THERMOCHEMISTRY

Chapter 11

Teaching Periods	Assessment	Weightage
8	1	9

Students will be able to:

- **Define** thermodynamics.
- **Define** the terms system, surrounding, boundary, state of system, state function, internal energy, enthalpy, entropy, heat of formation, standard heat of formation.
- **Classify** reactions as exothermic and endotermic.
- **Relate** change in enthalpy to the heat of reaction and heat of combustion of a reaction.
- **Relate** change in internal energy of a system with thermal energy at constant volume and constant pressure.
- **Explain** Hess's law with examples.
- **Apply** Hess's law to construct simple energy cycles.
- **Explain** reaction pathway diagram in terms of enthalpy changes of the reaction.

INTRODUCTION

Energy changes are the most important feature of a chemical process. When gasoline is ignited with air in a car engine, a certain amount of energy is released which some works in moving the piston due to which the wheels of the car rotate. Similarly, food can provide us with energy as it is burned up with oxygen in every cell of our body.

Heat and temperature are two different terms. Temperature describes the random movement of particles of a substance where as heat is associated with transfer of energy between two bodies with a temperature change. Chemical reactions are generally carried out with the transfer of heat to or from environment. **"The study of energy transference as heat during a chemical process is known as thermochemistry"**.

11.1 THERMODYNAMICS

Thermodynamics is a Greek word, its first part 'Thermo' represents heat and the second part 'dynamic' which epitomizes flow or movement. **"Thermodynamics is an essential branch of science which deals with the study of inter transformation of heat, work, and other forms of energies"**. Thermodynamics applies to a variety of science such as physics, chemistry, engineering, etc and plays an imperative role in our daily life.

Thermodynamics is a macroscopic science and concerns with the initial and final states of a physical or chemical process but does not tell anything about the molecular constitution of matter. Hence, it helps to predict whether the thermochemical process can occur at particular conditions. However, it is incapable of assessing the rate of reaction.

11.1.1 Thermodynamics Terms

System:

A thermodynamic system is a quantity of matter of fixed identity, around which we can draw a boundary. **"It is a distinct part of our universe which is under particular experimental debate and separated from surrounding by an imaginary or real surface and can change its shape or size is called a system"**. It may be some water contained in a beaker, some gas enclosed in a cylinder, or some solution filled in a calorimeter or the whole of the universe. All systems contain a certain quantity of matter and are characterized by particular macroscopic properties.

Surroundings:

Everything outside the arbitrarily selected boundaries of the system that affects the system or is affected by it is called surrounding. It is referred to as the remaining part of the universe other than a system from which energy or matter can be exchanged with the system. The system and surrounding together constitute the thermodynamic universe of that specific process.

Boundary:

It is a physical (real) or conceptual (imaginary) closed surface that separates a system from its surroundings.

For example if a reaction between zinc dust and dilute hydrochloric acid is carried out in a container.

- The contents of the container, (zinc and HCl) constitute the system because they are characterized by specific factors, like mass, volume, temperature, etc.
- The entire remaining part of the universe including the wall and empty part of the container specifies its surrounding.
- The surface of the reacting material which separates the system from its surrounding is said to be a physical boundary.

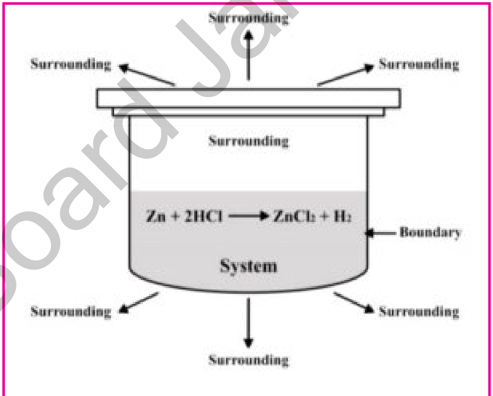


Fig 11.1: System, Surrounding & Boundary of Thermodynamic System

Thermodynamic systems are categorized into three main types on the basis of their ability to allow an interchange of mass and energy into environment thorugh their boundires.

Open System:

All such thermodynamic systems which communicate with the surrounding in term of both mass transfer and energy transfer are known as an open systems. The boundary of this type of system is open and non-insulated.

A boiling tea kettle is an open system because it transfers heat and matter (steam) to the surrounding.

Closed System:

All such thermodynamic systems which do not allow the exchange of mass but permit energy to be transferred with the environment are known as closed system. The boundary of a closed system is sealed but not insulated hence it is impermeable to mass only.

A pressure cooker is a good approximation to a close system where only heat transfers (except a little steam escapes through the top valved to prevent explosion).

Think of any other close systems around you!

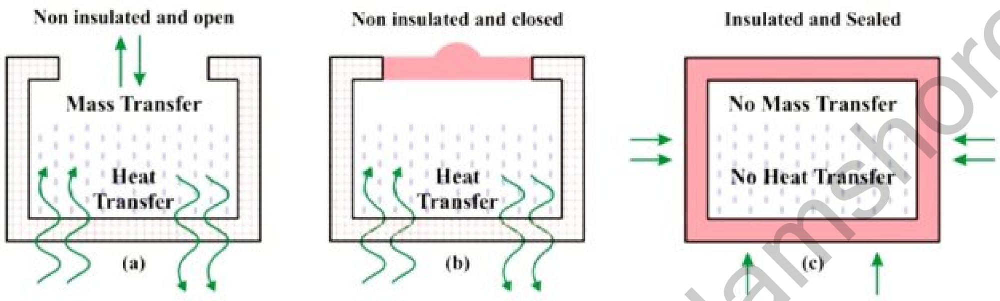


Fig 11.2: Three types of thermodynamic systems (a) open system (b) closed system (c) isolated system

Isolated System:

All such thermodynamic systems which neither exchange matter nor energy with the surrounding and hence totally independent of their surrounding are known as an isolated systems. The boundary of an isolated system is sealed and insulated.

A perfect isolated system does not exist as energy interaction in the form of heat radiation will always occur. However, some conceptually true isolated systems are thermo flask and insulated drink cooler.

Macroscopic Properties:

The description of a thermodynamic system is associated with some macroscopic quantities. These quantities can be measured if the system has large number of particles, thus macroscopic properties refers to the system having bulk amount. These are further classified into extensive and intensive properties depending upon whether they are proportional to the size of the system or not.

Entropy (S):

It is a measure of the disorder of the system. For example the arrangement of particles are more disordered in liquid and gases than solids. It is directly proportional to temperature.

State of System:

A thermodynamic system is said to be in a certain state if some macroscopic properties such as temperature pressure, volume, and moles are known. With the change of one or more of these macroscopic properties, the system changes its state.

Do You Know?

Intensive properties are those whose values are not dependent on quantity of matter in the given system. For example Pressure, density, Refractive index, surface tension, Melting point etc. Extensive Properties are those whose values for the entire system depend on the quantity of matter. For example Mass, Volume, Energy, Enthalpy, Moles etc.

The description of a system before the change occur is known as an initial state whereas it is said to be a final state when the change has occurred. The change in any macroscopic properties of the system is determined by taking the difference of their values at the final and initial state.

For example in a chemical reaction, the enthalpy of reactant is represented by H_1 (initial state), and the enthalpy of product is shown by H_2 (final state) hence ($\Delta H^\circ = H_2 - H_1$) is considered as the change in enthalpy in this chemical process.

State Function:

A state function is thermodynamic parameter which is dependent on initial and final state of the system and is independent of how the change is occurred. Examples of state function are internal energy, enthalpy, temperature, volume etc.

Enthalpy of a System:

Heat transfer in almost all physical and chemical process happens at constant volume. In the laboratory, for example, the reaction is usually carried out in open test tube, beakers or flask etc and hence the heat flow into or out of the reaction generally takes place under the condition of the constant pressure of air (approximately 1 atmosphere). In thios situation heat associated with the system may utilize both in altering the internal energy as well as performing work which may be seen by changing the volume of the reaction mixture in the reaction container.

To quantify the total heat contents of a system, chemists use a quantity named enthalpy (H). It defines as **"The sum of internal energy and algebraic product of its pressure and volume".**

$H = E + PV$ ---------------------------- (i)

Equation (i) specify that enthalpy of a system depends on the quantity of internal energy, pressure and volume. Since P, V and E are all state functions, we must say that enthalpy is also a state function.

Enthalpy change (ΔH) of a reaction is measured in Calorie (metric unit system) as well as Joule (S. I unit system). The interrelation between Joule and calorie is given as

$$\boxed{1\ \text{Cal} = 4.18\ \text{Joules}}$$

Experience shows that in many chemical reaction amounts of heat evolves or absorbs in thousands of joules per mol. Hence for convenient it is measured in KJ/mol.

Self Assessment

(i) What is meant by enthalpy of system? Mention its units.
(ii) Which of the following are not classified into state function.
Work (W), Enthalpy change (ΔH), Volume change (ΔV), Internal energy change (ΔE).

11.2 THERMOCHEMICAL REACTIONS

The progress of a chemical reaction i.e. the conversion of reactants into products involves the breaking of existing bonds of reactant particles for which energy has to be supplied and the formation of new bonds in which energy is released. Indeed, different bonds have different energy requirements for their breaking and re-forming thus to decide whether a chemical reaction takes place with the absorption or evolution of heat, we must know the energy difference of reactants and products. Since chemical reactions are usually taking place at constant pressure and the enthalpy of a system is stored in the chemical bond, the energy change in the formation of products from reactants is represented by ΔH.

Do You Know?

Gas welding is a combustion reaction between acetylene and oxygen. When the two gases contact to each other in a hand-held torch a relatively hot flame is produced having a temperature of 3000°C.

11.2.1 Exothermic Reactions

Exothermic reactions (Exo; out) are those in which heat is given out making the surrounding warmer. In the course of exothermic reactions, energy stored in the chemical bond of products is less than reactant hence these reactions are energetically favorable and often occur spontaneously but sometimes we need extra energy to get them started. The overall energy released in these reactions is represented by ΔH with a negative sign.


(a) (b)

Fig 11.3: Evolution and absorption of heat in thermochemical reaction (a) exothermic reaction (b) endothermic reaction

All combustion reactions including the burning of fuel and coal, oxidation of Sui gas, etc are exothermic reactions and can easily be noted by a rise of the surrounding temperature.

$$C + O_2 \longrightarrow CO_2 \quad (\Delta H = -ve)$$
$$CH_4 + 2O_2 \longrightarrow 2CO_2 + 2H_2O \quad (\Delta H = -ve)$$

11.2.2 Endothermic Reactions

Endothermic reactions (endo; taking in) are those in which heat is put into the system making the surrounding colder. In these reactions more energy is needed to break the bonds in the reactants than is released when new bonds are formed in the products. Since heat is used for the reaction to occur, these are referred to as non-spontaneous reactions. The net energy absorbed in these reactions is represented by ΔH with a positive sign.

An appropriate endothermic reaction is photosynthesis during which plants absorb solar heat through their chlorophyll parts and this heat is utilized for the conversion of CO_2 and H_2O into glucose.

$$2CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2 \quad (\Delta H = +\text{ve})$$

$$CH_4 \rightarrow C + 2H_2 \quad (\Delta H = +\text{ve})$$

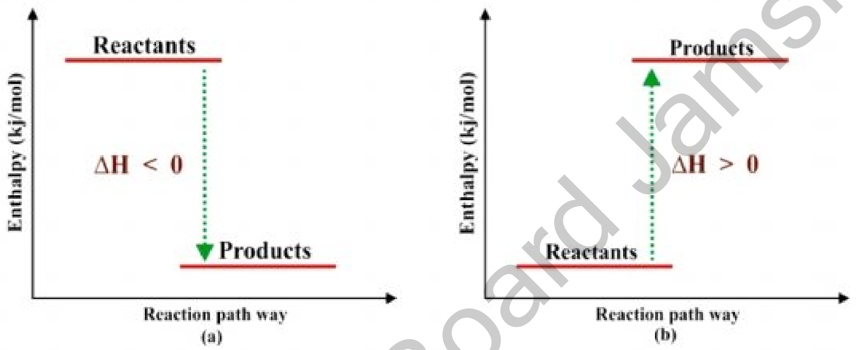


Fig 11.4: Energy diagram of thermochemical reaction
(a) exothermic reaction (b) endothermic reaction

Self Assessment

Classify each of the following processes as exothermic or endothermic.

(i) Synthesis of Ammonia
(ii) Decomposition of Lime
(iii) Oxidation of Coal
(iv) Neutralization of NaOH and HCl
(v) Combustion of Hexane
(vi) Burning of Sui gas

11.3 FIRST LAW OF THERMODYNAMICS

The first law of thermodynamic is an adaptation of the law of conservation of energy that governs the transference of energy between the system and surrounding in the form of heat and work. This concept was enunciated by J.R. Mayer (1841) and formulated by Helmholtz (1847).

11.3.1 Statement and Mathematical Derivation

This law may be stated as; **"In any physical or chemical process, the net energy of a system and its surroundings must remain constant"**. Or **"a system can not create or destroy energy, however, it can exchange energy with its surrounding in the form of heat and work"**. This law describes us that heat and work are mutually convertible but since energy can neither be created nor be destroyed, the total energy conversion remains constant.

To develop the mathematical approach of the law let us consider a system in its initial state having internal energy **E_1**. If "**q**" be the heat supplied to the system while **W** be the work done on the system, the internal energy increases to **E_2**. Then according to the law, the internal energy change ($E_2 - E_1$) may be formulated as

$$\Delta E = q + w \quad \text{--------------------------- (iii)}$$

Where

q = heat transfer across the system

W = work done

ΔE = change in the total energy of the system ($E_2 - E_1$)

The sign of '**q**' is taken positive if thermochemical process is concerned with heat absorbtion but in case of heat release it is taken as negative sign. The sign of **W** should be taken negative for thermochemical expansion and positive if it undergoes compression.

Equation (iii) may take the form $\Delta E = q$ if the heat is transferred to the system without work is being done but if work is done on the system without heat transfer it may change to $\Delta E = W$.

11.3.2 Derivation of Pressure-Volume Work Equation

Mechanical work due to expanding or squeezing of a system at constant external pressure is known as pressure-volume work.

Consider a gas confined in a cylinder fitted by a negligible weight, fraction less and movable piston of cross-section area **A** at a constant external pressure. If the force exerted by the gas on the inner wall of the piston is greater than external pressure, the piston move upward from a height **h_1** to **h_2** and hence does some work which may be formulated as

$$W = -F(h_2 - h_1)$$

Insertion of a negative sign indicates that external pressure opposes the expansion of gas. Since pressure is the force exerted on unit area ($P = F/A$) and thus the force is ($F = PA$), the work may be written as

$$W = -PA(\Delta h)$$

But A.Δh represents volume change (ΔV) of the system so work done on thermodynamics system is deduced as

$$W = -P\Delta V \quad \text{--------------------------- (iv)}$$

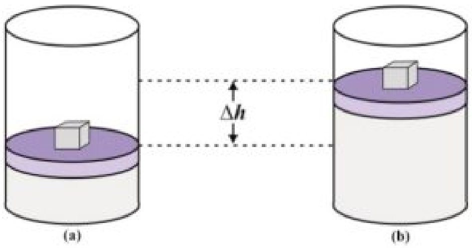


Fig 11.5: pressure-volume work in thermodynamic expansion process (a) volume at initial state (b) volume at the final state

As far as the unit of pressure-volume work is concerned, we may have two options; either it takes in Joules (J) or in atm.dm^3. In S.I measurement pressure is taken in Pascal (N/m^2) and volume in cubic meter (m^3), their product will be in Joules. However, it is more agreeable to express pressure in atmosphere and volume in dm^3, it makes the unit of work is atm.dm^3. The two work units are co-related as

$$1 \text{ atm.dm}^3 = 101.325 \text{ Joules}$$

Example 11.1

A gaseous chemical reaction is carried out in a cylinder under a constant external pressure of 1 atm. If during the reaction volume increases from 3dm^3 to 5dm^3 by moving the piston upward. Calculate the workdone and express in kJ.

Solution:

Since the work done in an expansion process has negative sign, the equation of pressure volume work should be $W = -P\Delta V$.

Work = $-P\Delta V$

Work = -1 atm (5dm^3 – 3dm^3)

Work = -2 atm dm^3

But 1 atm dm^3 = 101.325J, hence

Work = -202.65J = -0.20265KJ

Self Assessment

Convert the values of following quantities.

(i) 20 calories energy into Joule

(ii) 3.5 atm dm^3 work into KJ.

Internal Energy

Every system is made of particles (atoms, ions, or molecules) and has a specific amount of energy. This energy is associated with the sum of all microscopic energies of the particles of the system and mainly categorised as kinetic and potential energies. The kinetic energy comprises of particles motion such as translational, vibrational, rotational motions etc. potential energy includes attractive and repulsive interaction between particles and other chemical energies stored in the chemical bond. **"The total energy content of a thermodynamic system under a given set of conditions is known as internal energy"**.

Change in internal energy (ΔE) can be measured experimentally ($\Delta E = E_2 - E_1$). Internal energy change (ΔE) is a state function because it depends only upon the initial and final state and not by a path to which change occurs.

Example 11.2

Burning of petrol in an automobile engine gives carbondioxide and water vapours. If the gases do 675J work in pushing the piston outward and the system lose 435J heat to the surrounding, calculate the internal energy change in kJ.

Solution:

Since heat is given out, the value of **q** is taken with negative sign. Likewise sign of **W** is also taken negative because work is done by the system.

$q = -435J$

$W = -675J$

$\Delta E = ?$

$\Delta E = q + w$

$\Delta E = (-435) + (-675)$

$\Delta E = -1110J$

$\Delta E = -1.11KJ$

11.3.3 Applications at Constant Volume and Constant Pressure

So far we have learned categorically that heat absorb or evolve in a chemical process is related to its internal energy and PV work done. Now we will see that how the equation of First law of thermodynamics is applicable to the process that occur under constant pressure and constant volume.

The process at Constant Volume

When a reaction is carried out at constant volume ($\Delta V = 0$) no work is done on or by the system. In this situation internal energy change must equal to heat change of the reaction. The equation of the First law of thermodynamics may be reformed as $q_v = \Delta E$ (the subscript "**v**" specify constant volume process).

$q_v = \Delta E$ --------------------------- (v)

The process at Constant Pressure

It is a matter of fact that many chemical reactions in labs or workshops are carried out in open vessels. This means they carried out at constant pressure in a manner of thermochemical expansion. Thus according to the first law of thermodynamics, this constant pressure process may be illustrated as

$\Delta E = q_p - P\Delta V$

or $q_p = \Delta E + P\Delta V$ ---------------------- (vi)

Where q_p is the heat flow to or from the system at constant pressure, **ΔE** is internal energy change, and PΔV is work done with changing the volume.

$q_p = (E_2 - E_1) + P(V_2 - V_1)$

$q_p = (E_2 + PV_2) - (E_1 + PV_1)$

$q_p = H_2 - H_1$

And $q_p = \Delta H$ -------------------------- (vii)

Equation (vii) tells that, if a chemical process is occurred at constant pressure where only PV work is allowed due to compression of expansion the enthalpy change (ΔH) of system is equal to energy flow (q).

Substituting this value in equation (vi) we get

$\Delta H = \Delta E + P\Delta V$ -------------------------- (viii)

Equation (viii) represents gaseous reaction. However, for the reaction in which one or more solids or liquids are involved, the value of PΔV becomes almost zero because solids and liquids undergo very small volume change. Thus in this case enthalpy change (ΔH) will be equal to internal energy change (ΔE) and the equation of First law of thermodynamics is reformed as

$\Delta H = \Delta E$ -------------------------- (ix)

11.4 HESS'S LAW: (Enthalpy change calculations)

The change in enthalpy of some reactions are measured by calorimetric method. However, experimentally it is difficult to determine change in enthalpy of very slow and very fast reaction.

For example, combustion of carbon (graphite) to give carbon dioxide can be worked in a calorimeter, and ΔH° for this reaction can be conveniently measured.

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \quad (\Delta H^\circ = -393.5 \text{ KJ/mol}) \quad \text{(i)}$$

Further, the same is true for the oxidation of carbon monoxide to carbon dioxide.

$$CO_{(g)} + \tfrac{1}{2}O_{2(g)} \longrightarrow CO_{2(g)} \quad (\Delta H^\circ = -283.5 \text{ KJ/mol}) \quad \text{(ii)}$$

Contradictorily, the measurement of ΔH° in the combustion of carbon to carbon monoxide is quite difficult because some of the carbon monoxides is further oxidized to carbon dioxide. (Subracting equation ii from i)

$$C_{(s)} + \tfrac{1}{2}O_{2(g)} \longrightarrow CO_{(g)} \qquad (\Delta H^\circ = ?)$$

Enthalpy change of a reaction is a state function and it depends only on where the chemical process begins and finishes, but not on the route it takes from. Hence considering the energy cycle of the above three reactions (illustrated in fig 11.6), ΔH° of carbon monoxide can be measured indirectly.

G.H. Hess (1840) introduced a law of thermochemistry based on his observations on cyclic thermochemical changes which involve two or more different routes. This is known as Hess's law of enthalpy summation.

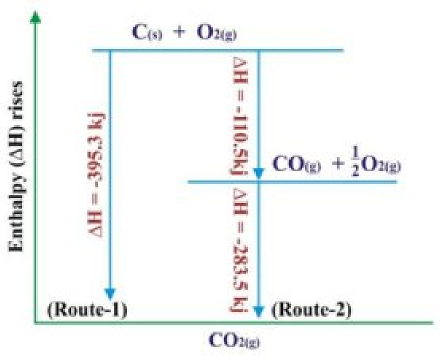


Fig 11.6: Energy cycle diagram for the formation CO_2(g) (a) route-1 (b) route-2

This law states as **“if a chemical reaction can be brought about in more than one path way, the net enthalpy change is the same provided that the initial and final states are the same”**.

11.4.1 Explanation of Hess’s Law

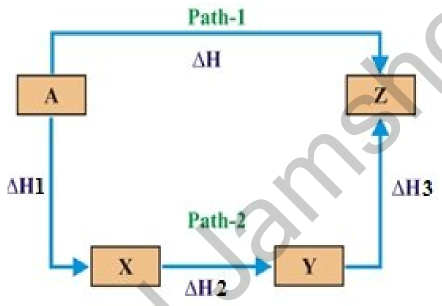


Fig 11.7: Illustration of Hess’s Law

Let us suppose a substance A is converted to Z by two different paths (illustrated in fig 11.7). It may either change directly to **Z** in one step or by involving some intermediate steps in which **X** and **Y** are formed. In both cases the total enthalpy change remains the same.

Path-1 = A $\xrightarrow{\Delta H}$ Z

Path-2 = A $\xrightarrow{\Delta H_1}$X $\xrightarrow{\Delta H_2}$Y $\xrightarrow{\Delta H_3}$Z

Thus $\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$

Standard Enthalpies of Formation

It defines as **“the enthalpy change of a chemical reaction in which one mole of a pure substance is formed from its elements with all substance in their standard state”**.

The standard enthalpy of formation is represented by the symbol ΔH_f° in which superscript zero signifies standard conditions of 1 atmospheric pressure and 25°C, whereas subscript “f” stands for formation.

Conventionally ΔH_f° of most of the elements (H_2, O_2, N_2, Na, etc) are taken as zero because no further change is needed to bring them to standard state condition, However, for those elements which exists in more than one allotropic forms, the most stable allotropic form is conventionally assumed to have $\Delta H_f = 0$. For example, graphite is a thermodynamically more stable allotropic form of carbon than diamond at 25°C and 1 atm pressure hence ΔH_f of graphite is taken as zero. Similarly, O_2 (oxygen) is a more stable allotropic form than O_3 (ozone), and therefore ΔH_f of O_2 is assumed to be zero. The same case in for Rhombic sulfur ($\Delta H_f = 0$)

Table 11.1 **The Standard States of various substances**

Substances	Standard States
All pure solids & liquids	25°C
All gaseous compounds	25°C and 1 atm
All substances in the solution	25°C and 1 molar conc.
All elements	25°C and 1 atm

Standard Enthalpy of Reaction

It is the enthalpy absorbed or evolved when fixed number of moles of reactants as represented in a balance chemical equation are completely reacted to form product with the condition that all reactants and products are in their standard states. It is represented by ΔH°. In general ΔH° in a balanced thermochemical equation is the sum of ΔH_f° of products minus the sum of ΔH_f° of reactants.

$$\Delta H^\circ_{reaction} = \left[\left(\Sigma \text{ np } \Delta H^\circ_{f\ (products)} \right) - \left(\Sigma \text{ nr } \Delta H^\circ_{f\ (\text{reactants})} \right) \right]$$

Where np and nr represent total number of moles of reactants and products take part in the reaction.

Table 11.2 **Standard Molar Enthalpy of Formation of some organic and inorganic substances at 25°C (In KJ/mol)**

Organic substances	ΔH_f° (KJ/mol)	Inorganic substances	ΔH_f° (KJ/mol)
$CH_{4(g)}$	– 74.85	$CO_{(g)}$	– 110.5
$C_2H_{6(g)}$	– 83.8	$CO_{2(g)}$	– 393.5
$C_3H_{8(g)}$	– 103.9	$SO_{2(g)}$	– 296.8
$C_2H_{4(g)}$	+ 52.30	$SO_{3(g)}$	– 396
$C_2H_{2(g)}$	+ 226.7	$H_2S_{(g)}$	– 20.17
$C_6H_{6(l)}$	+ 49.03	$NH_{3(g)}$	– 46.19
$CH_3OH_{(l)}$	– 239	$H_2O_{(l)}$	– 285.8
$C_2H_5OH_{(l)}$	– 277.7	$Fe_2O_{3(s)}$	– 824.2
$CH_3COOH_{(l)}$	– 484.2	$NaCl_{(s)}$	– 411

Use of Hess's Law in the determination of heat of reaction

There are two ways to calculate ΔH° of a reaction. It either determined calorimetrically or calculate from known values of ΔH_f° of all the susbstances involve in the reaction. Hess's law provides us a convenient way to find out the heat change involves in a chemical reaction by subtracting the sum of heat of formation of all reactants from the sum of heat of formation of all products.

Example 11.3

Calculate the enthalpy of combustion of propane at 25°C by the given informations.

$$C_3H_{8(g)} + 5O_{2(g)} \longrightarrow 3CO_{2(g)} + 4H_2O_{(g)} \qquad (\Delta H^\circ = ?)$$

ΔH_f° **of** $C_3H_{8(g)} = -103.9\,KJ/mol$

ΔH_f° **of** $CO_{2(g)} = -393.5\,KJ/mol$

ΔH_f° **of** $H_2O_{(\ell)} = -285.8\,KJ/mol$

Solution:

The mathematical form of heat of reaction ΔH° is given as.

$$\Delta H^\circ_{reaction} = \Big[\big(\Sigma\, np\, \Delta H^\circ_{f\,(products)}\big) - \big(\Sigma\, nr\, \Delta H^\circ_{f\,(reactants)}\big) \Big]$$

Substituting the values.

$$\Delta H^\circ_{reaction} = \Big[(-393.5 \times 3) + (-285.8 \times 4)\Big] - \Big[(-103.9 \times 1)\Big]$$

$$\Delta H^\circ_{reaction} = -2219.8\, KJ/mol$$

Use of Hess Law in the determination of Heat of formation

Realizing the fact that thermochemical equations can be added subtracted or multiplied like ordinary algebraic equations, Hess's law is useful to calculate the heat of formation of many compounds where an experimental determination is not possible.

To understand how is Hess's Law useful in thermochemistry, look at the oxidation of sulphur to sulphur trioxide.

$$S_{(s)} + \tfrac{3}{2}O_{2(g)} \longrightarrow SO_{3(g)}$$

Analyzing the reaction, we find that sulphur can not be directly oxidized into SO_3, therefore ΔH_f° of SO_3 can not be determined if we put sulphur and oxygen in a calorimeter. The only option is to go for an alternative route which consists of following two steps.

Step-1: $S_{(s)} + O_{2(g)} \longrightarrow SO_{2(g)} \quad (\Delta H_1 = -296.8KJ/mol)$

Step-2: $SO_{2(g)} + \tfrac{1}{2}O_{2(g)} \longrightarrow SO_{3(g)} \quad (\Delta H_2 = -99.2KJ/mol)$

Thus the ΔH_f° of $SO_{3(g)}$ is indirectly determined by adding enthalpy change of step 1 and step 2.

$$\begin{array}{l}
S_{(s)} + O_{2(g)} \longrightarrow SO_{2(g)} \quad (\Delta H_1 = -296.8KJ/mol) \\
SO_{2(g)} + \tfrac{1}{2}O_{2(g)} \longrightarrow SO_{3(g)} \quad (\Delta H_2 = -99.2KJ/mol) \\
\hline
S_{(s)} + \tfrac{3}{2}O_{2(g)} \longrightarrow SO_{3(g)} \quad (\Delta H_f^\circ = -396KJ/mol)
\end{array}$$

Example 11.4

Calculate the standard heat of formation of acetylene (C_2H_2) by using the data of the following thermochemical equations.

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \qquad (\Delta H = -393.5\ KJ) \text{ -------- (i)}$$

$$H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(\ell)} \qquad (\Delta H = -285.8\ KJ) \text{ -------- (ii)}$$

$$C_2H_{2(g)} + \frac{5}{2}O_{2(g)} \longrightarrow 2CO_{2(g)} + H_2O_{(\ell)} \qquad (\Delta H = -1299.5\ KJ) \text{ -------- (iii)}$$

The desired equation is

$$2C_{(s)} + H_{2(g)} \longrightarrow C_2H_{2(g)} \qquad (\Delta H_f^\circ = ?) \text{ -------- `(iv)}$$

Solution:

To determine ΔH_f value of C_2H_2, we have to generate the desired equation by manipulating and adding eq. (i), (ii) and (iii) together in such a way that all unwanted substances should be canceled.

In the desired equation (iv) we see that 2 moles of carbon and 1 mole of H_2 are needed as a reactant, this can be obtained by multiplying equation (i) by 2, which means that ΔH° will also be multiplied by 2.

$$2C_{(s)} + 2O_{2(g)} \longrightarrow 2CO_{2(g)} \ (\Delta H^\circ = -787\ KJ)$$

Next, we see that C_2H_2 is needed as a product. To do this, the equation (iii) must be reverse with changing the sign of ΔH° .

$$2CO_{2(g)} + H_2O_{(\ell)} \longrightarrow C_2H_{2(g)} + \tfrac{5}{2}O_{2(g)} \ (\Delta H = +1299.6\ KJ)$$

Now sum up these three manipulated equations to get the required reaction. Also, sum up the three modified ΔH° values to get ΔH_f° of the desired reaction.

$$2C_{(s)} + \cancel{2O_{2(g)}} \longrightarrow \cancel{2CO_{2(g)}} \qquad (\Delta H = -787\ KJ)$$

$$H_{2(g)} + \cancel{\frac{1}{2}O_{2(g)}} \longrightarrow \cancel{H_2O_{(\ell)}} \qquad (\Delta H = -285.8\ KJ)$$

$$\cancel{2CO_{2(g)}} + \cancel{H_2O_{(\ell)}} \longrightarrow C_2H_{2(g)} + \cancel{\frac{5}{2}O_{2(g)}} \qquad (\Delta H = +1299.6\ KJ)$$

$$2C_{(s)} + H_{2(g)} \longrightarrow C_2H_{2(g)} \qquad (\Delta H = \ 226.7KJ/mol)$$

11.4.2 Born Haber Cycle

Born Haber cycle is developed by two German chemists Max Born and Fritz Haber (1919) to correlate the lattice energy of ionic solids with some other energies involved in their formation. **"It is a cycle of enthalpy change in which an ionic solid is theoretically formed from its elements in their standard states"**. It is a


Max Born


Fritz Haber

specific application of Hess's law and generally use to determine lattice energy of ionic solids.

To understand, how the lattice energy of a binary ionic solid determines by using Born Haber cycle let's take solid Cesium fluoride (CsF) as an example. We start by writing a thermochemical equation for the formation of CsF from its elements at their standard states (25°C and 1 atm).

The standard enthalpy of formation of $CsF_{(s)}$ as mentioned in table 11.2 is -553.5 KJ/mol

$$Cs_{(s)} + \tfrac{1}{2}F_2 \longrightarrow CsF_{(s)} \qquad (\Delta H_f^{\circ} = -553.5\ KJ/mol)$$

Now various energies involved in the formation of $CsF_{(s)}$ are described in the following stepwise manner.

Step-1: Sublimation of Cesium It involves the vapourization of metallic cesium into gaseous atom. The process is endothermic because heat is always needed to sublime a solid.

$$Cs_{(s)} \longrightarrow Cs_{(g)} \qquad (\Delta H_{(sub)} = 76.5\ KJ/mol)$$

Step-2: Ionization of Cesium atom It involves the loss of electron from cesium gaseous atom. The enthalpy change corresponds to this process is always positive and known as ionization enthalpy.

$$Cs_{(g)} \longrightarrow Cs^{+}_{(g)} + \bar{e} \qquad (\Delta H_{(IE)} = 375.5\ KJ/mol)$$

Step-3: Dissociation of gaseous Fluorine It involves the breaking of F_2 molecule into fluorine gas atoms. The enthalpy related to this process is ever positive and labeled as enthalpy of dissociation or often known as enthalpy of atomization.

$$\tfrac{1}{2}F_{2(g)} \longrightarrow F_{(g)} \qquad (\Delta H_{(D)} = \tfrac{1}{2} \text{ x } 157\ KJ/mol)$$

Step-4: Formation of $\bar{F}$ ion It involves the absorbtion of electron into fluorine gas atom. The enthalpy change of this thermochemical process is negative and specify as electron affinity.

$$F_{(g)} \longrightarrow \bar{F}_{(g)} \qquad (\Delta H_{(EA)} = -328.2\ kJ/mol)$$

Step-5: Formation of Solid CsF It involves the electrostatic interaction of oppositely charged gaseous ions. The enthalpy change in this process is indeed negative and known as Lattice energy.

$$Cs^{+}_{(g)} + \bar{F}_{(g)} \longrightarrow CsF_{(s)} \qquad (\Delta H_{(LE)} = ?)$$

Intended with Hess's Law, the sum of enthalpy change of these five steps will be equal to the enthalpy of formation of $CsF_{(s)}$ being the overall enthalpy change of the energy cycle is zero. This may be set out in fig 11.10 and formulated as.

$$\Delta H_f^{\circ} = \Delta H_{sub} + \Delta H_{IE} + \tfrac{1}{2}\Delta H_D + \Delta H_{EA} + \Delta H_{LE}$$

Substituting the values of concerned energies, we get lattice energy.

$$(-553.5) = (76.5) + (375.5) + \left(\tfrac{1}{2} \times 157\right) + (-328.2) + (-\Delta H_{LE})$$

$$\Delta H_{LE} = -755.8\ KJ/mol$$

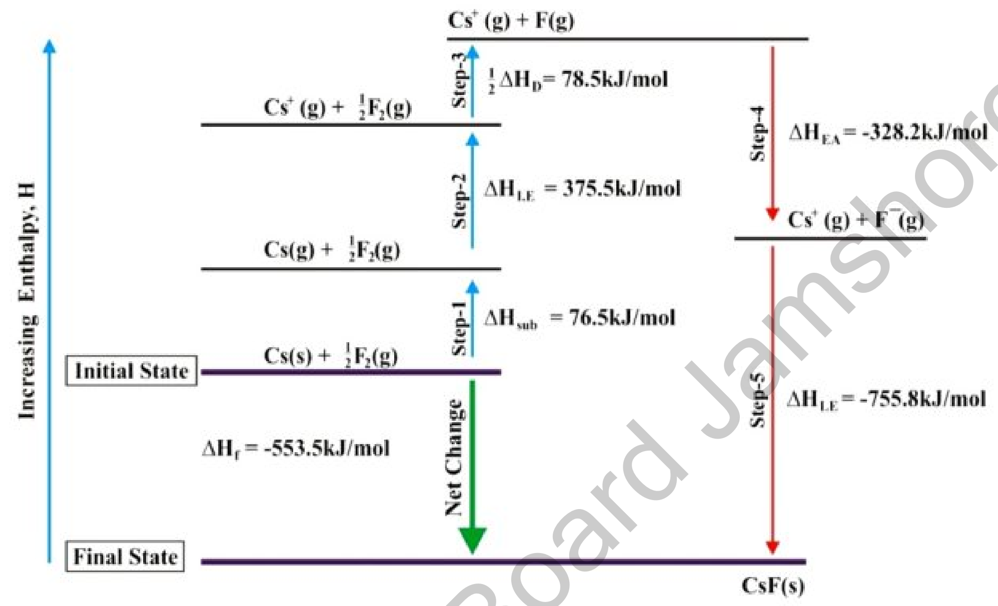


Fig 11.8: Born Haber cycle for the enthalpy change of formation of CsF(s)

Example 11.5

Use the data provided below for the formation of $RbCl_{(s)}$, write thermochemical equations for all the steps involved in the Born Haber cycle and determine the enthalpy of formation of $RbCl_{(s)}$.

Sublimation energy of $Rb_{(s)}$ = 82 KJ/mol

Ionization energy of $Rb_{(g)}$ = 403 KJ/mol

Dissociation energy of $Cl_{2(g)}$ = 242 KJ/mol

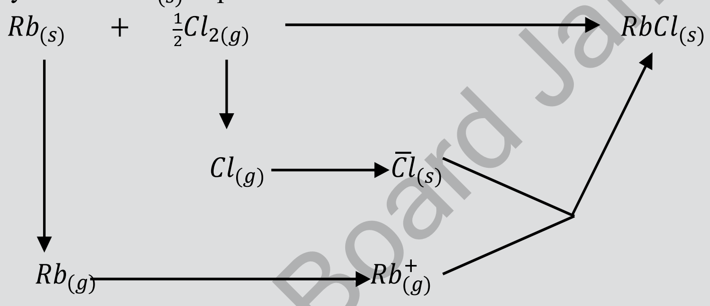
Electron affinity of $Cl_{(g)}$ = -348.5 KJ/mol
Lattice energy of RbCl = -689 KJ/mol

Solution:

Since, according to Hess's law overall enthalpy change of a cyclic thermochemical process is zero, the sum up of all five steps involved in the process will get heat of formation of RbCl. Thermochemical equations associated with Born Haber cycle in the formation of $RbCl_{(s)}$ maybe written as

$$\begin{array}{lcl}
Rb_{(s)} \longrightarrow Rb_{(g)} & & (\Delta H^{\circ}_{(sub)} = 82\text{KJ/mol}) \\
Rb_{(g)} \longrightarrow Rb^{+}_{(g)} & & (\Delta H^{\circ}_{(IE)} = 403\text{KJ/mol}) \\
\frac{1}{2}Cl_{2(g)} \longrightarrow Cl_{(g)} & & (\Delta H^{\circ}_{D} = \frac{1}{2} \times 242\text{KJ/mol}) \\
Cl_{(g)} \longrightarrow \bar{Cl}_{(g)} & & (\Delta H^{\circ}_{EA} = \text{-}348.5\text{KJ/mol}) \\
Rb^{+}_{(g)} + \bar{Cl}_{(g)} \longrightarrow RbCl_{(s)} & & (\Delta H^{\circ}_{LE} = -689\text{KJ/mol}) \\
\hline
Rb_{(s)} + \frac{1}{2}Cl_{2(g)} \longrightarrow RbCl_{(s)} & & (\Delta H^{\circ}_{f} = -431.5\text{KJ/mol}) \\
\hline
\end{array}$$

The Born Haber cycle on $RbCl_{(s)}$ is presented below



Heat of formation of RbCl(s) may also be calculated by summing up the individual steps involved in the following simple way.

$$\Delta H^{\circ}_{f} = \Delta H_{sub} + \Delta H_{IE} + \frac{1}{2}\Delta H_{D} + \Delta H_{EA} + \Delta H_{LE}$$

$$\Delta H^{\circ}_{f(RbCl)} = (82) + (403) + \left(\frac{1}{2} \times 242\right) + (-348.5) + (-689)$$

$$\Delta H^{\circ}_{f(RbCl)} = -431.5\ Kj/mol$$

Society, Technology and Science

Use of cold pouche for cooling

Endothermic reactions are all around us. You might have sprained on your wrist or swollen on the elbow, in these circumstances you often put an instant cold pack for quick relief. Let's imagine, what happens. The bag consists of ammonium nitrate and water in separate packing and when torn, they get mixed. The polar terminals of water molecules interact with ionic bond of ammonium nitrate and the energy needed for this process is absorbed from the surrounding which makes the water colder and thus bag feels chill.

$$4NH_4NO_{3(s)} \rightarrow NH^{+}_{4(aq)} + NO^{-}_{3(aq)}\ (\Delta\text{H} = +\text{ve})$$

Activity

You will always find a kitchen having usual cooking items such as vinegar (CH_3COOH) and baking soda ($NaHCO_3$). Can you deduce whether the chemical reaction between them is exothermic or it is an endothermic one?

For that, you need to have a glass tumbler and pour very little amount of acetic acid in it (1/5 of the volume). Check the temperature initially through a temperature probe (the one which you use to note the temperature of coffee). Let it be dipped in the tumbler. Now add a teaspoon of baking soda in it and keep yourself at a distance. You will observe bubbles forming rapidly. It appears as if something is boiling and your mind could misconceive it as an exothermic reaction but the temperature probe would show you a drop in temperature indicating that in actual it is an endothermic reaction.

SUMMARY
with Key Terms

- **Thermodynamics** is the branch of physical science which deals with the study of intertransformation of heat work and other forms of energies.
- **Thermochemistry** is the study of energy change associated with a physical or chemical process.
- **Thermodynamic System** is a distinct part of the universe that is under experimental debate and separated from surrounding by a boundary.
- **Internal Energy, E** is mainly associated with the sum of all kinetic and potential energies of the particles of a system under study.
- **Enthalpy, H** is the heat contents of a system under constant pressure and describe as $H = E + PV$.
- **State Function** is a thermodynamic parameter on which description of a system is made, it depends on the initial and final state of the change but not on the path.
- **Exothermic Reactions** are those in which heat is given out making the surrounding warmer.
- **Endothermic Reactions** are those in which heat is put into the system making the surrounding colder.
- **The First Law of Thermodynamics** states that the total energy of a system and its surroundings must remain constant.
- **Pressure-Volume Work** is mechanical work associated with expansion or compression of a thermodynamic system, under a constant external pressure.
- **Standard Enthalpy of Formation, ΔH_f°** is the heat evolve or absorb when 1 mole of a substance is produced from its constitutent elements under their standard states i.e 25°C and 1 atm pressure.
- **Standard Enthalpy of combustion ΔH_c°** heat energy given out when one mole of a substance burn completely in air.

- **Standard Enthalpy of Reaction, ΔH°** is the heat change of a chemical reaction and can be measured by subtracting the sum up values of ΔH_f° of products to the sum up values of ΔH_f° of reactants.
- **Hess's Law** tells that if a reaction is carried out through several steps then the enthalpy change for the overall reaction must be equal to the sum of enthalpy change of these individual steps.
- **Born Haber Cycle** is an application of Hess's Law and generally use to determine the Lattice of ionic compounds.

EXERCISE

Multiple Choice Questions

1. Choose the correct answer

(i) Least entropy found in which of the following state of water:

(a) Liquid water at 4°C (b) Liquid water at 25°C
(c) Steam at 100°C (d) Ice at 0°C

(ii) The energy corresponds to the given thermochemical process is labeled as:

$$Li^{+}_{(g)} + \bar{C}l_{(g)} \longrightarrow LiCl_{(s)}$$

(a) Ionization energy (b) Lattice energy
(c) Enthalpy of combustion (d) Enthalpy of atomization

(iii) Which of the following change is not an endothermic reaction:

(a) Decomposition of lime (b) Cracking of alkanes
(c) Combustion of butane (d) Photosynthesis

(iv) Heat transfer can not be feasible across the boundryof a:

(a) Open system (b) Close system
(c)Isolated system (d) Thermo permeable system

(v) Which of the following enthalpy change is always negative:

(a) Enthalpy of formation (b) Enthalpy of decomposition
(c) Enthalpy of combustion (d) Enthalpy of reaction

(vi) Standard enthalpy of formation of all of the following elements at 25°C and 1 atm pressure are zero except:

(a) $C_{(\mathbf{diamond})}$ (b) $C_{(\mathbf{graphite})}$
(c) O_2 (d) N_2

(vii) In the equation of First law of thermodynamics ($\Delta E = q + w$), the property(s) which depends upon initial and final state is (are):

` (a) ΔE (b) q
(c) W (d) Both q and W

(viii) Which statement is incorrect:
(a) For constant pressure process, $\Delta H = \Delta E + P\Delta V$
(b) For constant volume process, $\Delta E = q$
(c) For exothermic reactions, $\Delta H \ \rangle\ 0$
(d) For Hess law $\sum \Delta H^\circ_{(cycle)} = 0$

(ix) In a thermochemical process, no work is done if the system is kept at:
(a) Constant temperature (b) Constant pressure
(c) Constant volume (d) Constant mass

(x) Volume is a:
(a) State function (b) Path function
(c) Intensive properties (d) Colligative property

Short Questions

1. State precisely the meaning of each of the following terms.
(i) System and surrounding (ii) State and state function
(iii) Internal energy and Enthalpy

2. What is meant by Internal energy change (ΔE) and Enthalpy change (ΔH)? Under what conditions are ΔE and ΔH equal?

3. How can you define standard enthalpy of formation and standard enthalpy of reaction.

Descriptive Questions

1. State and explain First law of Thermodynamics. Derive pressure-volume work of a system.

2. Discuss the applications of the First law of thermodynamics at constant pressure and constant volume.

3. State and explain Hess's Law of enthalpy summation. Discuss its applications.

4. Explain Exothermic and Endothermic reactions with the help of the energy diagram.

Numerical Questions

1. A thermochemical process is carried out at constant pressure of 8.52atm. If it absorbs 15.4KJ energy from the surrounding due to which an expansion in the volume of 4.7dm^3 is occurred. Calculate its change in internal energy. [Ans: 11.34KJ]

2. Using the data in table 11.2, calculate the standard enthalpy change for each of the following reactions.

$$2H_2S_{(g)} + 3O_{2(g)} \longrightarrow 2H_2O_{(\ell)} + 2SO_{2(g)}$$

$$Fe_2O_{3(s)} + 3CO_{(g)} \longrightarrow 2Fe_{(s)} + 3CO_{2(g)}$$

3. In the manufacturing of HNO_3 by the Ostwald process, one of the most important exothermic reactions is the oxidation of ammonia.

$$4NH_{3(g)} + 5O_{2(g)} \longrightarrow 4NO_{(g)} + 6H_2O_{(\ell)}$$

Determine standard heat of reaction (ΔH°) from the following given data.

$$\Delta H_f^\circ \text{ of } NH_{3(g)} = -46.19KJ/mol$$
$$\Delta H_f^\circ \text{ of } NO_{(g)} = 90.25KJ/mol$$
$$\Delta H_f^\circ \text{ of } H_2O_{(\ell)} = -285.8KJ/mol$$

[Ans: – 1169.04 KJ/mol]

4. Iso octane (C_8H_{18}) is an efficient fuel with a high octane rating. The combustion of C_8H_{18} in an internal combustion engine is represented in the following thermochemical equation. Find its standard heat of combustion.

$$C_8H_{18(\ell)} + 12\tfrac{1}{2}O_{2(g)} \longrightarrow 8CO_{2(g)} + 9H_2O_{(\ell)} \quad (\Delta H_f^\circ = ?)$$

Given that ΔH_f° of CO_2 = – 393.5 KJ/mol

ΔH_f° of H_2O = – 285.8 KJ/mol

ΔH_f° of C_8H_{18} = – 223.8 KJ/mol

[Ans: – 5496.4 KJ/mol]

5. Glycerol ($C_3H_8O_3$) is a well known organic compound due to its versatile uses. Calculate the standard enthalpy of formation of Glycerol from the data given below.

$$3C_{(s)} + 4H_{2(g)} + \tfrac{3}{2}O_{2(g)} \longrightarrow C_3H_8O_{3(\ell)} \quad (\Delta H_f^\circ = ?)$$
$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \quad (\Delta H^\circ = -393.5 \text{ KJ/mol})$$
$$H_{2(g)} + \tfrac{1}{2}O_{2(g)} \longrightarrow H_2O_{(\ell)} \quad (\Delta H^\circ = -285.8 \text{ KJ/mol})$$
$$C_3H_8O_{3(\ell)} + 3\tfrac{1}{2}O_{2(g)} \longrightarrow 3CO_{2(g)} + 4H_2O_{(\ell)} \quad (\Delta H^\circ = -1654.1 \text{ KJ/mol})$$

[Ans: – 669.6 KJ/mol]

6. Draw a fully labeled Born Haber cycle for Rubidium chloride (RbCl) and determine the lattice energy by using the following values. (all in kJ/mol).

- I.P$_{1st}$ of Rb = 403
- Electron affinity of Cl = -349 KJ/mol
- Bond energy of Cl_2 = 242 KJ/mol
- Sublimation energy of Rb = 86.5 KJ/mol
- Heat of formation of $RbCl_{(s)}$ = -430.5 KJ/mol

[Ans: -692 KJ/mol]

ELECTROCHEMISTRY

Chapter 12

Teaching Periods	Assessment	Weightage
12	1	8

Students will be able to:

- **Give** the characteristics of a Redox reaction.
- **Determine** oxidation and reduction in term of change in oxidation number.
- **Determine** oxidation number of atom of an element in a molecule or polyatomic ion on the basis of some assigned rules.
- **Enlist** oxidizing and reducing agents.
- **Balance** redox reaction that takes place in acid solutions.
- **Break** a redox reaction into oxidation and reduction half reactions.
- **Balance** the redox equation by using half-cell reaction method.
- **Define** cathode, anode, electrode potential and S.H.E.
- **Identify** the substance oxidized and the substance reduced in batteries.
- **Describe** the cell potential and how it is determined.
- **Describe** the reaction that occurs when a lead storage battery is recharged.
- **Illustrate** how a fuel cell produces electrical energy.
- **Explain** the types and uses of batteries in daily life.
- **Define** corrosion and describe simple methods like electroplating and galvanizing for its prevention.

INTRODUCTION

In our daily life many chemical reactions provide electrical energy. Have you ever think how portable radio, children's toys, or an automobile battery works? In fact in all these devices electrical energy generates due to chemical change. In reverse situation, we have a large list of chemical process in which electrical energy is used to bring about chemical changes. For example recharging of battery, extraction and purification of metals etc. Electro chemistry deals with the chemical change happen due to electric current as well as the generation of electric current by chemical change. It is best defined as **"the study of interchange of chemical and electrical energy"**. Electrochemistry is generally investigated by the usage of electrolytic and galvanic cells where electrical energy either produces or utilize by incorporating redox reactions.

12.1 OXIDATION-REDUCTION CONCEPTS

Reduction and oxidation reactions, collectively known as redox reactions, are associated with the electrons transfer from one species to another. If one species in a reaction loses electrons, it is said to be oxidized and acts as a reducing agent, at the same time the other specie gains electrons and gets reduced, therefore acts as oxidizing agent. The number of electrons lost and gained must be equal. Various natural processes that we observe in daily routine such as rusting of iron, photosynthesis, fading of cloth's color, generation of electric current in batteries are all concerned with simultaneous reduction and oxidation reactions.

12.1.1 Oxidation and Reduction

Oxidation refers to the addition of oxygen or removal of hydrogen from a substance for example.

$$4Al + 3O_2 \longrightarrow 2Al_2O_3 \text{ (Al is oxidized to } Al_2O_3\text{)}$$

$$H_2S + Cl_2 \longrightarrow 2HCl + S \text{ (} H_2S \text{ is oxidized to elemental sulphur)}$$

Reduction originally describes the addition of hydrogen or removal of oxygen from a compound. For example

$$2CuO \longrightarrow 2Cu + O_2 \text{ (Copper oxide is reduced to elemental copper)}$$

$$WO_3 + 3H_2 \longrightarrow W + 3H_2O \text{ (Tungsten oxide is reduced to elemental tungsten)}$$

According to modern electronic concept, **"oxidation is the chemical process in which electron are lost by an atom or ion where as reduction involves the gain of electrons"**. Thus oxidation may result in producing or increasing the positive charge on the species or decreasing its negative charge. Contrarily reduction involves in producing or increasing the negative charge on the species or decreasing its positive charge.

Oxidation Process
$Fe \longrightarrow Fe^{+2} + 2\bar{e}$
$Hg^{+} \longrightarrow Hg^{+2} + \bar{e}$
$S^{-2} \longrightarrow S + 2\bar{e}$

Reduction Process
$Cl_2 + 2\bar{e} \longrightarrow 2Cl^{-}$
$O^{-1} + \bar{e} \longrightarrow O^{-2}$
$Cu^{+2} + 2\bar{e} \longrightarrow Cu$

According to oxidation number concept **"oxidation is a process in which the oxidation state of an element increases while reduction is a process in which the oxidation state of an element decreases"**.

Let us consider a redox reaction between zinc powder with dilute hydrochloric acid.

$$Zn^{0}_{(s)} + 2\overset{+1}{H}Cl_{(aq)} \longrightarrow \overset{+2}{Zn}Cl_{2(aq)} + H^{0}_{2(g)}$$

Reduction

Oxidation

Characteristics of Redox Reactions

There are some general characteristics of redox reactions.

(i) All redox reactions may involve the transfer of electrons.

(ii) Oxidation and reduction process always occur side by side thus if one substance is oxidized the other is reduced at the same time.

(iii) Not all atoms in a redox reaction need to change their oxidation states but at least one atom should be oxidized and one should be reduced.

12.1.2 Oxidation Number

Oxidation number is an apparent charge on an atom in a compound or ion. Its value may be positive, negative or zero depending upon charge of combined atoms in the molecule or ion.

Rules for Assigning Oxidation Number:

(i) Oxidation number of all elements in Free State (uncombined state) is taken as zero. For example: K°, Cl_2°, H_2° , O_2° , Cu° etc.

(ii) The oxidation number of a mono atomic ion is the same as the charge appear on it. For example: the oxidation number of Na^{+} ion is + 1 and Ca^{+} ion is +2.

(iii) The sum of oxidation numbers of all elements in a neutral compound is zero. For example: $H_2SO_4^{\circ}$ ($H_2^{+2}SO_4^{-2}$)

(iv) The oxidation number of oxygen in most of its compounds is -2. However in peroxides it is -1 (Na_2O_2 and H_2O_2), in super oxides is -1/2 (KO_2) and in oxy fluoride is +2 (OF_2).

(v) Oxidation of hydrogen in covalent compounds is assigned as +1. However in metal hydrides its oxidation number is taken as -1 (e.g. $Na^{+}H^{-}$, $K^{+}H^{-}$ etc).

(vi) The oxidation numbers of group IA and group IIA elements are generally assigned +1 and +2 respectively. Elements of group IA are Li, Na, K, Rb, Cs and group IIA are Be, Mg, Ca, Sr, Ba

(vii) The oxidation number of fluorine in all its compounds is always taken as -1 because it is most electronegative atom of all elements. The oxidation number of other halogen elements in binary compounds is also taken as -1 except when they are bonded to a more electronegative halogen or oxygen.

(viii) In polyatomic ion, the sum of oxidation numbers of all the atoms present in them is equal to the net ionic charge on the ion.

Example 12.1

Determine the oxidation number of (i) S in $Na_2S_2O_3$ (ii) Mn in MnO_4^{-}

Solution:

(i) $Na_2S_2O_3$ contains elements Na, S and O. From the rules given above, the oxidation number of Na is +1 and that of O is –2. Further the sum of oxidation number of all elements in a neutral compound is zero. Thus we may determine the oxidation number of sulphur in the following way.

$$2(+1) + 2(S) + 3(-2) = 0$$
$$+2 + 2S - 6 = 0$$
$$2S = +4$$
$$S = +2$$

(ii) Since sum of oxidation number of all the elements in a polyatomic ion is equal to its net ionic charge, we may determine oxidation number of Mn in MnO_4^{-} ion in the following way.

$$Mn + 4(O) = -1$$
$$(Mn) + 4(-2) = -1$$
$$Mn - 8 = -1$$
$$Mn = +7$$

Self Assessment

Determine the oxidation number in the following species.
(i) Cl in ClO_3^- (ii) Cr in $Cr_2(SO_4)_3$ (iii) P in $Ca(H_2PO_4)_2$

12.1.3 Balancing oxidation reduction equation by ion electron method

Equations of redox reactions are often difficult to balance by simple inspection. There are two methods by virtue of which the redox reactions are balanced, namely; oxidation number method and ion electron method.

In ion electron method only those reactants and products of redox reaction are balanced that contain the elements undergoing a change in oxidation state. That is to say, only those reactants and products are balanced which are actually oxidized or reduced. Following steps are involved in balancing of chemical equation by ion electron method.

(1) Write a skeleton equation which includes those reactants and products that contain the elements undergoing a change in oxidation state.

(2) Transform the molecular skeleton equation into ionic form. If the given equation is already in the ionic form, then this step is omitted.

(3) Split the ionic equation into two partial equations i.e. the oxidation and reduction equation

(4) Balance each partial equation in terms of atoms. In neutral or acidic medium, H_2O and H^+ are added for balancing oxygen and hydrogen respectively. The oxygen atoms are balanced first. In case of basic medium, OH^- and H_2O are added to balance oxygen and hydrogen respectively.

(5) Balance the charge in each partial equation by adding electrons on either left or right side of the equation. It will be found that electrons are added to the left in the partial equation for the reduction equation and to the right in the partial equation for oxidation reaction.

(6) Multiply each partial equation by a number so that the electrons in both the partial equations become equal in number.

(7) Add the two partial equations after cancelling the electrons. In the sum equation, cancel out any species common to both sides.

Example 12.2

Balance the following equation by ion electron method.

$$\mathbf{HNO_3 + H_2S \longrightarrow NO + S + H_2O}$$

Solution:

The skeleton equation is given as

$$HNO_3 + H_2S \longrightarrow NO + S + H_2O$$

Step-1: Transform the molecular equation into ionic form:

$$H^+ + NO_3^- + H_2S \longrightarrow NO + S + H_2O$$

The oxidizing agent is the nitrate ion (NO_3^-) since its nitrogen atom undergoes a decrease in oxidation state. The reducing agent is H_2S since sulphur atom undergoes an increase in oxidation state. H_2S could have been written as sulphide ion (S^{-2}), but H_2S is preferable due to slight degree of ionization.

Step-2: Split the equation into oxidation and reduction half equations.

$NO_3^- \longrightarrow NO$ Reduction (Nitrogen from +5 to +2)

$H_2S \longrightarrow S$ Oxidation (Sulphur from -2 to 0)

Step-3: Since the medium is acidic, oxygen atoms are balanced by adding $2H_2O$ on right hand side and hydrogen atom are balance by $4H^+$ on left hand side in the first partial equation.

$$NO_3^- + 4H^+ \longrightarrow NO + 2H_2O$$

In the second partial equation two protons are added to the right to balance two hydrogen atoms on the left.

$$H_2S \longrightarrow S + 2H^+$$

Step-4: Balance the charge in the partial equations by adding electrons.

In first partial equation, the oxidation number of nitrogen decreases from +5 to +2, hence 3 electrons are added to the left side.

$$NO_3^- + 4H^+ + 3\bar{e} \longrightarrow NO + 2H_2O$$

In the second partial equation, the oxidation of sulphur increases from –2 to zero hence 2 electron are added to make it zero on the left

$$H_2S \longrightarrow S + 2H^+ + 2\bar{e}^-$$

Step-5: In order to equalize the electrons lost and gain, first partial equation is multiplied by 2 and second by 3.

$$2NO_3^- + 8H^+ + 6\bar{e} \longrightarrow 2NO + 4H_2O$$
$$3H_2S \longrightarrow 3S + 6H^+ + 6\bar{e}$$

Step-6: Cancel out the electron and add the partial equations.

$$\begin{array}{l} 2NO_3^- + 8H^+ + 6\bar{e} \longrightarrow 2NO + 4H_2O \\ \underline{\quad 3H_2S \longrightarrow 3S + 6H^+ + 6\bar{e} \quad} \\ 2NO_3^- + 3H_2S + 2H^+ \longrightarrow 2NO + 3S + 4H_2O \end{array}$$

This equation may be converted back to molecular form by combining NO_3^- and H^+

$$2HNO_3 + 3H_2S \longrightarrow 2NO + 3S + 4H_2O$$

Example 12.3

Balance the following equation in basic aqueous solution by ion electron method.

$$\mathbf{Cr(OH)_3 + SO_4^{-2} \longrightarrow CrO_4^{-2} + SO_3^{-2}}$$

Solution:

To balance a chemical equation, we first identify the elements which undergo change in their oxidation number. In the given equation Cr and S are undergoing oxidation number change.

Step-1: Split the given equation into two half reactions mentioning oxidation and reduction on the bases of either the oxidation number of Cr and S decreases or increases.

$$Cr(OH)_3 \longrightarrow CrO_4^{-2} \text{ (oxidation)}$$
$$SO_4^{-2} \longrightarrow SO_3^{-2} \text{ (reduction)}$$

Step-2: According to balancing rule in basic medium, we balance the oxygen atoms of first half equation by adding $5O\bar{H}$ on left hand side and hydrogen atoms are balanced by adding $4H_2O$ on right hand side.

$$Cr(OH)_3 + 5O\bar{H} \longrightarrow CrO_4^{-2} + 4H_2O$$

In second half equation, oxygen atoms are balanced by adding $2O\bar{H}$ on right hand side and hydrogen atoms are balanced by adding H_2O on left hand side.

$$SO_4^{-2} + H_2O \longrightarrow SO_3^{-2} + 2O\bar{H}$$

Step-3: Since the oxidation number of Cr increases from +3 to +6, the charges of first half equation are balanced by adding three electrons on right hand side.

$$Cr(OH)_3 + 5O\bar{H} \longrightarrow CrO_4^{-2} + 4H_2O + 3\bar{e}$$

On the other hand in second half equation the oxidation number of sulphur decreases from +6 to +4; this change must be balanced by adding two electrons on left hand side.

$$SO_4^{-2} + H_2O + 2\bar{e} \longrightarrow SO_3^{-2} + 2O\bar{H}$$

Step-4: For equalizing the number of electrons lost in first half equation and gain in second half equation, we must multiply first half equation by 2 and second half equation by 3.

$$2 \times [Cr(OH)_3 + 5O\bar{H} \longrightarrow CrO_4^{-2} + 4H_2O + 3\bar{e}]$$
$$3 \times [SO_4^{-2} + H_2O + 2\bar{e} \longrightarrow SO_3^{-2} + 2O\bar{H}]$$

Now add the two half equations and cancel out electrons as well as H_2O in both side to get the net balanced ionic equation.

$$\begin{array}{rcl} 2Cr(OH)_3 + 10\,O\bar{H} & \longrightarrow & 2CrO_4^{-2} + 8H_2O + 6\bar{e} \\ 3SO_4^{-2} + 6\bar{e} + 3H_2O & \longrightarrow & 3SO_3^{-2} + 6O\bar{H} \\ \hline 2Cr(OH)_3 + 4O\bar{H} & \longrightarrow & 2CrO_4^{-2} + 3SO_3^{-2} + 5H_2O \end{array}$$

Self Assessment

Balance the following equation by ion electron method.

(i) $Cr_2O_7^{-2} + Cl^{-} \rightarrow Cr^{+3} + Cl_2$ (acidic medium)

(ii) $MnO_4^{-} + SO_3^{-2} \rightarrow Mn^{+2} + SO_4^{-2}$ (basic medium)

12.1.4 Chemistry of some important oxidizing and reducing agents

Electrons are neither created nor destroyed in a chemical reaction therefore oxidation and reduction always occurs simultaneously.

Consider the oxidation reduction process in the following reaction.

$$\begin{array}{c}\text{(Oxidation)}\\ \overset{\circ}{Zn}_{(s)} + 2HCl^{-}_{(aq)} \qquad ZnCl^{+2}_{2(aq)} + \overset{\circ}{H}_{2(g)}\\ \text{(Reduction)}\end{array}$$

Zinc is one reactant that oxidizes to $ZnCl_2$ while HCl is other reactant which reduces to H_2. **"In any redox reaction the species that oxidizes the other substance and itself get reduced is known as oxidizing agent where as the species that reduces other substance but itself get oxidized is identified as reducing agent"**.

Do You Know?

Transmission of nerve impulse in biological system is an electrochemical process and was observed by an Italian scientist Luigi Galvani (1737-1798) during his investigation on frog.

Table 12.1 List of some redox reactions mentioning oxidizing and reducing agent

Redox Reaction	Oxidizing Agent	Reducing Agent
Oxidation $Cl_2 + H_2S \longrightarrow 2HCl + S$ Reduction	Cl_2	H_2S
Oxidation $CuO + H_2 \longrightarrow Cu + H_2O$ Reduction	CuO	H_2
Oxidation $Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$ Reduction	Fe_2O_3	CO
Oxidation $Al + H_2SO_4 \longrightarrow Al_2(SO_4)_3 + SO_2 + H_2O$ Reduction	H_2SO_4	Al
Oxidation $K_2Cr_2O_7 + 6KI + 7H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + 4K_2SO_4 + 3I_2 + 7H_2O$ Reduction	$K_2Cr_2O_7$	KI
Oxidation $2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 \longrightarrow 2MnSO_4 + K_2SO_4 + 10CO_2 + 8H_2O$ Reduction	$2KMnO_4$	$H_2C_2O_4$

12.2 ELECTRODE, ELECTRODE POTENTIAL AND ELECTROCHEMICAL SERIES

The production or use of electric current through a chemical change is generally carried out in electrochemical cell which is a system consisting of electrodes that dips into an electrolytic solution.

Electrolytic Cell

An electrolytic cell is an apparatus containing two metallic rods or foils known as electrodes dipped in an electrolytic solution and connected to a battery wherein the electric current is used to derive a non-spontaneous redox reaction. The electrode connected to the negative terminal of battery is called cathode, through which electrons enter the solution whereas the electrode connected to the positive terminal of battery is called anode, through which electrons leave the cell. The electrodes are basically metallic plates, rods or foils through which the current enters or leaves the electrolyte. Cathode is the negative electrode (Reductions occurs) whereas anode is the positive electrode (Oxidation occurs). The electrolyte spontaneously dissociates to produce ions within the solution. The positive ions are known as cations while the negative ions are known as anions.

When the electric current is passed through the solution, anions move towards anode where they lose electrons to get oxidized. On the other hand, cations move towards cathode where they gain electrons to become reduced. By this we can say that oxidation occurs at anode while reduction occurs at cathode.

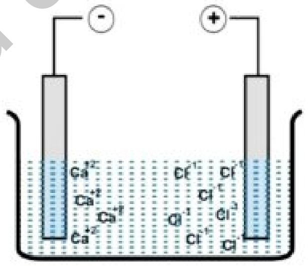


Fig 12.1: Process of electrolysis in an electrolytic cell

"The movement of cations and anions towards their respective electrodes accompanying all chemical changes in an electrolytic solution under the influence of electric current is known as electrolysis".

During the process of electrolysis, ions of electrolyte migrate towards their respective electrodes where they get oxidized or reduced. For example when aqueous calcium chloride is electrolyzed, the Ca$^+$ ions move towards cathode and the Cl$^-$ ions move towards anode.

$$Ca^{+2}_{(aq)} + 2\bar{e} \longrightarrow Ca_{(aq)} \text{ (Reduction at cathode)}$$

$$2Cl^{-}_{(aq)} \longrightarrow Cl_{2(g)} + 2\bar{e} \text{ (Oxidation at anode)}$$

Thus the reactions taking place in the electrolytic cell are redox reactions and the process of electrolysis remains continue in the electrolytic cell until all ions of the electrolyte change into neutral atoms.

Self Assessment

What is electrolysis? Describe the process of electrolysis for NaCl in an electrolytic cell.

Galvanic Cell

A Galvanic or voltaic cell is type of electrochemical cell in which current is generated by a spontaneous redox reaction. Galvanic cell is typically consist of two half cells which are inter connected electrically. Each half cell is made up of a strip of metal immersed into a solution of its metal ions.

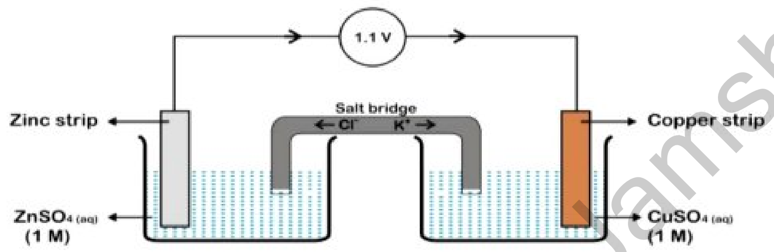


Fig 12.2: A Galvanic cell with zinc anode and copper cathode

"A salt bridge is a u-shaped glass tube in which an inert electrolyte is filled along with gel. It allows the flow of ions but prevent the mixing of solution". Thus maintain the electrical neutrality in each half cell.

The two half cell reactions and the net reaction can be written as

$$Zn_{(s)} \longrightarrow Zn^{+2}_{(aq)} + 2\bar{e} \text{ (Oxidation at zinc half cell)}$$

$$Cu^{+2}_{(s)} + 2\bar{e} \longrightarrow Cu_{(aq)} \text{ (Reduction at copper half cell)}$$

$$Zn_{(s)} + Cu^{+2}_{(s)} \longrightarrow Zn^{+2}_{(aq)} + Cu_{(aq)} \text{ (Net cell reaction)}$$

Galvanic cells are conveniently express in some short hand notations. For example Zinc-copper cell may be written as.

$$\underset{\textbf{(anode)}}{Zn_{(s)}} \,|\, Zn^{+2}_{(aq)} \underset{\textbf{salt bridge}}{||} Cu^{+2}_{(aq)} \,|\, \underset{\textbf{(cathode)}}{Cu_{(s)}}$$

Here single vertical line specifies the phase boundary between electrode and electrolytic solution where as double vertical lines indicate salt bridge.

Cell Potential

The electrical energy produce by voltaic cell is due to the electron flow from anode to cathode through an external wire. **"The driving force with which the electrons pushes out from anode into external circuit is known as electromotive force (emf) or cell potential or cell voltage".**

Just as each half cell reaction is a part of overall reaction, the potential of each half cell make up the overall emf of the cell. Thus, knowing the emf of the cell and electrode potential of any one of the half cell, we could obtained the other. The standard electrode potential of a single half cell is defined as **"The difference of potential created between metal electrode and 1 molar solution of its ions at 25°C and 1 atmospheric pressure"**. It is abbreviated by E° and measured in volt.

Electrode potential can be represented in term of oxidation potential or reduction potential. The capability of electrode to get oxidized in its electrolytic solution is known as oxidation potential where as the tendency of electrode to gain electrons and allows the positive ions of solution to deposit on it is called as reduction potential. IUPAC convention recommended that electrode potential is taken as reduction potential. Therefore while constructing a Galvanic cell, cathode should be of higher reduction potential and anode should be of lower reduction potential.

Do You Know?

Voltaic cell was first developed by Alessandro volta (1745-1827). He made it by fixing zinc and silver plates alternatively in a container and placed brine soaked card board between them. Since voltmeter was not invented at that time he checked the flow of current by hand shocked.

It is not possible to measure experimentally the electrode potential of a single electrode. The electrode potential of a single electrode can only be determine if it is coupled with another electrode having a known electrode potential. Chemists established an arbitrary standard known as reference electrode.

The most commonly used reference electrode is **standard hydrogen electrode (SHE)** which assigned as an electrode potential of 0.00 volt and thus the electrode potential of all other electrodes can be measured relative to it.

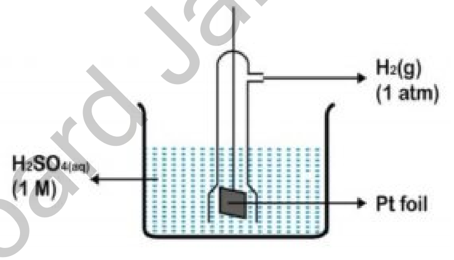


Fig. 12.3: Standard Hydrogen Electrode (SHE)

A standard hydrogen electrode (SHE) is a gas electrode and consists of a platinum rod coated with finely divided platinum which is immersed in 1M solution of H_2SO_4. Pure hydrogen gas is passed continuously through the solution under a pressure of 1 atm and 25°C. Platinum absorbs hydrogen gas on its surface. When it is connected to another half cell, the hydrogen gas at platinum electrode either pass into solution and form H^+ ions or the H^+ ions of solution reduced at platinum electrode to form hydrogen gas.

$$H_2 \longrightarrow 2H^+ + 2\bar{e} \text{ (Oxidation)}$$
$$2H^+ + 2\bar{e} \longrightarrow H_2 \text{ (Reduction)}$$

If oxidation takes place at platinum electrode, it serves as anode but if reduction occurs, it behaves as cathode.

Standard electrode potential of Galvanic cell (E°_{cell}) is the algebraic difference between the standard reduction potential of two half cells and can be expressed as

$$E^\circ_{cell} = E^\circ_{(cathode)} - E^\circ_{(anode)}$$

Experimental Determination of Electrode Potential of Zinc and Copper

Standard electrode potential of an electrode can be measured by using a reference electrode such as SHE. Let consider we want to determine the electrode potential of zinc. For this purpose we have to construct a voltaic cell made of Zinc–SHE electrodes. The first half cell consists of a strip of zinc immersed in 1M $ZnSO_4$ solution while the other half cell consists of platinum foil immersed in 1M H_2SO_4 solution at standard conditions.

A salt bridge is made of KCl jelly which completes the circuit between the two half cells and prevent the mixing of solutions. Both electrodes are connected to each other through an external wire by means of a voltmeter.

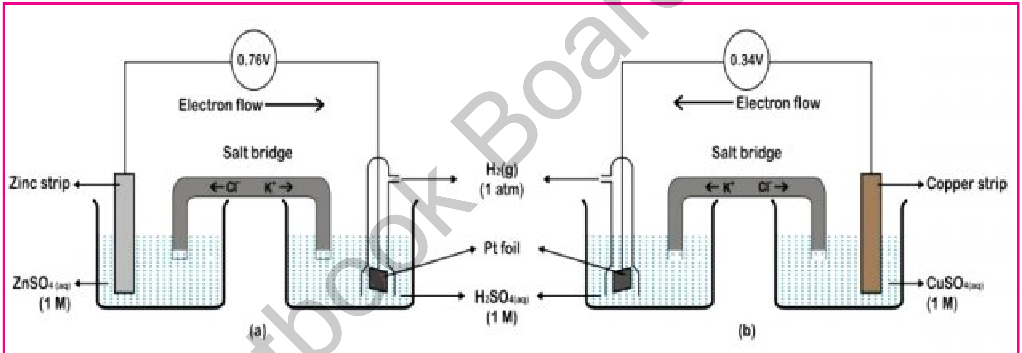
Whenever the construction is completed and Galvanic cell is operational, the voltmeter shows emf of the cell which comes out to be 0.76 volt. Now note the flow of electrons in the external circuit. It should be from zinc electrode to SHE. Thus electrons must have originated at zinc and zinc is anode where oxidation takes place.

Half cell reactions on zinc and SHE electrode are written as

$$Zn_{(s)} \longrightarrow Zn^{+2}_{(aq)} + 2\bar{e} \text{ (Oxidation at anode)}$$
$$2H^{+} + 2\bar{e} \longrightarrow H_2 \text{ (Reduction at cathode)}$$

The electrode potential of zinc is now determined as

$$E^{\circ}_{(cell)} = E^{\circ}_{(cathode)} - E^{\circ}_{(anode)}$$
$$0.76 = (0.0) - E^{\circ}_{(Zn)}$$
$$E^{\circ}_{(Zn)} = -0.76 \text{ volt}$$



$$Zn_{(s)} \longrightarrow Zn^{+2}_{(aq)} + 2\bar{e}$$
$$2H^{+} + 2\bar{e} \longrightarrow H_{2(g)}$$

$$H_{2(g)} \longrightarrow 2H^{+}_{(aq)} + 2\bar{e}$$
$$Cu^{+2} + 2\bar{e} \longrightarrow Cu_{(s)}$$

$Zn \mid Zn^{+2}(1M) \,||\, 2H^{+}(1M) | H_2$ (1 atm); Pt

H_2 (1 atm); Pt$| \, 2H^{+}(1M) \,||\, Cu^{+}(1M) | Cu$

Fig 12.4: Galvanic cell of (a) zinc-SHE couple (b) copper-SHE couple

The electrode potential of copper and other substances can be determined in the same way.

Electrochemical Series

Taking SHE as a reference electrode, chemists determine the electrode potential of many substances and arranged in the order of increasing reduction potential, is known as electro chemical series.

The E° value of each electrode in ECS represents its relative tendency to undergo reduction as compared to the hydrogen ion at standard conditions.

Some important features of electrochemical series are given below:

(i) Electrodes above hydrogen in ECS have negative electrode potential. They have stronger tendency to lose electron (oxidation) then hydrogen, these substance thus acts as reducing agent (anode).

(ii) Electrodes which are placed below hydrogen in ECS have positive electrode potential. They have greater ability to gain electrons (reduction) as compared to hydrogen and hence serve as oxidizing agent (cathode).

Table 12.2 Standard reduction potential at 25°C for some half reactions

Electrodes	Reduction Half – Reaction	E° (V)
Li^+/Li	$Li^+ + e^- \rightarrow Li$	-3.05
K^+/K	$K^+ + e^- \rightarrow K$	-2.93
Na^+/Na	$Na^+ + e^- \rightarrow Na$	-2.71
Mg^{2+}/Mg	$Mg^{2+} + 2e^- \rightarrow Mg$	-2.37
Zn^{2+}/Zn	$Zn^{2+} + 2e^- \rightarrow Zn$	-0.76
Fe^{2+}/Fe	$Fe^{2+} + 2e^- \rightarrow Fe$	-0.44
Cd^{2+}/Cd	$Cd^{2+} + 2e^- \rightarrow Cd$	-0.40
Ni^{2+}/Ni	$Ni^{2+} + 2e^- \rightarrow Ni$	-0.25
Pb^{2+}/Pb	$Pb^{2+} + 2e^- \rightarrow Pb$	-0.13
H^+/H_2	$2H^+ + 2e^- \rightarrow H_2$	0.000
Cu^{2+}/Cu	$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34
Ag^+/Ag	$Ag^+ + e^- \rightarrow Ag$	+0.80
MnO_2/Mn^{2+}	$MnO_2 + 4H^+ + 4e^- \rightarrow Mn^{2+} + 2H_2O$	+1.28
$Cr_2O_7^{2-}/Cr^{3+}$	$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	+1.33
Cl_2/Cl^-	$Cl_2 + 2e^- \rightarrow 2Cl^-$	+1.36
MnO_4/Mn^{2+}	$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	+1.51
H_2O_2/H_2O	$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	+1.78
$F_2/2F^-$	$F_2 + 2e^- \rightarrow 2F^-$	+2.87

Increasing strength of oxidizing agent ↓

Increasing strength of reducing agent ↑

12.3 BATTERIES

So far we have understood that how a Galvanic cell generate electricity. Indeed the current produce by it is not sufficient for commercial use, practically we combine two or more cells and make a battery.

"A battery consists of two or more Galvanic cells connected in series and is used to convert chemical energy into electrical energy by means of reduction-oxidation (redox) reactions".

Have you ever seen battery in your automobile car, or the devices like cellular phone, radio, torch, toys etc? You might note that these are light weight, compact in size and work at constant voltage, a commercial battery should fulfill all these criteria.

Batteries are classified into following two types.

12.3.1 Primary Cells/Battery

In this type of batteries redox reaction takes place in only one direction and cannot be reversed. Thus these batteries cannot be recharged or reused. When all amount of electrolyte present in the cell is consumed, they become dead. The most inexpensive and commonly used primary cell is dry cell which we often use in remote control, transistors, flash lights and many other domestic works.

Do You Know?

Technologically, electrochemistry plays an imperative role in many ways in our lives. For example

(i) Batteries that power a variety of appliances vehicles and devices become more compact light weight and consumable day by day due to the research progress in electrochemistry.

(ii) Other domains of modern science in which electrochemistry is significantly involves are electro refining, electroplating, corrosion, protection, electrophoresis etc.

Dry Cell

The common dry cell was first invented by a French chemist Leclanche. The outer body of this cell is made up of zinc which serves as anode where as a graphite rod located at the centre works as cathode. The whole zinc container is lined with porous paper which works as a separator. The region between cathode and anode is filled with a paste of MnO_2, Carbon, NH_4Cl and $ZnCl_2$.

When the cell starts working Zn anode oxidizes to Zn^{+2} ions whereas at graphite cathode Mn^{+4} ions reduces to Mn^{+3} ions.

$$Zn \longrightarrow Zn^{+2} + 2\bar{e} \text{ (anode)}$$

$$2NH_4^+ + 2MnO_2 + 2\bar{e} \longrightarrow Mn_2O_3 + 2NH_3 + H_2O \text{ (cathode)}$$

The electrons generated at anode flow out to the external circuit. This cell produces 1.5 volt electric current and become dead after complete utilizing zinc electrode. 0

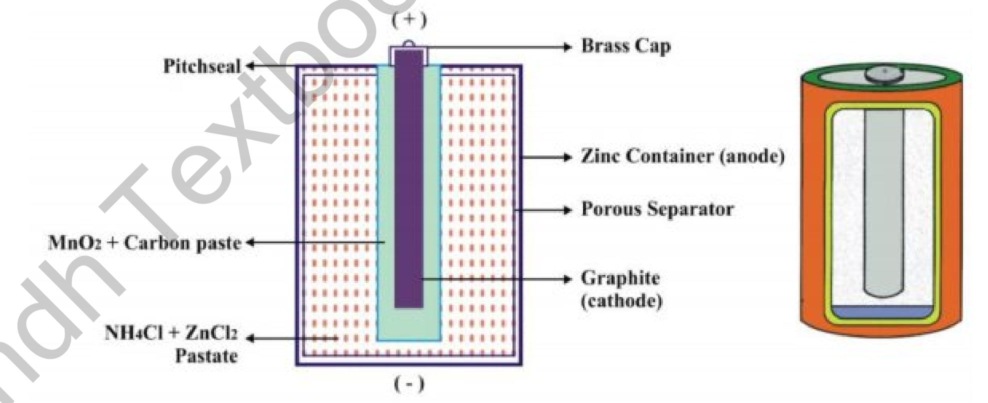


Fig 12.5: Structure of common dry cell

12.3.2 Secondary Battery

These batteries can be recharged by reversing the electricity flow through the cell by utilizing a source of external power supply after every use. Lead storage battery which is commonly known as car battery is an example of secondary battery.

A 12 volt car battery is made up of six Galvanic cells connected in a series each of which has an emf of 2 volt. All anode plates are made up lead (Pb) while all cathode plates consists of lead coated with PbO_2. Both groups of plates are alternatively suspended into a dilute solution of H_2SO_4 of specific gravity 1.25.
When the battery starts working, lead atoms at anode oxidize to form lead ions.

$$Pb_{(s)} \longrightarrow Pb^{+2}_{(aq)} + 2\bar{e} \text{ (Oxidation at anode)}$$

The Pb^{+2} ions combine with SO_4^{-2} ions to form solid $PbSO_4$ which is deposited on anode.

$$Pb^{+2}_{(aq)} + SO^{-2}_{4(aq)} \longrightarrow PbSO_{4(s)}$$

The electrons generate at anode pushes out into external circuit and then re-enter into cell from cathode (PbO_2) where PbO_2 reduces to Pb^{+2} ions.

$$PbO_{2(s)} + 4H^{+}_{(aq)} + 2\bar{e} \longrightarrow Pb^{+2}_{(aq)} + 2H_2O_{(l)} \text{ (Reduction at cathode)}$$

The Pb^{+2} ions again combine with SO_4^{-2} ions of electrolyte and produce solid $PbSO_4$ which is deposited at cathode plates.
The net chemical change at anode and cathode during discharge may be written as.

$$Pb_{(s)} + SO^{-2}_{4(aq)} \longrightarrow PbSO_{4(s)} + 2\bar{e} \text{ (anode)}$$
$$PbO_{2(s)} + 4H^{+}_{(aq)} + SO^{-2}_{4(aq)} + 2\bar{e} \longrightarrow PbSO_{4(s)} + 2H_2O_{(l)} \text{ (cathode)}$$

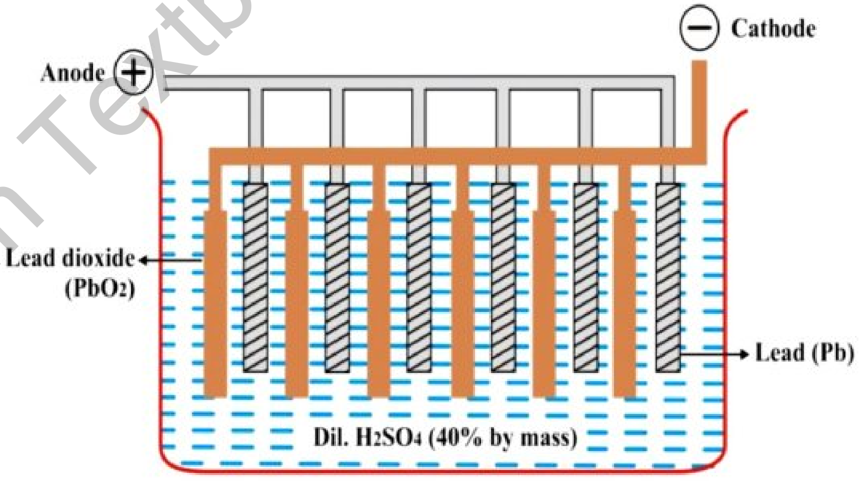


Fig 12.6: Structure of lead storage battery

As long as lead battery works, its electrolyte (H_2SO_4) uses up gradually which results in covering the electrodes with $PbSO_4$. Thus it becomes unable to release electricity and said to be discharge. This can be checked by lowering in the specific gravity of acid as well as drop of voltage.

How is car battery recharged?

When the battery is needed to be recharged, its anode (Pb) is connected to negative terminal and cathode (PbO_2) is connected to positive terminal of external power supply. In doing so, the redox reaction becomes reverse and may be written as

$$PbSO_{4(s)} + 2\bar{e} \longrightarrow Pb_{(s)} + SO^{-2}_{4(aq)}$$

$$PbSO_{4(s)} + 2H_2O_{(l)} \longrightarrow PbO_{2(s)} + 4H^{+}_{(aq)} + SO^{-2}_{4(aq)} + 2\bar{e}$$

Thus H^+ ions conc. increases gradually in the electrolyte until the specific gravity again reaches the original value and the voltage of the battery is restored.

12.3.3 Fuel Cell

A hydrogen oxygen fuel cell is unique type of Galvanic cell which is based on the reaction between hydrogen and oxygen to produce water and the heat release in the reaction is use to produce electricity. Unlike other batteries, it cannot store reactants hence reactants are fed continuously which utilize in the reaction and the product thus formed remove out continuously. The most familiar Fuel cell is hydrogen oxygen fuel cell. It consists of two porous carbon electrodes having a thin platinum paste. Platinum serves as catalyst. The compartment between the two electrodes is filled with concentration solution of KOH which works as electrolyte. Hydrogen gas fed into the cell from anode side and oxygen from cathode side. These gases after bubbling through their concerned electrode enter into electrolytic solution.

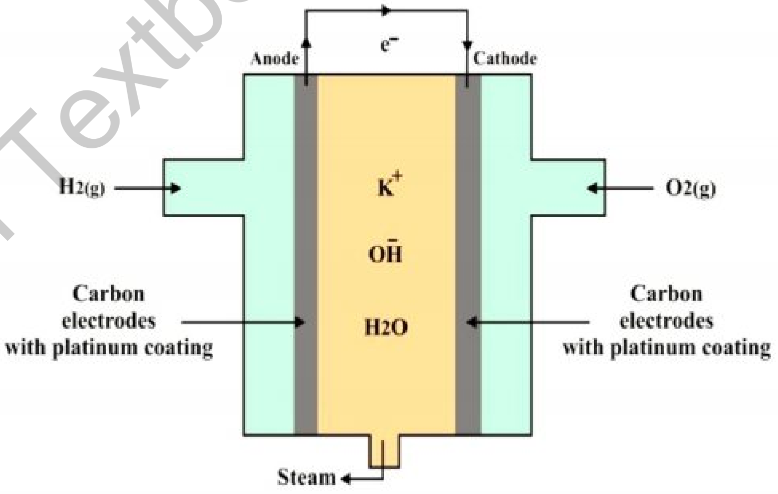


Fig 12.7: Structure of hydrogen oxygen fuel cell

The reaction at cathode and anode are given below:

$$2H_{2(g)} + 4O\bar{H}_{(aq)} \longrightarrow 4H_2O_{(l)} + 4\bar{e} \text{ (anode)}$$
$$O_{2(g)} + 2H_2O_{(l)} + 4\bar{e} \longrightarrow 4O\bar{H}_{(aq)} \text{ (cathode)}$$
$$\overline{\quad 2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)} \text{ (overall reaction)} \quad}$$

12.4 CORROSION AND ITS PREVENTION

We often noted that metals on exposure to air lose their luster and strength. A brown, green or grayish layer develops on their surface which makes them dull. It is due to chemical interaction between metal and the environment such as oxygen of air and moisture. **"A spontaneous process in which surface atoms of metals get oxidized (harmful oxides) due to the action of surrounding medium is known as corrosion"**. Generally, corrosion occurs on the surface of metal but when the upper surface gets corroded, the atoms in the inner layer get exposed to air and become corroded. This process remains continue up to a certain depth which makes the metal brittle, and weak. However some metals are self protective to corrosion since only the atoms of outer layer oxidize.


Fig 12.8: Corrosion of Iron

The most familiar type of corrosion which we see in daily life is the **"rusting of iron"**. Rust is a brown powderly material produce on the surface of iron appliances due to an oxidation reaction of iron atoms with moist air.

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

Various theories describes the phenomena of corrosion but the most adequate is the electrochemical theory which tells that metal atoms serves as cathode and anode and water containing O_2 and CO_2 works as electrolyte which involves in the flow of electrons. In the light of this theory **"corrosion is an electrochemical process"**.

Prevention against corrosion

We aware that iron, copper and various other metals are essentially used in many commercial as well as domestic purpose. To keep them for long period, they should be protected against corrosion by using certain temporary or permanent techniques. Iron Gate of our house is painted so that paint resists the contact of moist air with the metal atoms. Coating of grease or oil in machineries and tools are commonly seen for corrosion control. Often a thin layer of another metal such as zinc, tin or chromium is coated on the metal. For more permanent safety, alloying of metals is carried out.

Galvanizing

"The process of coating a thin layer of zinc on a metal is known as galvanizing". Since zinc is placed above iron in ECS, it preferably oxidizes and consumes rather than iron and thus protects the iron against corrosion. Galvanizing is carried out either by spraying molten zinc on the surface of iron made material or by dipping the iron sheets into molten zinc.

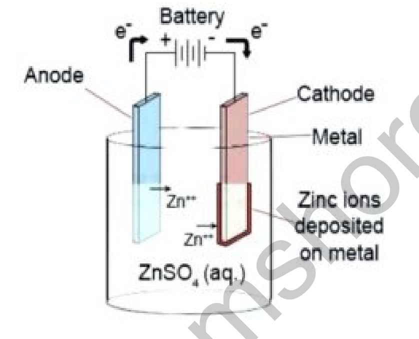


Fig 12.9: Galvanizing of metal sheet

Electroplating

We have studied in sec 12.2 that during the process of electrolysis metal cat ions of electrolytic solution deposited on cathode. Thus a thin layer of tin, chromium etc can be coated on given metal, this process is known as electroplating. Its most common use is electroplating of tin. **"Electroplating is the coating of one metal on the surface of another by involving electrolysis"**. Vegetable oil, food and juice containers are generally tin plated. Tin plating protects iron as long as it remains coated, if scratched then iron exposed to air and starts to get corrosion.

In the electrolytic process, the iron sheets after cleaning, washing and drying are suspended into a bath containing a mixture of stannous chloride and hydrochloric acid. Pure tin is made the anode and the iron sheet works as cathode. On passing the current through the bath, tin starts depositing on the iron sheet and thus iron sheets are tinned electrolytically.

Society, Technology and Science

Solar cell as a source of energy

Solar cell or photovoltaic cell is a device which converts solar energy into useable electricity. The material of most of the solar cell is silicon which serves as semiconductor. When exposed to sun light, it absorbs radiations and transfer energy of photons into electrons of silicons. The electrons after absorbing this energy jump out into the external circuit.

Solar technology provides us an opportunity to make saving in electricity bills. Although the cost of solar panels installation is high but it produces free electricity. Further, remote areas which are beyond electric power transmission, this method of renewable energy becomes popular day by day.

Activity

The combination of copper and aluminum strips in the citric acid of the lemon serves as the source of electric energy in this activity.
Just insert aluminum foil and copper coin in the lemon such that they remain as far as possible from each other. Now connect these metals to a bulb with the help of wires. The lemon's citric acid serves as an electrolyte. Since aluminum is located in the upper side of ECS, so it oxidizes and releases electrons to the external circuit. Copper on the other hand, undergoes reduction by gaining the electrons and thus bulb is lit by an electric current.

SUMMARY
with Key Terms

- **Oxidation** is a chemical process in which electrons are lost by an atom or ion. During this process oxidation number of an element increases.
- **Reduction** is a chemical process in which electrons are gained by an atom or ion. During this process oxidation number of an element decreases.
- **Oxidizing agent** is the specie which oxidizes the other substance and itself get reduced in a redox reaction. Stronger oxidizing agents found in the lower region of ECS. Thus strongest oxidizing agent is fluorine.
- **Reducing agent** is the specie which reduces the other substance but itself get oxidized in a redox reaction. Stronger reducing agent is located on upper region of ECS. Thus strongest reducing agent is Li.
- **Redox reactions** are associated with electron transfer from one species to another. Each redox reaction can be broken into two half reactions, one comprises with the loss of electron and other with the gain of electrons.
- **Electrochemical cell** is a system in which electric current is either producing or use through chemical change.
- **Electrolysis** is the process in which a non spontaneous reaction takes place at the expense of electric energy. During this process ions of electrolyte migrate towards their respective electrodes where they get oxidized or reduced.

- **Galvanic cell** is a device in which electricity is generated by spontaneous redox reaction. It consists of two half cells and each is made up of a strip of metal immersed into a solution of its metal ions. Cathode in this cell is positive and anode is negative.

- **Salt bridge** is a U-shaped glass tube is which an inert electrolyte is filled along with gel. It allows the flow of ions but prevent the mixing of solution.

- **Cell Potential** (E°_{cell}) of a Galvanic cell is the deriving force with which the electrons push out from anode into external circuit. It is measured by connecting two half cells through a voltmeter.

- **Standard electrode potential** (E°) is the difference of potential created between a metal electrode and one molar solution of its ions at 25°C and 1 atmospheric pressure.

- **Standard hydrogen electrode (SHE)** is a reference electrode which assigned as electrode potential of 0.0 volt. It consists of a platinum rod immersed in 1M acid solution where pure hydrogen gas at 1 atmospheric pressure and 25°C is passed.

- **Electrochemical series (ECS)** is an arrangement of various electrode potential in order of their increasing values. All the electrodes above hydrogen in ECS have negative values and they are reducing agent where as below hydrogen electrode potential values are positive indicating that they are oxidizing agent.

- **Corrosion** is electrochemical process in which atoms on the metal surface get oxidized due to environment oxygen and moisture.

- **Galvanizing** is the coating of thin layer of zinc on the metal to protect it form corrosion.

- **Electro tinning** is the coating of tin on metal sheet by using the process of electrolysis. It helps in preventing a metal from corrosion.

- **Battery** is the source of direct current and construct by connecting two or more galvanic cells.

- **Primary batteries/Cells** are not rechargeable; thus when their chemicals have been consumed, they stop doing chemical reactions.

- **Secondary batteries/Cells** are galvanic cells in which chemical reactions are easily being reversible. These cells can be recharged by flowing current in reverse direction.

- **Dry Cell** is a primary cell in which metallic zinc is oxidized to Zn^{+2} ions and liberates electrons which flow along the container to the external circuit.

- **Lead storage battery** is a portable secondary battery use in automobile in which lead serves as anode and lead oxide (PbO_2) works as cathode.

- **Fuel Cell** is a special type of Galvanic cell which generates electricity by chemical reactions but a continuous supply of reactants and a continuous removal of product are required.

EXERCISE

Multiple Choice Questions

1. Choose the correct answer

(i) The outer body of dry cell serves as anode, it is made up of:
(a) Copper (b) Zinc
(c) Lead (d) Iron

(ii) The conduction of electricity through an electrolytic solution is due to the flow of:
(a) Electrons (b) Ions
(c) Atoms (d) Molecules

(iii) During electrolysis, the reaction that takes place at anode is:
(a) Oxidation (b) Reduction
(c) Hydrolysis (d) Simultaneous oxidation and reduction

(iv) This statement is not correct for lead storage battery:
(a) It can be recharged (b) It is a primary battery
(c) Anode is made up of lead (d) Cathode is made up of lead oxide

(v) In Zn-SHE voltaic cell, the half reaction occurs at anode is:
(a) $Zn^{+2} + 2\bar{e} \longrightarrow Zn$ (b) $Zn \longrightarrow Zn^{+2} + 2\bar{e}$
(c) $2H^{+} + 2\bar{e} \longrightarrow H_2$ (d) $H_2 \longrightarrow 2H^{+} + 2\bar{e}$

(vi) The strongest oxidizing agent in the electro chemical series is:
(a) Li (b) H_2
(c) Cu (d) F_2

(vii) Galvanized rode of iron is coated with:
(a) Nickel (b) Zinc
(c) Chromium (d) Carbon

(viii) Fuel cell is a typical Galvanic cell which is based on the reaction between:
(a) Nitrogen and oxygen (b) Hydrogen and oxygen
(c) Methane and oxygen (d) Hydrogen and zinc

(ix) Oxidation number of Cr in $Na_2Cr_2O_7$ is:
(a) + 3 (b) + 6
(c) + 8 (d) + 12

(x) Which of the following half cell reaction show oxidation:
(a) $Fe^{+3} \rightarrow Fe^{+2}$ (b) $Cl_2 \rightarrow 2Cl^{-}$
(c) $SO_4^{-2} \rightarrow SO_4^{-3}$ (d) $Zn \rightarrow Zn^{+2}$

Short Questions

1. Define the following:
   - Primary and secondary cell
   - Oxidizing agent and reducing agent
   - Redox reactions
   - Oxidation and reduction
   - Oxidation number

2. What is meant by oxidation number? Determine the oxidation number in following.
   (i) Cr in H_2CrO_4 (ii) S in $K_2S_4O_6$
   (iii) Fe in Fe_3O_4 (iv) Cl in $HClO_4$

3. Define the term standard electrode potential and hydrogen electrode.

4. In the process of electroplating the item to be plated is made cathode, give reason?

5. What is corrosion? What causes it to form? What can be done to prevent its formation?

6. How can you define an electrochemical series? Give its properties.

Descriptive Questions

1. (a) What is meant by electrode potential and standard Hydrogen electrode (SHE).
   (b) Describe how the electrode potential of copper is determined.

2. Sketch a copper-zinc Galvanic cell, write the cell reaction and show the direction of electron flow.

3. What is the difference between a primary cell and secondary cell sketch a diagram of dry cell and explain its working.

4. Balance the following equations by ion electron method.
   (i) $Cr_2O_7^{-2} + I_2 \longrightarrow Cr^{+3} + IO_3^{-}$ (acidic medium)
   (ii) $MnO_4^{-} + SO_3^{-2} \longrightarrow Mn^{+2} + SO_4^{-2}$ (basic medium)
   (iii) $MnO_4^{-} + Cl^{-} \longrightarrow Mn^{+2} + Cl_2$ (acidic medium)
   (iv) $Cl_2 + O\bar{H} \longrightarrow Cl^{-} + ClO_3^{-} + H_2O$ (basic medium)
   (v) $MnO_4^{-} + C_2O_4^{-2} + H^{+} \longrightarrow Mn^{+2} + CO_2 + H_2O$ (acidic medium)
   (vi) $Fe^{+2} + Cr_2O_7^{-2} + H^{+} \longrightarrow Fe^{+3} + Cr^{+3} + H_2O$ (acidic medium)

MCQS ANSWER KEYS

Chap #	MCQs No.									
	(i)	(ii)	(iii)	(iv)	(v)	(vi)	(vii)	(viii)	(ix)	(x)
1	c	d	a	a	a	c	a	b	b	b
2	b	c	d	d	c	b	b	c	a	a
3	c	b	d	a	c	c	c	a	d	c
4	d	b	c	c	b	d	d	d	a	c
5	d	a	c	b	d	b	a	b	a	a
6	d	c	c	c	b	d	a	c	a	c
7	a	c	d	b	d	a	d	c	a	a
8	c	c	d	d	c	a	c	d	b	c
9	c	a	c	c	a	c	b	d	b	b
10	d	c	c	d	b	b	d	d	c	b
11	d	b	c	c	c	a	a	c	c	a
12	b	b	a	b	b	d	b	b	b	d

APPENDIX - 1

Multiples and Submultiples of SI Units

Prefixes	Symbols	Multiplying Factor	
tera	T	10^{12}	1 000 000 000 000
giga	G	10^{9}	1 000 000 000
mega	M	10^{6}	1 000 000
kilo	K	10^{3}	1 000
hecto	H	10^{2}	100
deca	Da	10	10
deci	D	10^{-1}	0.1
centi	C	10^{-2}	0.01
milli	M	10^{-3}	0.001
micro	U	10^{-6}	0.000 001
nano	n	10^{-9}	0.000 000 001
pico	p	10^{-12}	0.000 000 000 001

APPENDIX - 2

Atomic Numbers & Atomic Weights

Element	Symbol	Atomic Number	Atomic Weight
Hydrogen	H	1	1.008
Helium	He	2	4.003
Lithium	Li	3	6.938
Beryllium	Be	4	9.0121
Boron	B	5	10.821
Carbon	C	6	12.0116
Nitrogen	N	7	14.007
Oxygen	O	8	15.999
Fluorine	F	9	18.998
Neon	Ne	10	20.179
Sodium	Na	11	22.989
Magnesium	Mg	12	24.307
Aluminum (aluminium)	Al	13	26.9815385
Silicon	Si	14	28.086
Phosphorus	P	15	30.973
Sulfur (sulphur)	S	16	32.059
Chlorine	Cl	17	35.446
Argon	Ar	18	39.948
Potassium	K	19	39.098
Calcium	Ca	20	40.078

Element	Symbol	Atomic Number	Atomic Weight
Scandium	Sc	21	44.955
Titanium	Ti	22	47.867
Vanadium	V	23	50.941
Chromium	Cr	24	51.996
Manganese	Mn	25	54.938
Iron	Fe	26	55.845
Cobalt	Co	27	58.933
Nickel	Ni	28	58.693
Copper	Cu	29	63.546
Zinc	Zn	30	65.380
Gallium	Ga	31	69.723
Germanium	Ge	32	72.630
Arsenic	As	33	74.921
Selenium	Se	34	78.971
Bromine	Br	35	79.907
Krypton	Kr	36	83.798
Rubidium	Rb	37	85.467
Strontium	Sr	38	87.62
Yttrium	Y	39	88.905
Zirconium	Zr	40	91.224

Element	Symbol	Atomic Number	Atomic Weight
Niobium	Nb	41	92.906
Molybdenum	Mo	42	95.950
Technetium	Tc	43	97
Ruthenium	Ru	44	101.07
Rhodium	Rh	45	102.905
Palladium	Pd	46	106.42
Silver	Ag	47	107.868
Cadmium	Cd	48	112.414
Indium	In	49	114.818
Tin	Sn	50	118.710
Antimony	Sb	51	121.760
Tellurium	Te	52	127.600
Iodine	I	53	126.904
Xenon	Xe	54	131.293
Cesium (caesium)	Cs	55	132.905
Barium	Ba	56	137.327
Lanthanum	La	57	138.905
Cerium	Ce	58	140.116
Praseodymium	Pr	59	140.907
Neodymium	Nd	60	144.242

Element	Symbol	Atomic Number	Atomic Weight
Promethium	Pm	61	145
Samarium	Sm	62	150.36
Europium	Eu	63	151.964
Gadolinium	Gd	64	157.25
Terbium	Tb	65	158.925
Dysprosium	Dy	66	162.500
Holmium	Ho	67	164.930
Erbium	Er	68	167.259
Thulium	Tm	69	168.934
Ytterbium	Yb	70	173.045
Lutetium	Lu	71	174.966
Hafnium	Hf	72	178.49
Tantalum	Ta	73	180.947
Tungsten (wolfram)	W	74	183.84
Rhenium	Re	75	186.207
Osmium	Os	76	190.23
Iridium	Ir	77	192.217
Platinum	Pt	78	195.084
Gold	Au	79	196.966
Mercury	Hg	80	200.592

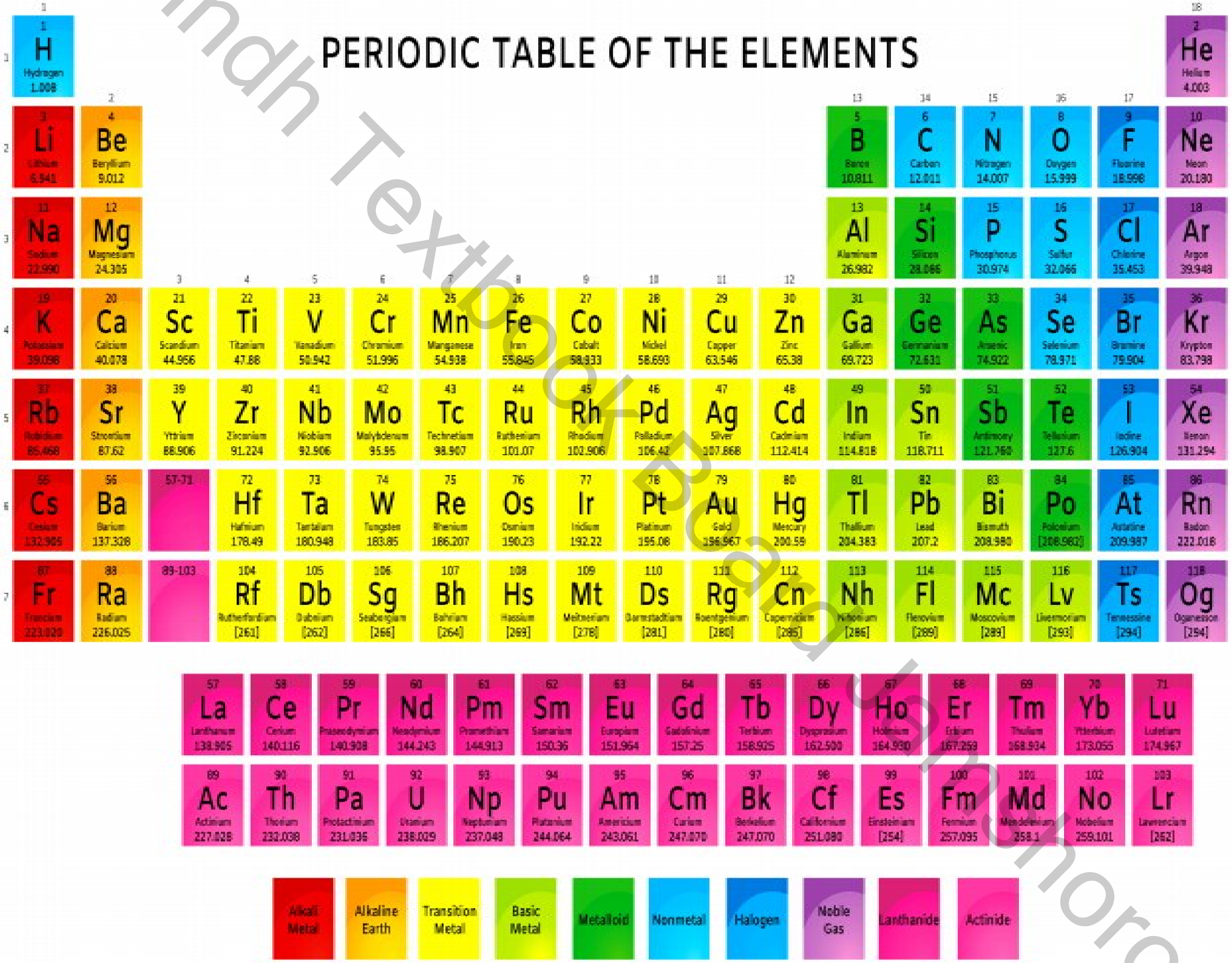
Element	Symbol	Atomic Number	Atomic Weight
Thallium	Tl	81	204.385
Lead	Pb	82	207.2
Bismuth	Bi	83	208.980
Polonium	Po	84	209
Astatine	At	85	210
Radon	Rn	86	222
Francium	Fr	87	223
Radium	Ra	88	226
Actinium	Ac	89	227
Thorium	Th	90	232.037
Protactinium	Pa	91	231.035
Uranium	U	92	238.028
Neptunium	Np	93	237
Plutonium	Pu	94	244
Americium	Am	95	243
Curium	Cm	96	247
Berkelium	Bk	97	247
Californium	Cf	98	251
Einsteinium	Es	99	252
Fermium	Fm	100	257

Element	Symbol	Atomic Number	Atomic Weight
Mendelevium	Md	101	258
Nobelium	No	102	259
Lawrencium	Lr	103	262
Rutherfordium	Rf	104	263
Dubnium	Db	105	268
Seaborgium	Sg	106	271
Bohrium	Bh	107	270
Hassium	Hs	108	270
Meitnerium	Mt	109	278
Darmstadtium	Ds	110	281
Roentgenium	Rg	111	281
Copernicium	Cn	112	285
Ununtrium	Uut	113	286
Flerovium	Fl	114	289
Ununpentium	Uup	115	289
Livermorium	Lv	116	293
Ununseptium	Uus	117	294
Ununoctium	Uuo	118	294

APPENDIX - 3

Constant Values

Physical Constant	Symbols	Values
Speed of light	C	3×10^8 m/s
Planck constant	H	6.625×10^{-34} J.S
Boltzmann constant	K	1.38×10^{-23} J/K
Universal gas constant	R	8.314 J/(mol.K) 0.082 atm dm^3/mol.K
Avogadro's number	N_A	6.023×10^{23}
Charge of electron	E	1.602×10^{-19} Coulomb
Permitivity of vacuum	$\in_0$	8.84×10^{-12} C^2/J.m
Mass of electron	m_e	9.1×10^{-31} kg
Mass of proton	m_p	1.6726×10^{-27} kg
Mass of neutron	m_n	1.6749×10^{-27} kg
Rydberg constant	R_h	1.09678×10^7 m^{-1}
Bohr radius	a_0	0.529×10^{-10} m
Molar Volume	V(STP)	22.4dm^3
Standard Temperature	T (STP)	273 K = 0°C
Standard Pressure	P (STP)	101325 Pa = 1 atm
Standard Hydrogen Electrode	SHE	0 volt
Density of water at 4°C	ρ_{H2O}	1 g/cm^3
Specific heat of water	C_{H2O}	4200 J/Kg.K
Ionization constant of water	KW(125°C)	1×10^{-14}



PERIODIC TABLE OF THE ELEMENTS

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H Hydrogen 1.008																	2 He Helium 4.003
2	3 Li Lithium 6.941	4 Be Beryllium 9.012											5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180
3	11 Na Sodium 22.990	12 Mg Magnesium 24.305											13 Al Aluminum 26.982	14 Si Silicon 28.086	15 P Phosphorus 30.974	16 S Sulfur 32.066	17 Cl Chlorine 35.453	18 Ar Argon 39.948
4	19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.88	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Capper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.631	33 As Arsenic 74.922	34 Se Selenium 78.971	35 Br Bromine 79.904	36 Kr Krypton 83.798
5	37 Rb Rubidium 85.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.95	43 Tc Technetium 98.907	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.414	49 In Indium 114.818	50 Sn Tin 118.711	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.904	54 Xe Xenon 131.294
6	55 Cs Cesium 132.905	56 Ba Barium 137.328	57-71	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.85	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.967	80 Hg Mercury 200.59	81 Tl Thallium 204.383	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium [208.982]	85 At Astatine 209.987	86 Rn Radon 222.018
7	87 Fr Francium 223.020	88 Ra Radium 226.025	89-103	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [278]	110 Ds Darmstadtium [281]	111 Rg Roentgenium [280]	112 Cn Copernicium [285]	113 Nh Nihonium [286]	114 Fl Flerovium [289]	115 Mc Moscovium [289]	116 Lv Livermorium [293]	117 Ts Tennessine [294]	118 Og Oganesson [294]

57 La Lanthanum 138.905	58 Ce Cerium 140.116	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.243	61 Pm Promethium 144.913	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.500	67 Ho Holmium 164.930	68 Er Erbium 167.259	69 Tm Thulium 168.934	70 Yb Ytterbium 173.055	71 Lu Lutetium 174.967
89 Ac Actinium 227.028	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium 237.048	94 Pu Plutonium 244.064	95 Am Americium 243.061	96 Cm Curium 247.070	97 Bk Berkelium 247.070	98 Cf Californium 251.080	99 Es Einsteinium [254]	100 Fm Fermium 257.095	101 Md Mendelevium 258.1	102 No Nobelium 259.101	103 Lr Lawrencium [262]

Alkali Metal	Alkaline Earth	Transition Metal	Basic Metal	Metalloid	Nonmetal	Halogen	Noble Gas	Lanthanide	Actinide