SYLLABUS

MAHARISHI DAYANAND UNIVERSITY, ROHTAK

PHYSICAL CHEMISTRY

B.Sc.–2nd (4th Semester)

Time : 3 Hrs. *Marks : 30*

Note : *Examiner will set nine questions and the candidates will be required to attempt five questions in all. Questions number one will be compulsory containing six short answer type questions convering the entire syllabus and will be of six marks. Further, examiner will set two questions from each section and the candidates will be required to attempt one question from each section which will be of six marks each.*

SECTION-A

Thermodynamics-III

Second law of thermodynamics, need for the law, different statements of the law, Carnot's cycles and its efficiency. Carnot's theorem. Thermodynamics scale of temperature. Concept of entropy - entropy as a state function, entropy as a function of V & T, entropy as a function of P & T, entropy change in physical change, entropy as a criteria of spontaneity and equilibrium. Entropy change in ideal gases and mixing of gases.

SECTION-B

Thermodynamics-IV

Third law of thermodynamics : Nernst heat theorem, statement of concept of residual entropy, evaluation of absolute entropy from heat capacity data. Gibbs and Helmoholtz functions; Gibbs function (G) and Helmholtz function (A) as thermodynamic quantitites, A & G as criteria for thermodynamics equilibrium and spontaneity, their advantage over entropy change. Variation of G and A with P, V and T.

SECTION-C

Electrochemistry-IV

Electrolytic and Galvanic cells : reversible & irreversible cells, conventional representation of electrochemical cells. EMF of cell and its measurement. Weston standard cell, activity and activity coefficients.

Calculation of thermodyanmics quantities of cell reaction (ΔG, ΔH & K).

Types of reversible electrodes : metal-metal ion gas electrode, metal-insoluble salt anion and redox electrodes. Electrode reactions, Nernst equations, derivation of cell EMF and single electrode potential. Standard Hydrogen electrode, reference electrodes, standard electrodes potential, sign conventions, electrochemical series and its applications.

SECTION-D

Electrochemistry-IV

Concentration cells with and without transference, liquid junction potential, application of EMF measurement *i.e.*, valency of ions, solubility product activity coefficient, potentiometric titration (acid-base and redox). Determination of pH using Hydrogen electrode. Quinhydrone electrode and glass electrode by poentiometric methods.

Note : This is only an outline of the syllabus for Complete and correct see at University Syllabus.

CONTENTS

1

THERMODYNAMICS

(Second Law of Thermodynamics)

Limitation of first law of Thermodynamics—Need for the second law of Thermodynamics

First law of thermodynamics deals with the conservation and conversion of energy. According to first law, when a thermodynamic process is carried out, the energy is neither gained nor lost. Energy only transforms from one form into another form and the energy balance is maintained. There are various phenomenon which cannot be explained by the first law of thermodynamic. The first law is not sufficient and posseses certain limitations which are discussed below :

1. First law does not explain the direction of flow of Heat : First law of thermodynamic give relationship between the heat absorbed and the work done by the system. But according to first law it is possible to heat water using ice without external agencies (fig-1) the first law is unable to tell the direction of flow of heat. If water get heated by using ice the following processes can be occured.

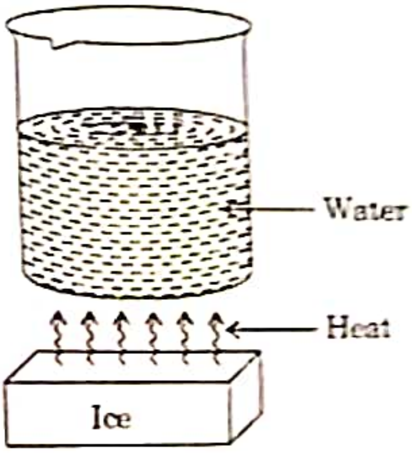


Fig. 1. Non Spontaineity of a Process

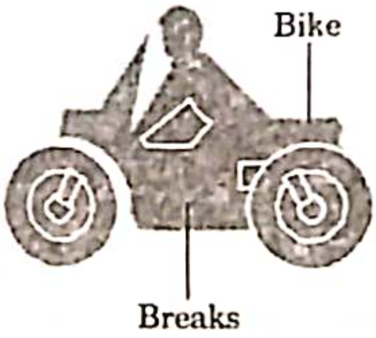


Fig. 2. Conversion of K.E. into Heat Energy

(i) Consider, A running vehicle stopped by applying breaks, the kinetic energy of vehicle changes into heat energy (fig-2) because breakes get heated up.

The increase in energy of breaks, according to first law of thermodynamics. But actually the reverse process *i.e.* cooling of breaks cannot be converted back into mechanical work.

(ii) Similarly on sliding a block down a rough plane, (fig-3) it become warmer. But the reverse process where the block slide up the plane and become cooler is not true.

(iii) Fuels burns in air and to form the products (fig-4). Once the fuel burnt cannot be converted back into its original form.

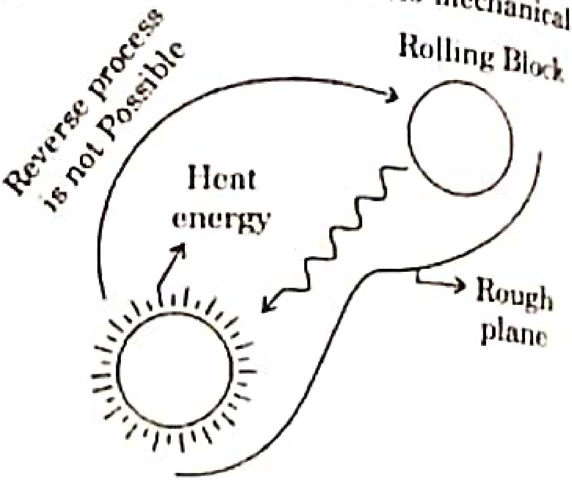


Fig. 3. Sliding of Block along the rough Plane

(iv) Churring of a liquid by paddle, rises the temperature of the vessel (fig. 5) This liquid cannot be change into its original form on cooling.

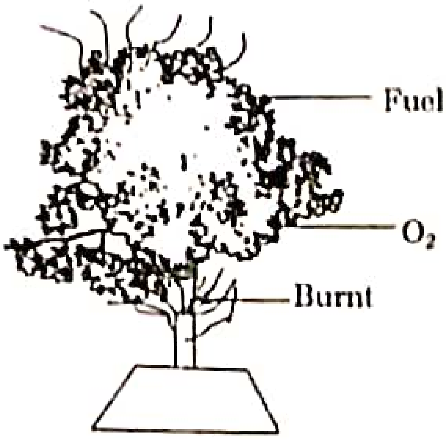


Fig. 4. Burning of fuel

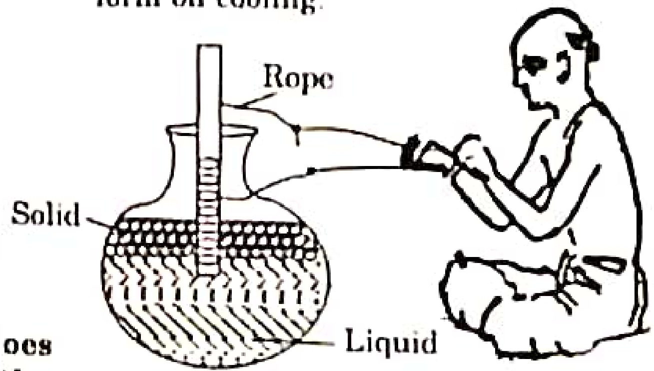


Fig. 5. Churring of Liquid

2. The first law of thermodynamic does not give any information about the spontaineity of a process : There are many processes which take place in one direction only, but cannot proceed in reverse direction, for examples

(i) Flow of water from higher level to lower level (fig-6) and the reverse of this process is not possible without using external agencies such as electric motor.

(ii) Flow of heat from warmer body to colder body but there reverse is not true (fig-7).

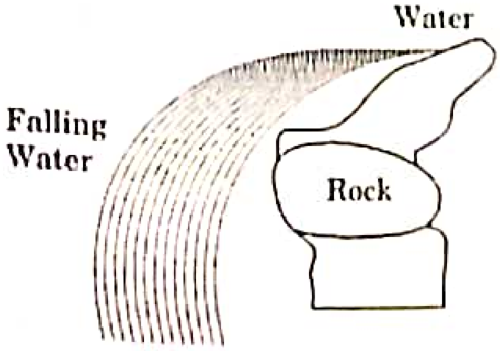


Fig. 6. Flow of Water down hill

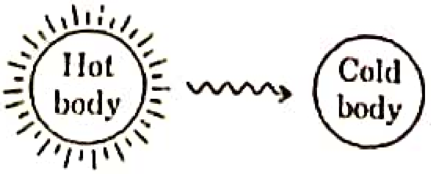


Fig. 7. Flow of Heat

Thermal or Heat reservoir

3

It is a part of environment that can exchange heat energy with a system. Its heat capacity value is very large and its temperature not affected by the quantity of heat transferred to or from it. Its temperature remain constant because transfer of heat to or from it is a very slow process ∴ it is quasi static. The thermal reservoir that supplies heat is called **heat source** while the reservoir which is at low temperature, to which heat is transferred is called **heat sink** fig 12.

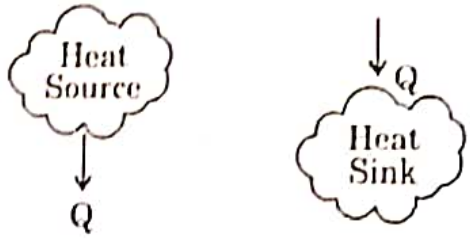


Fig. 12. Heat Source and Heat Sink

Example : Sun is the heat reservoir which is at high temperature while atmospheric air, ocean and river act as heat sink fig. 13.

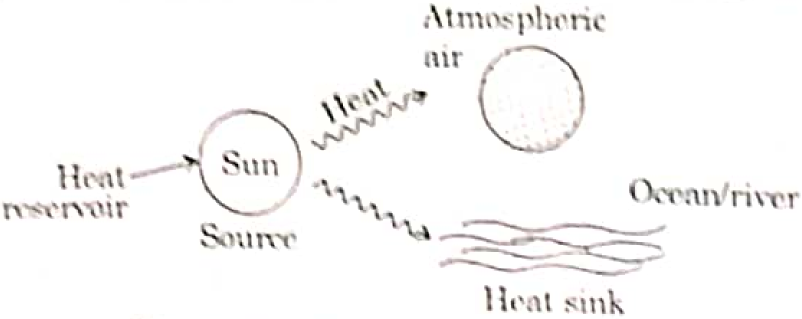


Fig. 13. Heat Source and Heat sink

Heat Engine, Refrigerator and Heat Pump

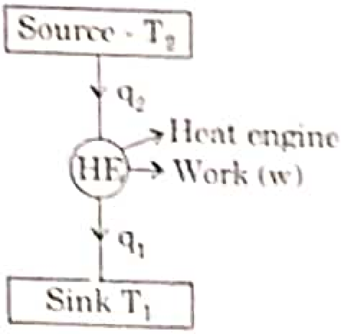


Fig. 14. Heat source and Heat sink

Heat engine : It is a device that used for continuous production of work from heat when operating in a cyclic process (fig. 14).

A heat engine characterises by the following features :

1. Absorption of heat q_2 from a source of high temperature, T_2
2. Partial conversion of heat into mechanical work.
3. Transfer of remaining heat, q_1 to a low temperature T_1, sink.
4. And its cyclic operation, so that, working substance flowing through the engine.

The functioning of any machine can be expressed as the ratio of net work output to the total heat supplied. This ratio is called as thermal efficiency (η). It is the measure of degree of utilization of heat received in a heat engine. The heat efficiency (η) given as

$$\eta = \frac{\text{net work output}}{\text{total heat supplied}}$$

According to first law of thermodynamics, the heat engine that undergoes a cyclic change gives

$$w = q_2 - q_1$$

$$\therefore \quad \eta = \frac{q_2 - q_1}{q_2} = 1 - \frac{q_1}{q_2}$$

So, thermal efficiency of a heat engine (HE) operating between two thermal reservoirs (Source and Sink) is always less than unity. To increase the thermal efficiency (η).

it is necessary to reduce q_1 (heat transferred to sink) so that q_2 remain constant. Thermal efficiency become equal to unity if $q_2 \to \infty$ and $q_1 = 0$.

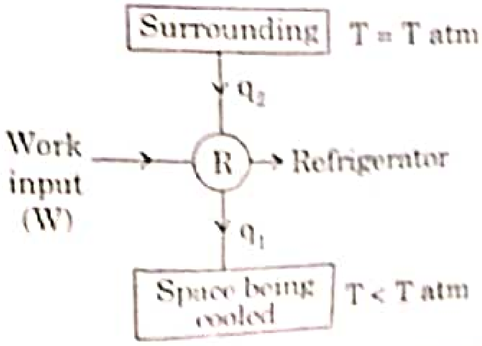


Fig. 15. Refrigerator and flow of heat

Refrigerators : It is reverse of the heat engine. It means the direction of heat and work are in opposite than that of heat engine (fig. 15).

The refrigerator remove heat from a body at low temp. and then transfer this heat to another body at high temp. This device operates between the temperature of surroundings and a temperature below that of the surroundings. It is generally used to preserve food items and drugs at low temperature.

The Carnot Cycle

It is a hypothetical cycle consisting of four distict processes i.e. two reversible isothermal processes and two reversible adiabatic processes. The cycle was proposed in 1824 by a young french engineer, Sadi Carnot.

The essential components needed for making this cycle are (fig. 17).

1. A working substance which is assumed to be a perfect gas i.e. 1 mole of ideal gas.
2. Two heat reservoirs, the hot reservoir (heat source) at temperature T_2 and the cold reservoir (heat sink) at temperature, T_1.
3. The arrangement of piston cylinder for getting the work out of the working substance. The piston and cylinder walls are taken as perfect heat insulators. The head of cylinder (bottom) is covered with perfect heat conductor and an adiabatic cover (perfect heat insulator.)

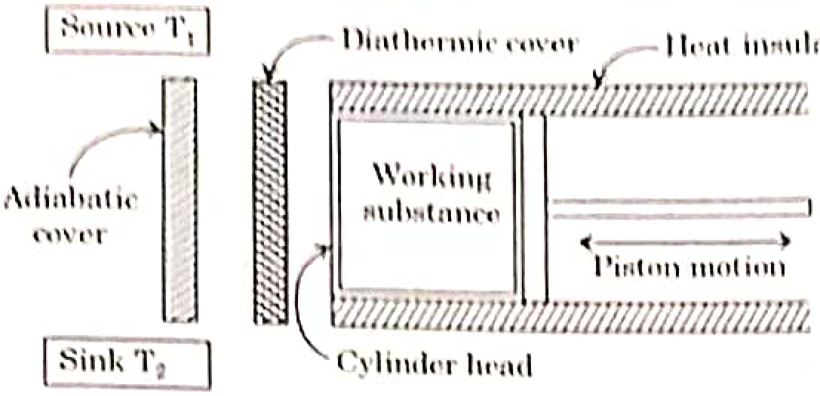


Fig. 17. Essential elements for a Carnot Cycle

The four reversible steps of Carnot cycle are discussed as one by one :

(i) Isothermal Expansion
(ii) Adiabatic Expansion
(iii) Isothermal Compression
(iv) Adiabatic Compression

These processes represented on a pressure-volume diagram (fig.18).

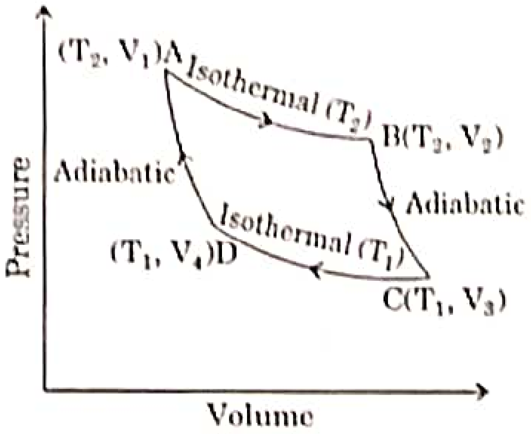
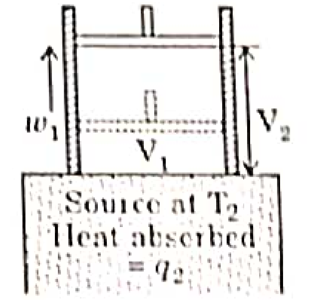


Fig. 18. Four steps of Carnot Cycle.

1. Step–1 : Isothermal Reversible Expansion

The cylinder containing one mole of an ideal gas, occupying a volume (V_1) placed in contact with a source (heat reservoir) at temperature, (T_2) The gas absorb q_2 amount of heat from the source and expand isothermally and reversibly so, that its volume has increased (V_2). The path represented by the curve AB. The work done (w_1) by the system given as (fig. 19).

$$-w_1 = RT_2 \ ln \frac{V_2}{V_1} \quad \text{... (1)}$$



Step 1.
Isothermal expansion

Fig. 19. Isothermal Reversible expansion

As the process is isothermal so ΔE or $\Delta U = 0$

$\therefore$ work done by the system is equal to heat absorbed (q_2).

So that we have

$$-w_1 = q_2 = RT_2 \ ln \frac{V_2}{V_1} \quad \text{... (2)}$$

$$\boxed{\begin{aligned} \Delta E &= q_2 + w \\ 0 &= q_2 + w \\ &\boxed{q_2 = -w} \end{aligned}}$$

Statement of Second Law of Thermodynamics

1. Kelvin Statement : From Carnot heat engine, we have

$$\frac{T_2 - T_1}{T_1} < 1 \text{ so that, } w < q_2$$

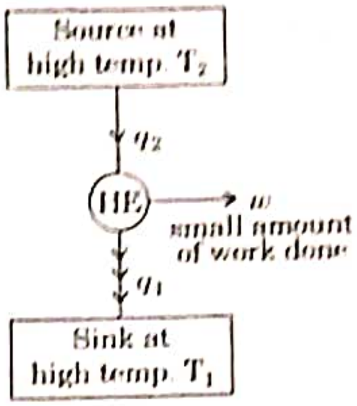


Fig. 24. Conversion of heat into work

it means, work done by the system is less than heat absorbed, so we can say, only a part of absorbed heat, by the system at higher temperature (T_2) is converted into work. The remaining part of heat (q_1) is given by the system to the surrounding (low temperature, T_1)

So, Kelvin statement of second law of thermodynamics given as

"It is impossible for a cyclic process that the heat of reservoir, completely converted into work without transfering it from hotter body to colder body.

Or

It is impossible to convert heat completely into mechanical work without leaving some effect in the system or surrounding.

Moreover it can be stated as "work can be converted into heat but the complete conversion of heat into work does not occur at all the conditions".

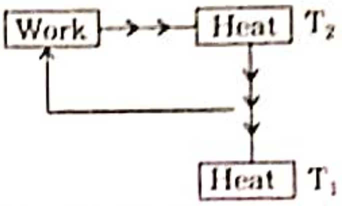


Fig. 25. Impossibility of Conversion of heat totally into mechanical work

2. Kelvin Planck Statement : In Carnot heat engine when $T_1 = T_2$ *i.e.*, two temperatures are same, the work done in the carnot cycle is zero

where
$$T_1 = T_2$$
$$w = 0$$

So, the Kelvin Planck statement of second law given as

It is impossible to construct a perpetual motion machine that work continuously by removal of heat from thermal reservoir

Or

In Carnot cycle, when a system connected to a single heat reservoir to produce positive amount of work in the surroundings

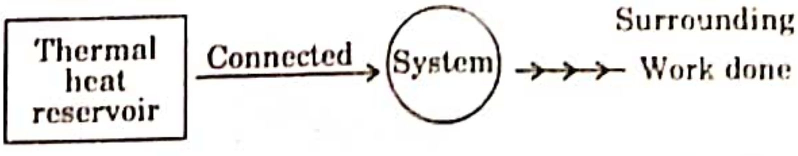


Fig. 26 Impossibility to construct a perpetual motion machine

3. Clausius Statement : In Carnot cycle, the heat engine (HE) can perform work only by the absorption of heat from a reservoir at higher temperature (T_2) and transfer the remaining heat (q_1) to another reservoir at lower temperature (T_1) (fig. 27). The heat absorbed by the lower temperature (T_1) reservoir is given as the difference between heat absorbed and work done by

ENTROPY

The function entropy came into existence from the work of Carnot.

In 1850, the function of state (S) introduced by the **Clausius.**

For a reversible **Carnot cycle**, functioning between temperatures T_2 and T_1, the efficiency (η) is given as

$$\eta = \frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2} \quad \dots (1)$$

Where, q_2 is the heat absorbed at temp, T_2 while q_1 is the heat lost isothermally at temp; T_1 (fig. 30)

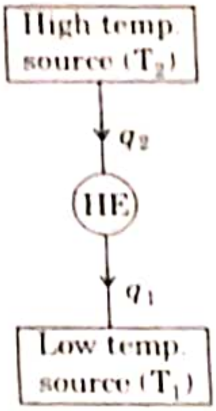


Fig. 30. Absorption and emission of heat

The above equation (1) can be written in simplified form

$$1 - \frac{q_1}{q_2} = 1 - \frac{T_1}{T_2}$$

or

$$\frac{q_2}{T_2} = \frac{q_1}{T_1} \quad \dots (2)$$

Thus, from equation (2) we have

$$\frac{q_{rev\ ,\ isothermally}}{T} = \text{Constant} \quad \dots (3)$$

So, we conclude that the heat absorbed or lost isothermally and reversibly devided by the absolute temperature at which heat is absorbed or lost is a constant quantity

For a given system

By using SI–conventions we take positive sign for heat absorbed and negative sign for heat lost where in equation (2), q_2–amount of heat is absorbed and q_1 is the amount of heat lost, then equation becomes

$$\frac{q_2}{T_2} = -\frac{q_1}{T_1}$$

$$\frac{q_2}{T_2} + \frac{q_1}{T_1} = 0$$

But for a cyclic process $q \neq 0$

$\therefore$ q is not a function of state

Thus we have

$$\sum \frac{q}{T} = 0$$

Entropy Change in Irreversible Process

The whole process will be irreversible, if any part of the process is irreversible. Suppose, total heat lost by the surrounding is q_{irrev} (fig. 33). This heat is absorbed by the system. But change in entropy of the system does not depend upon the heat actually absorbed but depends upon the heat absorbed reversibly i.e. q_{rev}

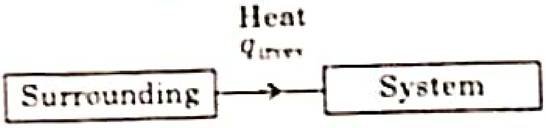


Fig. 33. Heat Lost irreversibly by the surrounding

Thus we have

$$\Delta S_{system} = \frac{q_{rev}}{T}$$

Suppose, heat (q_{irrev}) is lost by the surroundings isothermally at a temperature T, in infinitesimally small steps, then change in entropy of the surroundings will be given by (fig. 34)

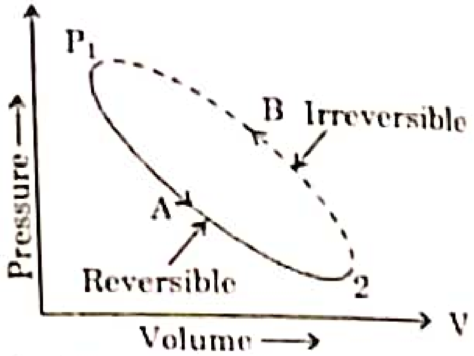


Fig. 34. Change in entropy in irreversible process

$$\Delta S_{surroundings} = -\frac{q_{irrev}}{T}$$

Then, the total change in entropy of the system and surroundings will be given as

$$\Delta S_{Total} = \Delta S_{System} + \Delta S_{surrounding}$$

$$= \frac{q_{rev}}{T} - \frac{q_{irrev}}{T} \qquad \text{...(1)}$$

But we know , for a reversible process work done is maximum *i.e.*

$$w_{rev} > w_{irrev}$$

First law for a reversible process, can be written as

$$\Delta E \text{ or } \Delta U = q_{rev} - w_{rev} \qquad \text{... (2)}$$

When the same process carried out irreversibly, then we have first law

$$\Delta E \text{ or } \Delta U = q_{irrev} - w_{irrev} \qquad \text{... (3)}$$

But the ΔE or ΔU is a function of state $\therefore$ its value is same whether the process is carried out reversibly or irreversibly. So, from equation (2) and equation (3) we get

$$q_{rev} - w_{rev} = q_{irrev} - w_{irrev}$$

But we know that

$$w_{rev} > w_{irrev}$$

Hence we concluded that

$$q_{rev} > q_{irrev}$$

or

$$\frac{q_{rev.}}{T} = \frac{q_{irrev.}}{T}$$

or

$$\frac{q_{rev.}}{T} - \frac{q_{irrev.}}{T} > 0 \qquad \text{... (4)}$$

On comparing equation (1) by equation (4) we get

$$\Delta S_{system} + \Delta S_{surroundings} > 0$$

Entropy Change for an Ideal Gas with Change in P,V and T

Consider, one mole of an ideal gas enclosed in a cylinder fitted with the frictionless piston (fig 42) The value of this ideal gas will change with the state variables such as T, P and V. Here, we study the variation of entropy by taking two variables at one time *i.e.* T and V or P and T.

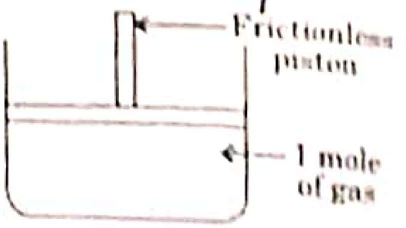


Fig. 42 Gas enclosed in a vessel of frictionless piston

1. Entropy as a function of T and V : Consider, one mole of an ideal gas that expand reversibly (fig. 43) Acc. to first law of thermodynamics we have the equation

$$dq_{rev} = dU - dW \quad \ldots (1)$$

if work done is the work of expansion, then for an infinitesimal increase in volume (dV) against the pressure (P), we have

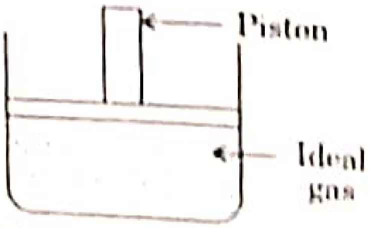


Fig. 43. Gas enclosed in a Vessel of Frictionless piston

$$-dW = P\,dV$$

Put the value of – dw in equation (1), we get equation (2)

$$dq_{rev} = dU + PdV \quad \ldots (2)$$

if dq_{rev} is the amount of heat given to the system isothermally and reversibly at a temperature, T, the increase in entropy of gas is given by

$$dS = \frac{dq_{rev}}{T} \quad \ldots (3)$$

On substituting the value of dq_{rev} in equation (3) we get

$$dS = \frac{dU + PdV}{T}$$

On rearranging we get,

$$TdS = dU + PdV \quad \ldots (4)$$

But we know that

$$C_v = \frac{dU}{dT} \quad \text{(for one, mole of ideal gas)}$$

or

$$dU = C_v dT \quad \ldots (5)$$

(C_v–Molar heat capacity at constant volume)

IMPORTANT QUESTIONS WITH ANSWER

1. **Derive the formula $\eta = \frac{w}{q_2} = \frac{T_2 - T_1}{T_2}$.** 10

Or

State and describe Carnot's cycle. Derive the mathematical expression for the efficiency of a reversible heat engine.

Ans. Carnot's cycle : A process in which a system when subjected to successive changes returns back to original state. Such type of process is called as a cyclic process.

Carnot chose a reversible hypothetical heat engine for calculation of efficiency. It consists of four steps applied successively on hypothetical heat engine.

Step-I : One mole of ideal gas (volume = V_1) after absorbing heat q_2 from heat reservoir at temperature T_2 is allowed to expand isothermally and reversibally to volume V_2.

11)

Then work done is given by

$$-W_1 = RT_2 \, ln \frac{V_2}{V_1} \qquad [\Delta U = 0 \text{ for isothermal expansion}]$$

and it is equal to q_2 the heat absorbed

$$q_2 = -W_1 = RT_2 \, ln \frac{V_2}{V_1} \qquad \text{...(i)}$$

Step-II : In second step, the gas expands adiabatically and reversibly to volume V_3 the temperature decreases from T_2 to T_1.

The work done is given by the expression

$$-W_2 = C_V(T_2 - T_1) \qquad [q = 0 \text{ from 1st law of thermodynamics and } \Delta U = -W_2$$

$$-W_2 = -C_V(T_1 - T_2) \qquad \text{...(ii)}$$

Step-III : The gas is again subjected to isothermal reversible expansion at temperature T_1 and the volume decreases from V_3 to V_4. According to convention q_1 will be negative and W_3 the work done will be positive.

Then

$$-q_1 = W_3 = RT_1 \, ln \frac{V_4}{V_3} \qquad \text{...(iii)}$$

Step-IV : Again the gas is subjected to adiabatic reversible compression till the original volume V_1 is attained and the temperature rises from T_1 to T_2. According to convention the work done is positive. So

$$W_4 = C_V(T_2 - T_1) \qquad \text{...(iv)}$$

Net work done *i.e.*, W is given as

$$\begin{aligned} W &= (-W_1) + (-W_2) + W_3 + W_4 \\ &= RT_2 \, ln \frac{V_2}{V_1} - C_V(T_2 - T_1) + RT_1 \, ln \frac{V_4}{V_3} + C_V(T_2 - T_1) \\ &= RT_2 \, ln \frac{V_2}{V_1} - RT_1 \, ln \frac{V_4}{V_3} \qquad \text{...(v)} \end{aligned}$$

For adiabatic steps it follows

$$\frac{V_2}{V_1} = \frac{V_3}{V_4}$$

or

$$\frac{V_4}{V_3} = \frac{V_1}{V_2}$$

Substituting in eqn. (*v*)

$$\begin{aligned} W &= RT_2 \, ln \frac{V_2}{V_1} + RT_1 \, ln \frac{V_1}{V_2} \\ &= RT_2 \, ln \frac{V_2}{V_1} - RT_1 \, ln \frac{V_2}{V_1} \\ &= R(T_2 - T_1) ln \frac{V_2}{V_1} \qquad \text{...(vi)} \end{aligned}$$

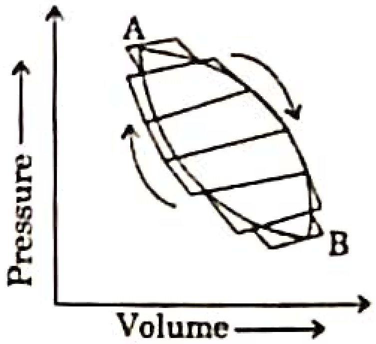


Fig. : Carnot cycles drawn across the reversible cycle

Dividing eqn. (vi) by (i)

$$\frac{W}{q_2} = \frac{R(T_2 - T_1) ln \frac{V_2}{V_1}}{RT_2 \, ln \frac{V_2}{V_1}} = \frac{T_2 - T_1}{T_2}$$

$$W = q_2\left(\frac{T_2 - T_1}{T_2}\right)$$

All heat engines will have same efficiency when operation are carried out using same heat reservoirs. So efficiency η

$$\eta = \frac{W}{q_2} = \frac{T_2 - T_1}{T_2}$$

Since $\frac{T_2 - T_1}{T_2}$ is always less than one. Hence the efficiency is always less than unity.

For a reversible Carnot's cycle working between temperature T_2 and T_1.

Then $$\frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2}$$

or $$1 - \frac{q_1}{q_2} = 1 - \frac{T_1}{T_2}$$

or $$\frac{q_1}{q_2} = \frac{T_1}{T_2}$$

or $$\frac{q_1}{q_2} = \frac{q_2}{q_1}$$

So $$\frac{q}{T} = \text{constant}$$

And for infinite number of Carnot's cycle

$$\boxed{\sum \frac{q}{T} = 0}$$

THIRD LAW OF THERMODYNAMICS

We have alreay learnt that, net change in entorpy of system and surrounding is

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{Surroundings}$$

Its value can be determined whether a process proceed spontaneously or not. If the value of $\Sigma S_{total} > 0$, the process will be spontaneous or irreversible, if $\Delta S_{total} = 0$ the process will be spontaneous i.e there is no net change in a state of equilibrium. For the determination of change in values of entropy change, some other state functions are required which depends upon the state of system only. Two such function are the work function and free energy function represented by A and G respectively.

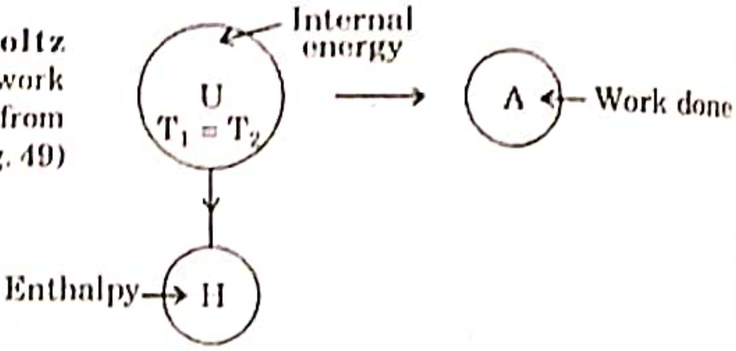


Fig. 49. Work function and internal energy

Work function (A), (Helmholtz function/Helmholtz free energy) : The work function symbolize by symbol, A It is derived from Germen word Arbeit which mean work. (fig. 49)

It is defined as mathematically

$$A = U - TS$$

Where

U — Internal energy

S — entropy

T — temperature

All these function U, S and T are the function of state *i.e.*, A is also a state function, it means its value depend upon the initial and final state of the system.

To understand exactly about the work function (A)

Consider, a process proceed isothermally at temperature, T

A_1, U_1 and S_1 are the values of these three function in initial state while , A_2, U_2 and S_2 are the values of these three state function in final state

Then we have

$$A_1 = U_1 - TS_1 \quad \text{(in initial state)}$$

$$A_2 = U_2 - TS_2 \quad \text{(in final state)}$$

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The change in value of work function is given by

$$A_2 - A_1 = (U_2 - TS_2) - (U_1 - TS_1)$$

or

$$A_2 - A_1 = (U_2 - U_1) - T(S_2 - S_1)$$

or

$$\boxed{\Delta A = \Delta U - T\Delta S} \quad \text{...(1)}$$

Where,

ΔU — change in internal energy

ΔS — change in entropy of the system at a temperature, T

For a reversible process that proceed at a temperature, T and heat is absorbed is q_{rev} then we have

$$\Delta S = \frac{q_{rev.}}{T} \quad \text{...(2)}$$

But we know, the equation of first law for a isothermal and reversible process is

$$\Delta U = q_{rev} + w_{max}$$

When work is done by the system, it is taken as negative ($-w$)

We have

$$\Delta U = q_{rev} - w_{max} \quad \text{...(3)}$$

On substituting the value of ΔS and ΔU from equation (2) and equation (3) into equation (1), we get

$$\Delta A = (q_{rev} - w_{max}) - T\,\frac{q_{rev}}{T}$$

$$\boxed{-\Delta A = w_{max}}$$

Thus, from this equation we conclude, that decrease in work function (A) represents the maximum work that can be done by the system. Therefore the function, A gives its name as the work function or the Helmholtz free energy.

Gibb's Free Energy

The Gibb's free energy symbolised by the symbol, G. It is defined as (fig. 50)

$$G = H - TS$$

Where H — enthalpy of the system

S — entropy of the system

T — Temperature of the system

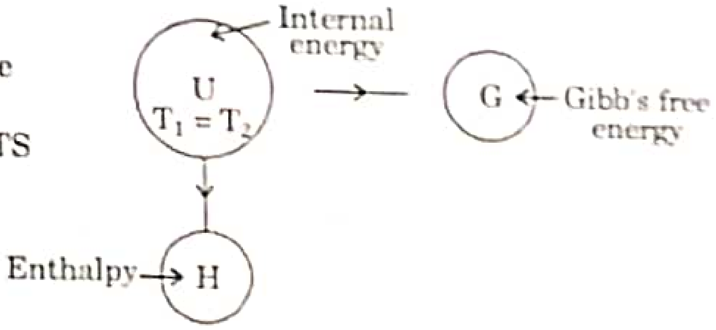

Fig. 50. Gibbs free energy and internal energy

These three functions, H, S and T are the function of state, therefore G is also a state function. The value of G depends upon the initial and final state of the system.

Let, G_1, H_1 and S_1 are the state function for initial state of the system G_2, H_2 and S_2 are the state function for final state of the system where, T is kept constant for an isothermal processes.

Therefore the equation for initial and final state can be written as

$$G_1 = H_1 - TS_1 \quad \text{(in initial state)}$$

$$G_2 = H_2 - TS_2 \quad \text{(in final state)}$$

The change in Gibb's free energy is given as

$$G_2 - G_1 = (H_2 - TS_2) - (H_1 - TS_1)$$
$$= (H_2 - H_1) - T(S_2 - S_1)$$

$$\boxed{\Delta G = \Delta H - T\Delta S} \quad \text{.... (5)}$$

Where,

$\Delta G = G_2 - G_1$ is the change in free energy

$\Delta H = H_2 - H_1$ change in enthalpy

$\Delta S = S_2 - S_1$ change in entropy of the system.

Variation of Helmholtz Function (Work Function) with, T and V

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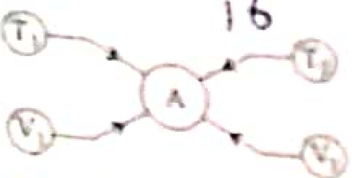

Fig. 52 : Variation of A with T and V

The work function is related by the equation

$$A = U - TS \quad \text{...(1)}$$

on differentiation, we get the equation (2)

$$dA = dU - TdS - SdT \quad \text{...(2)}$$

By the definition of entropy change we have,

$$dS = \frac{\delta q_{rev}}{T} \quad \text{...(3)}$$

and from the first law of thermodynamic we have

$$\delta q_{rev} = dU - \delta w \quad \text{...(4)}$$

Suppose, the work is restricted to the work of expansion i.e. reversible pressure volume work, then we have

$$-\delta w = PdV \quad \text{...(5)}$$

Substitute the value of δw from equation (5) in equation (4), we get equation (6)

$$\delta q_{rev} = dU + PdV \quad \text{...(6)}$$

On substituting the value of equation (6) in equation (3) we get

$$dS = \frac{dU + PdV}{T}$$

$$TdS = dU + PdV \quad \text{...(7)}$$

Putting this value of equation (7) in equation (2), we get

$$dA = dU - dU - PdV - SdT$$

$$dA = -PdV - SdT \quad \text{...(8)}$$

(i) If process is isothermal, *i.e.*, temperature is kept constant, $dT = 0$, then the equation (8) reduce to

$$(dA)_T = (-PdV)_T \text{ or } \left(\frac{\partial A}{\partial V}\right)_T = -P \quad \text{...(9)}$$

(ii) If process is isochoric i.e. volume is kept constant, $dV = 0$, then the equation (8) reduce to

$$(dA)_v = -(SdT)_v$$

$$\left(\frac{\partial A}{\partial T}\right)_v = -S \quad \text{...(10)}$$

The equation (9) and equation (10) give the variation of work function with volume and temperature.

The change in work function for a complete process under isothermal conditions can be calculated as

For isothermal condition of an infinitesimal change, the equation (9) written as

$$(dA)_T = -PdV \quad \text{...(12)}$$

Let the work function (A_1) in the initial state and work function (A_2) in the final state when the change in volume is V_1 to V_2 at constant temperature (fig. 53) then, on integrating equation (12), the change in work function (ΔA) is given by

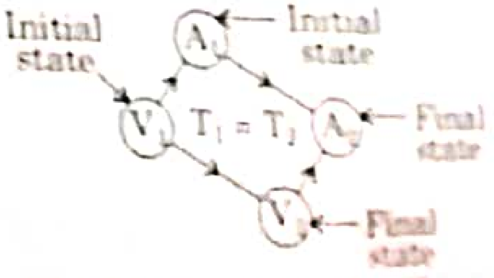

Fig. 53 : Variation in values of work function with volume

$$(\Delta A)_T = -\int_{V_1}^{V_2} PdV \qquad \text{...(12)}$$

For one mole of an ideal gas we have

$$PV = nRT$$

$$P = \frac{nRT}{V} \qquad (n = 1)$$

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

Substitute the value of P in equation (13), we get

$$(\Delta A)_T = \int_{V_1}^{V_2} \frac{RT}{V}\, dV$$

or

$$(\Delta A)_T = -RT\, ln\, \frac{V_2}{V_1}$$

For n moles of gas

$$(\Delta A)_T = -nRT\, ln\, \frac{V_2}{V_1} \qquad \left(\text{But } nRT\, ln\, \frac{V_2}{V_1} = w_{max}\right)$$

$$(\Delta A)_T = -W_{max}$$

CRITERIA FOR SPONTANEITY (FEASIBILITY) FOR A PROCESS

The net change in entropy for combined system and surroundings can serve as the criteria for spontaineity of a process. We know very well that

(i) If $\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings} > 0$ the process is spontaneous or irreversible.

(ii) If $\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings} = 0$ the process is in a state of equilibrium or reversible.

The net result of these two parameters are

$$\Delta S_{system} + \Delta S_{surroundings} \geq 0 \qquad \dots (1)$$

Where the sign 'greater than' refers to a spontaneous or irreversible process while the sign 'equal to' refers to a state of equilibrium or reversible process.

The other thermodynamics variables such as H, A, U and G also responsible for spontaineity of a process. These variables may be derived as follows.

For an infinitesimal process, the above criteria may be written as

$$\Delta S_{system} + \Delta S_{surroundings} \geq 0 \qquad \dots (2)$$

Where,

$>$ Stands for irreversible process

$=$ Stands for reversible process

Let, heat (δq) is lost by the surrounding isothermally and reversibly at temperature, T then we have

$$dS_{surroundings} = -\frac{\delta q_{rev}}{T} \qquad \dots (3)$$

From the first law of thermodynamics, we have

$$\delta q_{rev} = dU + PdV \qquad \dots (4)$$

On substituting the value of equation (4) in equation (3) we get

$$dS_{surroundings} = -\frac{dU + PdV}{T} \qquad \dots (5)$$

Substitute the value of equation (5) in equation (2) we get

$$dS_{system} - \frac{dU + PdV}{T} \geq 0$$

or $$TdS - dU + PdV \geq 0$$

$$\boxed{TdS \geq dU + PdV} \qquad \text{... (6)}$$

In this equation sign 'greater than' (>) refers to spontaneous process while sign 'equal to' (=) refers to a reversible process The equation (6) is the basic equation leading to a number of criteria for predicting the spontaineity of a process, that may be deduced as follows :

(i) In term of change in entropy of the system : If the internal energy (U) and volume (V) of a system are kept constant in an isothermal process we have (fig. 56).

$$dU = 0 \text{ and } dV = 0$$

Then the equation (6) reduce to

$$(TdS)_{U,V} \geq 0$$

or $$(dS)_{U,V} \geq 0$$

Where,

the sign (>) used for irreversible process

the sign (=) used for reversible process

While the subscripts U and V indicate the constancy of these properties

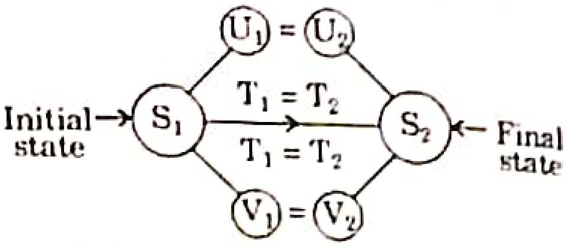

Fig. 56. Change in entropy at Constant U, V and T

(ii) In term of change in internal energy of the system : If the entropy and the volume of the system are kept constant (Fig. 57)

$$dS = 0 \text{ and } dV = 0$$

On substituting the value of dS and dV in equation (6), it reduce to

$$0 \geq (dU)_{S,V}$$

or $$\boxed{(dU)_{S,V} \leq 0}$$

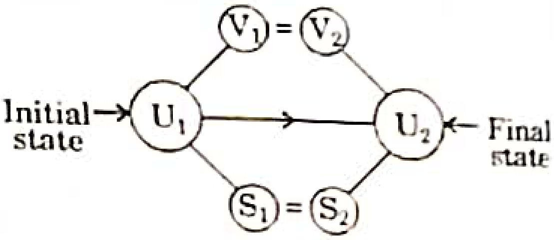

Fig. 57. Change in Internal Energy at Constant S and V

Where, the sign (<) stands for irreversible process the sign (=) stands for reversible process while the subscripts S and V indicate the constancy of these properties.

(iii) Criteria in term of change in enthalpy : By definition the expression for enthalpy is given as

$$H = U + PV$$

On differentiation this equation becomes

$$dH = dU + PdV + VdP$$

or $$dU + PdV = dH - VdP$$

Substitue the value of $dU + PdV$ in equation (6), we get

$$TdS \geq dH - VdP$$

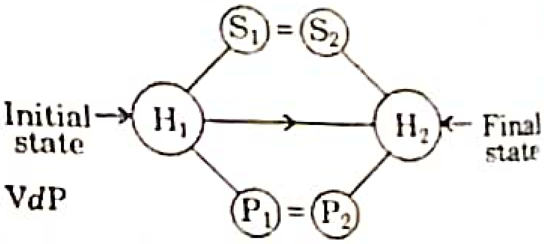

Fig. 58. Change in enthalpy at constant P and S

If the entropy and pressure of the system are kept constant (fig. 58)

$dS = 0$ and $dP = 0$ so, that we have

$$0 \geq (dH)_{S,P}$$

$$\boxed{(dH)_{S,P} \leq 0}$$

where, the sign (<) refers to the irreversible process while sign (=) refers to the reversible process, while the subscripts S and P indicate the constancy of these properties.

(iv) In term of Change in work function of the system : By definition, the expression for work function (A) given as

$$A = U - TS$$

On differentiation this equation becomes

$$dA = dU - SdT - dA$$

On substituting this value in equation (5) it becomes

$$dU - SdT - dA \geq dU + PdV$$

$$-SdT - dA \geq PdV$$

$$SdT + dA \leq -PdV$$

If the volume and temperature of the system kept constant (fig. 59)

$$dT = 0 \text{ and } dV = 0$$

So, that we have the equation

$$\boxed{(dA)_{T,V} \leq 0}$$

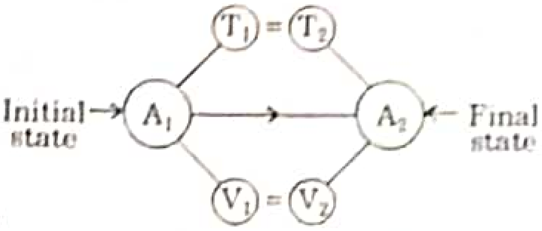

Fig. 59. Change in Work function at constant V ad T

Where, the sign (<) refers to the irreversible process while sign (=) refers to the reversible process. While the subscripts T and V indicate the constancy of these properties.

(v) In term of change in free energy : By definition, the expression for change in free energy given as

$$G = H - TS$$

Further $\quad H = U + PV$

Therefore $\quad G = U + PV - TS$

On differentiation this equation we get

$$dG = dU + PdV + VdP - TdS - SdT$$

or $\quad dE + PdV = dG - VdP + TdS + SdT$

On substituting the value in equation (6) we get

$$\cancel{TdS} \geq dG - VdP + \cancel{TdS} + SdT$$

$$0 \geq dG - VdP + SdT$$

or $\quad dG - VdP + SdT \leq 0$

If the temperature and pressure are kept constant (fig. 60)

$dP = 0$ and $dT = 0$ then we have

$$(dG)_{P,T} \leq 0$$

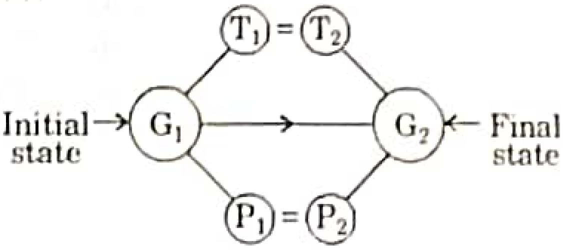

Fig. 60. Change in free energy at constant T and P

Where, the sign (<) refers to irreversible process while sign (=) refers to reversible process. The subscripts P and T indicate the constancy of these properties.

The Criterion in term of change in free energy is most signficant because most of the process proceed at constant pressure and constant temperature. The value of ΔG determines, whether the process is spontaneous or non spontaneous.

(i) If the $(dG)_{T,P} < 0$, the process is spontaneous or irreversible.

(ii) If the $(dG)_{T,P} = 0$, the process is reversible or is in equilibrium.

(iii) If the $(dG)_{T,P} > 0$, the process is non spontaneous i.e. does not occur at all.

Maxwell Relationships

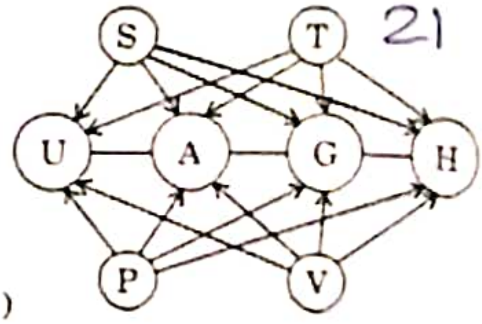

Fig. 61 : Relation between U, A, G and H with S, P, V and T

The various expression that relates the enthalpy (H), internal energy (U), Helmhotlz free energy (A) and Gibb's free energy (G) with the entropy and thermodynamics variables like T, P and V are given as (fig. 61)

$$dU = TdS - PdV \quad \text{... (1)}$$

$$dH = TdS - VdP \quad \text{... (2)}$$

$$dA = -SdT - PdV \quad \text{... (3)}$$

$$dG = -SdT - VdP \quad \text{... (4)}$$

For constant volume *i.e.* $dV = 0$, the equation (1) becomes

$$dU = TdS$$

or

$$\left(\frac{\partial U}{\partial S}\right)_V = T \quad \text{... (5)}$$

For constant value of entropy *i.e.* $dS = 0$, the equation (1) becomes

$$dU = -PdV$$

$$\left(\frac{\partial U}{\partial V}\right)_S = -P \quad \text{...(6)}$$

On differentiating, the equation (5) w.r.t. V, keeping entropy constant *i.e.* $dS = 0$, we get the expression

$$\frac{\partial^2 U}{\partial S \times \partial V} = \left(\frac{\partial T}{\partial V}\right)_S \quad \text{... (7)}$$

On differentiating, the equation (6) w.r.t S, keeping volume constant *i.e.* $dV = 0$, we get the expression

$$\frac{\partial^2 U}{\partial V \times \partial S} = -\left(\frac{\partial P}{\partial S}\right)_V \quad \text{... (8)}$$

On comparing equation (7) with equation (8) we get

$$\boxed{\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V} \quad \text{... (9)}$$

For constant value of pressure *i.e.* $dP = 0$ the equation (2) becomes

$$\left(\frac{\partial H}{\partial S}\right)_P = T \quad \text{... (10)}$$

For constant value of entropy *i.e.* $dS = 0$ the equation (2) becomes

$$\left(\frac{\partial H}{\partial P}\right)_S = V \quad \text{... (11)}$$

On differentiating, the equation (10) w.r.t. pressure, keeping entropy constant *i.e.*, $dS = 0$ we get the expression

$$\frac{\partial^2 H}{\partial S \times \partial P} = \left(\frac{\partial T}{\partial P}\right)_S \quad \text{... (12)}$$

On differentiating, the equation (11) w.r.t entropy, keeping the pressure constant *i.e.* $dP = 0$, we get the expression

$$\frac{\partial^2 H}{\partial P \times \partial S} = \left(\frac{\partial V}{\partial S}\right)_P \quad \text{... (13)}$$

On comparing the equation (12) with equation (13) we get

$$\boxed{\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P} \quad \text{... (14)}$$

Similarly, by applying the same above mentioned procedure for equation (3) and equation (4) we get the following expression

Expression for equation (3) is

$$\boxed{\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V} \quad \text{... (15)}$$

and expression for equation (4) is

$$\boxed{\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P} \quad \text{... (16)}$$

The expression (9), (14), (15) and (16) are called as maxwell's relationships

Other set of Maxwell's relationship can be derived are given as.

Expression from equation (1) and (2)

$$\left(\frac{\partial U}{\partial S}\right)_V = -\left(\frac{\partial H}{\partial S}\right)_P \quad \text{... (17)}$$

Expression from equations (1) and (3)

$$\boxed{\left(\frac{\partial U}{\partial V}\right)_S = \left(\frac{\partial A}{\partial V}\right)_T} \quad \text{... (18)}$$

Applications of Gibb's Helmholtz equation

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1. The equation (10) *i.e.* Gibb's Helmholtz equation can be applied to calculate change in enthalpy ΔH or ΔU when ΔG or ΔA at two different temperature are given
2. If the speed or rate of change of free energy with temperature remains practically constant, the known value of ΔG at a given temperature can be helpful in calculating the value at other temperature.
3. The equation can be used to calculate the e.m.f. of reversible cells. It was shown by Gibb's and Helmholtz that the electrical energy produced in a reversible electro chemical cell was equal to decrease in free energy ($-\Delta G$). The equation for this is

$$-\Delta G = nFE$$

Where

E – EMF of the cell

n – number of electron lost or gained by the electrode

F – Faradays constant i.e. (1 F = 96500C)

Substitute the value of (ΔG) from equation (13) into equation (10) we get

$$-nFE = \Delta H + T\left(\frac{\partial(-nFU)}{\partial T}\right)_P$$

or

$$\boxed{nFE = -\Delta H + T\ nF\left(\frac{\partial U}{\partial T}\right)_P}$$

Where,

$\left(\frac{\partial U}{\partial T}\right)_P$ represents the temperature coefficient of the *e.m.f.*

i.e. rate of change of EMF with temperature at constant pressure

By using this equation, the value of ΔH can be calculated by knowing the value of temperature coefficient of the cell, if U is known and vice-versa.

4. The equations like Van't Hoff equation and Clausius clapeyron equation can be deduced.

11. **Explain the concept of Helmhotz function(A) and its significance.** — 24

Ans. Helmhotz function (work function)

It is represented A and is defined as

$$A = U - TS \quad \text{...(i)}$$

U = Internal energy

S = Entropy

and T is the temperature in Kelvin

Physical significance : Suppose a system changes from state-I to state-II at constant temperature

$$\begin{array}{ccc} \text{I} & \rightarrow & \text{II} \\ A_1 & & A_2 \end{array}$$

A_1 = Work function of state-I

A_2 = Work function of state-II

According to definition of work function

$$A_1 = U_1 - TS_1 \quad \text{...(ii)}$$

$$A_2 = U_2 - TS_2 \quad \text{...(iii)}$$

Change in work function is given by subtracting eqn. (i) from (ii)

$$A_2 - A_1 = U_2 - U_1 - T(S_2 - S_1)$$

$$\Delta A = \Delta U - T\Delta S \quad \text{...(iv)}$$

[ΔU = Change in internal energy and ΔS = Change in entropy]

According to definition of entropy

$$\Delta S = \frac{q_{rev.}}{T}$$

or

$$T\Delta S = q_{rev} \quad \text{...(v)}$$

From 1st law of thermodynamics

$$q_{rev.} = \Delta U + W_{max.} \quad \text{...(vi)}$$

Substituting the value of $q_{rev.}$ in eqn. (vi)

$$T\Delta S = \Delta U + W_{max.}$$

$$-W_{max} = \Delta U - T\Delta S$$

$$-W_{max} = \Delta A$$

[According to relationship $\Delta A = \Delta U - T\Delta S$

As useful work done can never be negative

So

$$W_{max} = -\Delta A$$

Hence larger the decrease in work function maximum work is done by the system.

12. State the third law of thermodynamics. How this law help in determination of absolute entropy of a substance from heat capacity.

Ans. Third law–At absolute zero temp, entropy of all perfectly crystalline substance is taken as zero

Calculation of absolute entropy of a substance from heat capacity : With the help of third law of thermodynamics absolute values of entropies can be determined.

Infinitesinual change in entropy is given as

$$dS = \frac{dq}{T} \qquad \ldots(i)$$

From the defination of heat capacity at constant pressure *i.e.*, Cp is given as

$$Cp = \frac{dq}{dT} \text{ or } dq = C_p dT \qquad \ldots(ii)$$

Substituting dq in eqn. (i)

$$dS = Cp\frac{dT}{T}$$

So entropy change cna be obtained when temperature changes from 0K to particular temperature T

$$\int_{S=S_0}^{S=S} dS = \int_{T=0}^{T=T} Cp\frac{dT}{T}$$

or

$$S - S_0 = \int_0^T Cp\frac{dT}{T}$$

S = Entropy at temperature T

and S_0 = Entropy at 0K

According to third law of thermodynamics

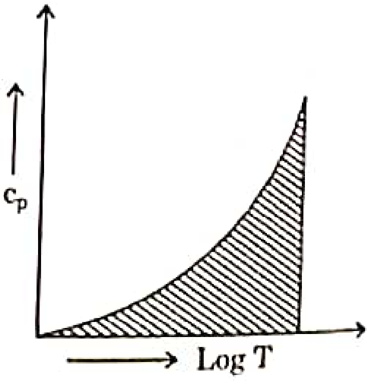
$$S_0 = 0$$

Then

$$S = \int_0^T Cp\frac{dT}{T}$$

or

$$S_T = \int_0^T Cp\, d\, lnT \qquad \ldots(iii)$$



The eqn. (iii) is elevated by plotting a graph between *Cp vs d lnT i.e., Cp vs* 2.303 logT and then by measuring the area under the curve and *Cp* is almost constant in the temperature 0 – T*k* range, the eqn. (iii) reduces to

$$S = Cp\, ln\, T = 2.303\, Cp \log T$$

(This is valid for solid only)

When the substance undergoes phase change *i.e.*, solid to liquid to gas and taking the value of entropy of crystalline solid as zero, then entropy S is obtained by adding the different changes

$$S = \int_0^{T_m} Cp(s)\frac{dT}{T} + \frac{\Delta H_m}{T_m} + \int_{T_m}^{T_b} Cp(l)\frac{dT}{T} + \frac{\Delta H_v}{T_b} + \int_{T_b}^{T} Cp(g)\frac{dT}{T}$$

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where T_m = melting point
ΔH_m = latent heat of melting
T_b = boiling point
ΔH_v = latent heat of vapouristion
T = Temperature

When the substance is solid and entropy is to be calculated at a particular temperature say 298K, then for all the above steps, values are determined and added to get the required result.

2

ELECTRO CHEMISTRY

Redox Reactions

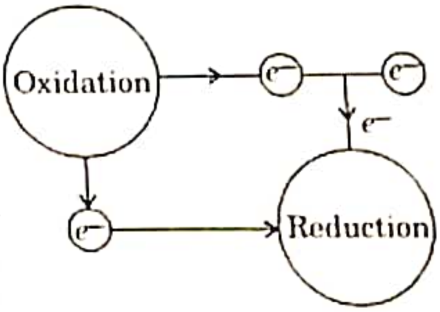


Fig. 1 : Redox Reaction

Oxidation and reduction reactions are called as Redox reaction. Oxidation is a process, by which a substance loss one or more electrons while reduction is a process by which a (fig-1) substance gain one or more electrons. In Redox reactions, electrons are transferred from one substance to other substance. The substance which can give its one or more electrons to other substance is called as reducing agent or reductant while the substance which aquires one or more electrons from the other substance is called as oxidising agent or oxidant, simply we can say, reducing agent is a substance that reduce other and itself get oxidised, while oxidising agent is a substance that oxidise other and itself get reduced.

Consider, a reaction between Zinc and copper sulphate solution, occuring in a beaker.

Reduction-gain of $2e^-$

$$\underset{0}{Zn}(s) + \overset{2+}{Cu}SO_4(aq) \longrightarrow \overset{2+}{Zn}SO_4(aq) + \overset{0}{Cu}(s)$$

Oxidation-loss of $2e^-$

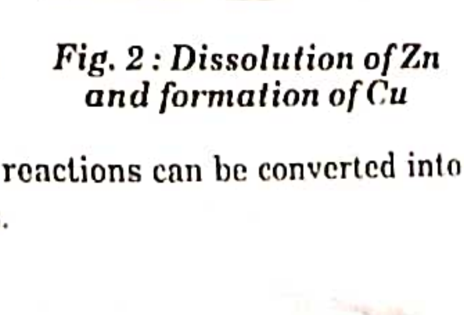


Fig. 2 : Dissolution of Zn and formation of Cu

In this reaction the element zinc loses electrons and get oxidised while Cu^{2+} ions from $CuSO_4$ solution gain electrons and get reduced. Thus, element zinc act as reducing agent and Cu^{2+} ions act as oxidising agent.

In this reaction, the size of zinc rod get decreased while precipitate of solid copper get formed. (fig.-2.)

Here, we will study how the chemical energy of a redox reactions can be converted into electrical form of energy. The redox reactions are of two types.

1. Direct Redox Reaction : These are types of redox reactions that proceed in a single beaker, it is noticed that the solution becomes hot.

For example : When a rod of zinc is placed in a solution of copper sulphate, the solution is found to become hot as the reaction proceed. (fig-3)

$$Zn\,(s) + CuSO_4\,(aq) \rightarrow ZnSO_4\,(aq) + Cu\,(s)$$

The similar observation is obtained when a rod of copper is placed in a solution of silver nitrate. (fig-4)

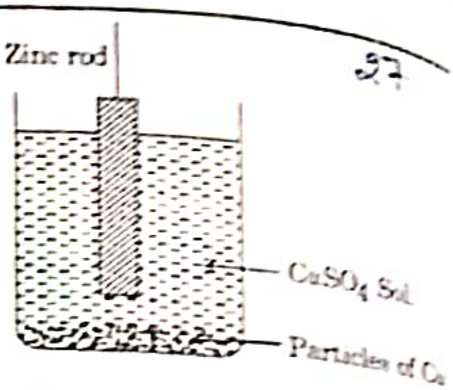


Fig. 3 : Direct Redox Reaction

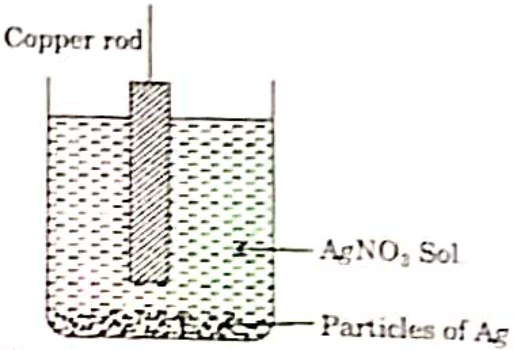


Fig. 4 : Direct Redox reaction between Cu and $AgNO_3$

$$Cu(s) + 2AgNO_3\,(aq) \rightarrow Cu(NO_3)_2\,(aq) + 2Ag(s)$$

Conclusion : From these observation it was concluded that when redox reaction proceed in a single beaker, the chemical energy in the form of heat energy is produced.

Indirect Redox reaction or Electrochemical cell or Galvanic cell or voltaic cell

When a redox reactions proceed in two seperate beakers connected by a wire are called as indirect redox reaction. The indirect redox method converts chemical form of energy into electrical form of energy. Thus, a device that used to convert the chemical energy of a redox reaction into electrical form of energy is called as electrochemical cell or chemical cell.

The electrochemical cell also called as Galvanic cells or voltaic cells, in the honour of name of scientist Luigi Galvani (1780) and Alessandro Volta (1800) who were first to perform experiments.

To explain the working of electrochemical cell with the help of following examples.

(i) Redox reaction between Zinc and copper sulphate :

The reaction between Zn and $CuSO_4$ solution given as

$$Zn\,(s) + CuSO_4\,(aq) \rightarrow ZnSO_4\,(aq) + Cu$$

or

$$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$$

In this electrochemical cell, a rod of zinc is placed in a solution of zinc sulphate in one beaker and a rod of copper is placed in a solution of copper sulphate in another beaker. The two

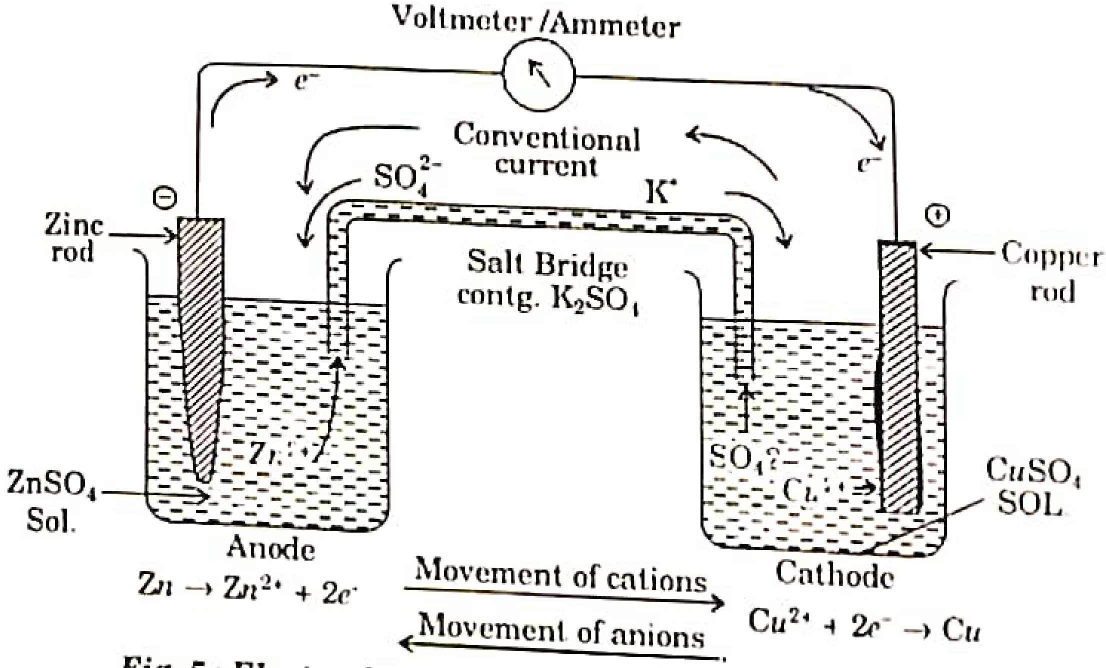


Fig. 5 : Electrochemical cell based on the redox reaction

$$Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu$$

(i) The zinc electrode at which oxidation takes place is called anode while the copper electrode at which reduction takes place is called cathode. The reaction taking place at the anode and cathode are given as

At anode — $Zn \rightarrow Zn^2 + 2e^-$ oxidation half reⁿ

At Cathode — $Cu^{2+} + 2e^- \rightarrow Cu$ reduction half reⁿ

$Zn + Cu^2+ \rightarrow Zn^{2+} + Cu$ overall reaction.

The reaction of anode is called oxidation half reaction and the reaction at the Cathode is reduction half reaction. The reaction obtained by adding these two half reactions is called overall reaction.

(ii) The electrons are produced at the zinc electrode, being negative charge on e^-, it is designated as negative pole. The other electrode (Cu) act as positive pole because it aquires negative charge (electron deficient).

(iii) The electrons flow from negative pole to positive pole, in the external circuit while current is said to flow in opposite direction (conventional direction.)

(iv) The oxidation of zinc produce excess of zinc ions in the left beaker and reduction of copper ion of $CuSO_4$ solution to copper atom leaves the excess of sulphate ions (SO_4^{2-}) in the right beaker. To maintain the electrical balance between the solution of two beakers. Salt bridge play role, and to complete the inner circuit.

(v) As the reaction proceed, the copper from $CuSO_4$ solution is deposited on the copper electrode. So, conc. of copper sulphate solution decreases. Consequently, current carrying tendency also decreases with the passage of time.

(vi) As the cell works, the weight of zinc rod decrease and weight of copper rod increase.

The cell based on the above reaction is commonly called as Daniell cell. A popular form of cell, (fig-6) in which salt bridge is replaced by the porous pot through which SO_4^{2-} ions migrates from $CuSO_4$ (aq) to $ZnSO_4$ (aq)

Difference between electrochemical cell and electrolytic cell

The difference between electrochemical and electrolytic cell given as –

Electrochemical cell	Electrolytic cell
1. A device that convert chemical form of energy into electrical form of energy.	1. A device that convert electrical form of energy into chemical from of energy.
2. It is an example of spontaneous reaction for the production of electrical form of energy.	2. It is an example of non-spontaneous redox reaction and electrical form of energy is required for the reaction to occur..
3. Two seperate beakers are taken, which are connected via salt bridge.	3. Both the electrodes are placed in the same solution of electrolyte.
4. Anode is positively charged and cathode is negatively charged.	4. Anode is positively charged and Cathode is negatively charged.
5. Migration of electrons occur from anode to cathode in the external circuit.	5. Migration of electrons takes place through the cathode to anode. These electrons are supplied by the external source *i.e.* battery.

Representation of an Electrochemical Cell

The following conventions are used to represent an electrochemical cell. These conventions given as :

(i) An Electrochemical cell is represented by writing anode (oxidation) on the left hand side (LHS) and cathode (reduction) on the right hand side (RHS).

$$\underset{\text{oxidation}}{\text{L.H.S.}} \longleftrightarrow \underset{\text{Reduction}}{\text{R.H.S.}}$$

For simplicity use formula

$$\underset{\text{Reduction}}{\overset{\text{R}}{\downarrow}} \quad \underset{\text{Right}}{\overset{\text{R}}{\downarrow}} \quad \underset{\text{Oxidation}}{\overset{\text{O}}{\downarrow}} \quad \underset{\text{Left}}{\overset{\text{L}}{\downarrow}}$$

(ii) The anode of the electrochemical cell represented by the symbol of an element along with there phase (solid, liquid or gas) in the brackett and then followed the symbol of cation of the electrolyte while the cathode of electrochemical cell represented by writing the symbol of anion first followed by the symbol of metal or element along with there phase (solid, liquid or gas). The metal and their ion seperated either by semicolon or by vertical line (that give information about the boundry of beakers.) Similary for cathode, the metal ion and there metal seperated by a vertical line or semicolon. The concentration of an electrolyte is also mentioned with in brackett after the cation.

i.e., **For anode,**

$Zn\,(s);\,Zn^{2+}(C_1)$ or $Zn(s)\,|\,Zn^{2+}\,(1M)$

For cathode

$Cu^{2+}(C_2);\,Cu(s)$ or $Cu^{2+}(1M)\,|\,Cu(s)$

3. The salt bridge indicated by the two vertical lines, which seperate the two half cells. *i.e.*,

$Zn\,(s)\,|\,Zn^{2+}(C_1)||Cu^{2+}(C_2);\,Cu(s)$

The pictorial notation of electrochemical cell represented as (fig. 10)

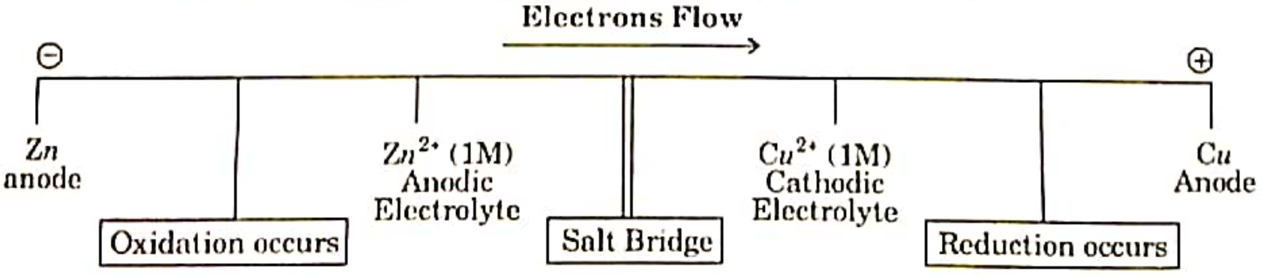


Fig. 10 : Flow diagram for representation of cell

Sometime, negative and positive signs are shown on the electrodes that represents the loss of electrons (*–ve* sign) by the anode and gain of electrons (+ve sign) by the cathode. These signs give information about the movements of electrons from anode to cathode in the external circuit, on the other hand current moves in opposite conventional direction.

Cell Potential or EMF of a Cell

3)

The force which responsible for flow of electrons from one electrode to other electrode and result in the flow of current is called electromotive force. It is represented by E.M.F. and measured in volts (fig. 16).

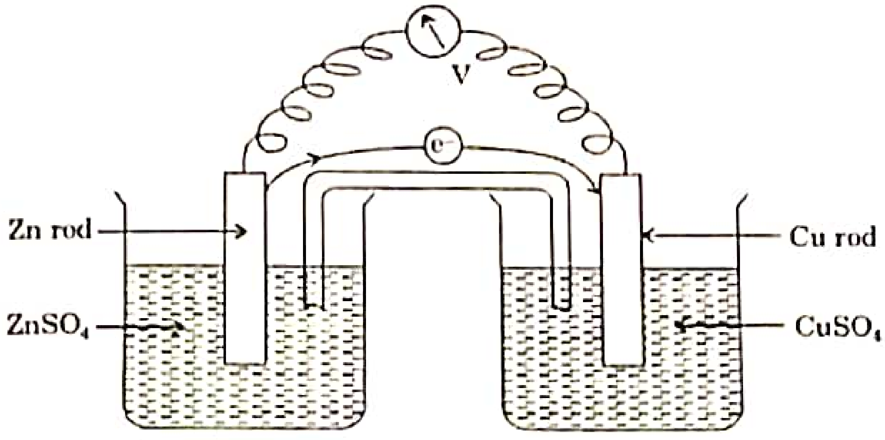


Fig 16 : Flow of e- from one electrode to other

or

It may also defined as the difference in potentials between two electrodes which causes the current to flow from an electrode at higher potential to an electrode at lower potential. If the EMF determined at a temperature of 25°C, the EMF is standard EMF.

Measurement of EMF : The EMF of a cell can be measured by connecting two electrodes to a voltmeter, the voltage or potential difference can be read directly from the voltmeter. But, this method suffer from the following limitations.

1. Some current drawn by the voltmeter of the cell. ∴ emf of the cell get changed.
2. Due to appreciable flow of current a part of e.m.f. will be utilized to overcome the internal resistance of the cell.

These objections can be overcome by using potentiometric method is based upon principle of poggendroff compensation. This principle help in determination of accurate value of e.m.f. of the cell. In this method, unknown value of e.m.f. opposed by another known value of e.m.f., until these two are equal.

The principle involved in the determination of emf of the cell may be explained as. Its simple representation made up of a stretched wire AB of uniform thickness a standard cell, S, whose EMF is known. It is connected to the end of wire A and B. X is a cell whose EMF is to be determined. One end of the cell, X is connected to the end A and the other end to the sliding jockey (J) through the galvanometer (G) in such a manner that it sends EMF in a direction opposite to that of the standard cell(s). The jockey is moved along the stretched wire AB, till at a particular point–C, no deflection is observed in the galvanometer. (Fig.–17) At the null point

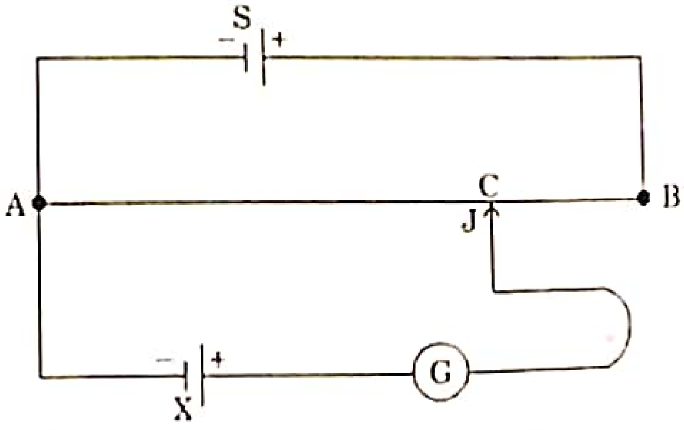


Fig 17 : Poggendroff's compensation method for measuring EMF

$E_s \propto$ length AB

and $E_x \propto$ length AC

Where, E_s – EMF of standard cell

E_x – EMF of experimental cell

$$\frac{E_x}{E_s} = \frac{\text{length AC}}{\text{length AB}}$$

Hence,

$$E_x = \frac{\text{length AC} \times E_s}{\text{length AB}}$$

Thus, knowing the value of Es, the value of Ex can be determined. The accuracy of this method should follows the conditions

(i) The value of Es should be greater than the value of Ex

(ii) The stretched wire (AB) should be uniform

(iii) The sensitivity of galvanometer should be high.

Alternatively, The following arrangement discussed as :

A cell S^1 (Storage battery) whose voltage greater than that of standard cell, S or that of experimental cell, X is connected to the ends A and B of the stretched uniform wire AB, via the variable resistance, R. The Jockey is fixed at a point, C′, on inserted key at point, *a*. So that, standard cell S is in the circuit. The resistance, R is adjusted till there is no deflection in the galvanometer, G (fig-18). Thus, we have

$$E_s \propto \text{length AC}'$$

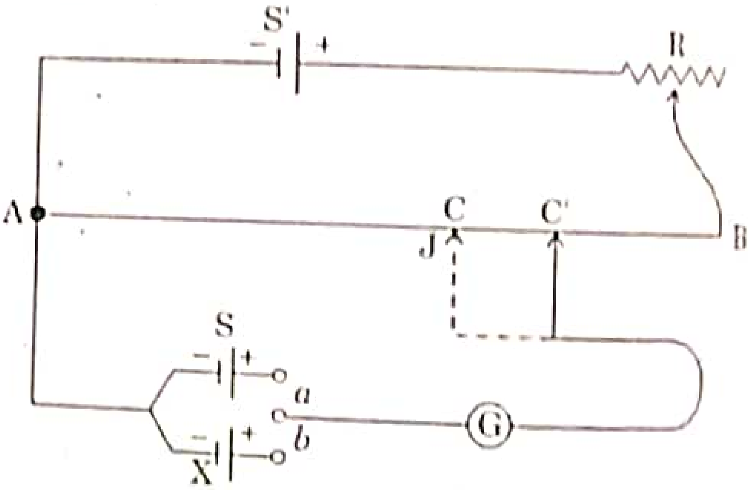


Fig. 18 : *Potentiometer method for measurement of EMF*

Es–EMF of the standard cell. Now, remove the key from position *a*, and insert key at point, *b*. So, the experimental cell, X is in the circuit. The jockey, J moved along the wire AB till no deflection is observed in the galvanometer. Suppose that null point is C. Then we have

$E_x \propto$ length AC.

E_x – Unknown EMF

$$\frac{E_x}{E_s} = \frac{\text{length AC}}{\text{length AC}'}$$

or
$$E_x = \frac{\text{length AC} \times E_s}{\text{length AC}'}$$

Thus, knowing Es, the value of Ex can be calculated.

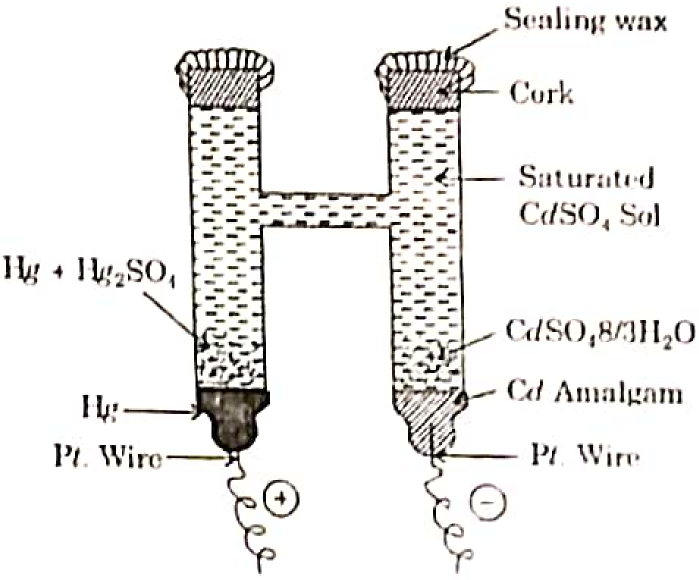
Standred Cell: A cell is said to be standard cell, if it fulfils the following requirements

(i) It has a constant value of EMF which is reproducible.

(ii) The EMF of cell does't change with the passage of time.

(iii) It has a small temperature coefficient. The best form of cell, that fulfils the above mentioned requirements is Wetson standard cell.

Wetson cell is made up of H-shaped glass vessel. Its one limb contain mercury, covered with a paste of mercurous sulphate (Hg_2SO_4) and mercury (Hg). This limb act as anode while the other limb contain cadmium amalgam *i.e.* 12-13 % Cd by weight covered with crystals of solid $3CdSO_4\ 8H_2O$ and then with saturated $CdSO_4$ solution. This limb generally act as cathode (fig. 19) A platinum wire is sealed at the bottom of each tube. The limbs are closed finally with cork and sealing wax. The crystal of $3CdSO_4 . 8H_2O$ always keep the solution of $CdSO_4$, saturated at all the temperatures. The EMF of this cell is usually 1.0185 volt at 15°C, 1.01830 volts at 20°C and 1.0181 volts at 25°C. The EMF of the cells are slightly varies with temperature. This cell can give constant value of their emf for a number of years. The reactions taking place in the cell are as follows :



at anode

$$Cd + \cancel{SO_4^{2-}} \rightleftharpoons CdSO_4 + \cancel{2e^-}$$

at cathode

$$Hg_2SO_4 + \cancel{2e^-} \rightleftharpoons 2Hg + \cancel{SO_4^{2-}}$$

complete reaction is

$$Cd + Hg_2SO_4 \rightleftharpoons CdSO_4 + 2Hg$$

Fig. 19 : Weston standard cell

Reversible and Irreversible Cell

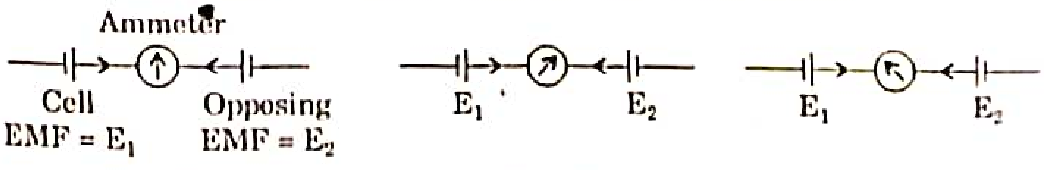
According to thermodynamics, a reversible process is that process in which driving force is infinitesimally different from the opposing force and that can be reversed by applying force infinitesimally greater than the force already acting or the cell sends infinitesimally small current so that, the cell reaction always remain in a state of equilibrium.

A reversible cell must fulfils the following conditions These are :

(i) If an opposing emf (applied from out side source) is equal to the emf of the cell, then no current flowing through the circuit and hence no chemical reaction should takes place. fig. 20 (i)

(ii) If opposing emf slightly smaller than the emf of the cell, an infinitesimally small amount of current flow through the cell and only a small amount of reaction occur in the cell. fig 20 (ii)

(iii) It opposing emf slightly greater than the emf of the cell, an infinitesimally small amount of current flow through the cell in opposite direction and small amount of chemical reactions also occur in opposite direction. [fig-20 (iii)]



$E_2 = E_1$ (*i*)　$E_2 < E_1$ (*ii*)　$E_2 > E_1$ (*iii*)

Fig. 20 : Concept of reversible cell

If the above mentioned conditions not full filled by the cell, it is said to be irreversible.

All the electrochemical cells are reversible consider, an example of Daniel cell. This cell is made up of Zn electrode immersed in a solution of $ZnSO_4$ and Cu-electrode immersed in a solution of $CuSO_4$. These two solution are seperated from each other by placing one solution in porous pot and other solution in the surrounding vessel (fig.–21). The representation of cell given as

$$Zn\,(s) \mid ZnSO_4(aq) \| CuSO_4\,(aq) \mid Cu(s)$$

The directon of arrow indicates the movement of electrons/ current through the cell. During the passage of current, the Cu^{2+} ions deposited on the Cu-electrode from the solution, while Zinc electrode start dissolving in the solution. The two cell reaction in combined form is

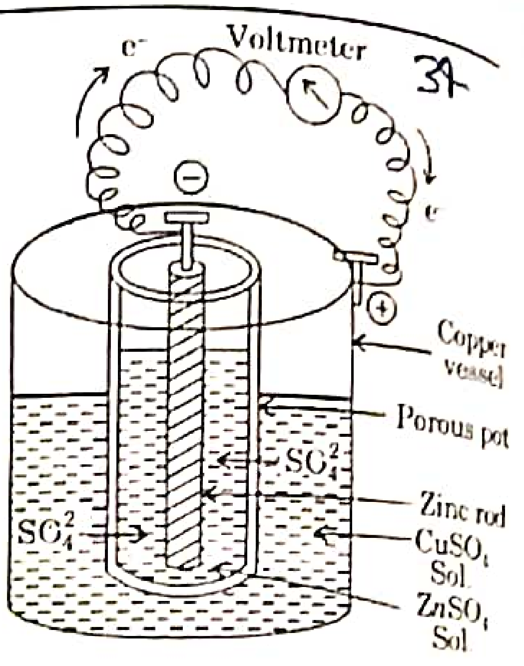


Fig. 21 : Daniell cell

$$Zn + Cu^{2+} \rightarrow Cu + Zn^{2+}$$

In this cell, if emf greater than the emf of the cell is applied, then current flow in the opposite direction and cell reactions is reversed. Thus Daniel cell and other electrochemical cell are reversible only when infinitesimally small amount of current passed and the system remain always in a state of equilibrium.

Irreversible Cell : If a cell (electrochemical) donot fulfils the condition of reversibility, the cell is called as irreversible cell.

Consider a cell, in which a Zinc rod and a silver rod dipped in dilute sulphuric acid. When these rod are connected through the wire, the following reactions have occured *i.e.,*

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$$

i.e., in this reaction, the Zinc dissolve at one electrode while $H_2(g)$ evolved at the other electrode (at silver-Ag electrode). However, when cell are connected with the external source of emf which is slightly greater than the emf of the cell, the following reaction occur *i.e.,*

$$2Ag \rightarrow 2Ag^+ + \cancel{2e^-}$$

$$2H^+ + \cancel{2e^-} \rightarrow H_2(g)\text{(at zinc electrode)}$$

∴ the overall reaction is given as

$$2Ag + 2H^+ \rightarrow 2\,Ag^+ + H_2\text{ (at Zinc)}$$

This reaction indicate, element silver dissolve with the evolution of $H_2(g)$. The cell not [illegible] second condition, because when external emf slightly greater than the emf of the cell is applied, the cell reactions is not reversed and cell behave as irreversibly.

Reversible electrode : The electrodes of a reversible cell are called reversible electrodes, because in reversible cell, half cell reaction proceed in one direction and other half cell reaction proceed in reverse direction.

Electrochemical Series

The standard electrode potential of large number of electrodes has been determined by using SHE *i.e.*, standard hydrogen electrode as the reference electrode. The electrode potential of SHE arbitrary fixed as Zero. It is convenient to take electrode potential of an electrode as reduction potentials. The reduction potential of any electrode can be obtained from oxidation potential by simply changing the sign. ∴ the reduction potential values all the electrodes, are arranged in the form of a series known as electrochemical series. This series is an "arrangement of electrode potential of various electrodes in an decreasing order of their reduction potential value." The electrochemical series also known as activity series. The electrode potentials along with their reduction potential values given in the table–2.

Electrode	Electrode reaction (Oxidized form + $ne^- \rightarrow$ Reduced form)			E° (V)
$F_2\|F^-$	$F_2(g) + 2e^-$	→	$2F^-(aq)$	2.87
$Co^{3+}\|Co^{2+}$	$Co^{3+} + e^-$	→	Co^{2+}	1.81
$H_2O_2\|H_2O$	$H_2O_2 + 2H^+ + 2e^-$	→	$2H_2O$	1.78
$MnO_2, H^+\|Mn^{2+}$	$MnO_2(s) + 4H^+ + 2e^-$	→	$Mn^{2+} + 2H_2O$	1.61
$Au^{3+}\|Au$	$Au^{3+} + 3e^-$	→	$Au(s)$	1.50
$MnO_4^-\|Mn^{2+}$	$MnO_4^- + 8H^+ + 5e^-$	→	$Mn^{2+} + 4H_2O$	1.49
Cl_2, Cl^-	$Cl_2(g) + 2e^-$	→	Cl^-	1.36
$Cr_2O_7^{2-}, H^+\|Cr^{3+}$	$Cr_2O_7^{2-} + 4H^+ + 6e^-$	→	$Cr^{3+} + 7H_2O$	1.33
$O_2, H^+\|H_2O$	$O_2 + 4H^+ + 4e^-$	→	$2H_2O$	1.23
Br_2, Br^-	$Br_2(l) + 2e^-$	→	$2Br^-$	1.09
$NO_3^-, H^+\|NO$	$NO_3^- + 4H^+ + 3e^-$	→	$NO(g) + 2H_2O$	0.97
$Hg^{2+}\|Hg_2^{2+}$	$2Hg_2 + 2e^-$	→	Hg_2^{2+}	0.92
$ClO^-\|Cl^-$	$ClO^- + H_2O + 2e^-$	→	$Cl^- + 2OH^-$	0.89
$Hg^{2+}\|Hg$	$Hg^2 + 2e^-$	→	Hg	0.85
$Ag^+\|Ag$	$Ag^+ + e^-$	→	Ag	0.80
$Hg_2^+\|Hg$	$Hg_2^+ + e^-$	→	$2Hg$	0.79
$Fe^{3+}\|Fe^{2+}$	$Fe^{3+} + e^-$	→	Fe^{2+}	0.78
$MnO_4^-\|MnO_4^{2-}$	$MnO_4^- + e^-$	→	MnO_4^{2-}	0.56
$I_2\|I^-$	$I_2 + 2e^-$	→	$2I^-$	0.54
$Cu^{2+}\|Cu$	$Cu^+ + e^-$	→	Cu	0.52
$Cu^{2+}\|Cu$	$Cu^{2+} + 2e^-$	→	Cu	0.34
$AgCl\|Ag$	$AgCl + e^-$	→	$Ag + Cl^-$	0.22
$Cu^{2+}+Cu$	$Cu^{2+} + e^-$	→	Cu^+	0.15
$AgBr\|Ag$	$AgBr + e^-$	→	$Ag + Br^-$	0.10

Strongest oxidizing agent

Weakest reducing agent

Strength of Oxidizing Agent

Strength of reducing Agent

Application of Electrochemical Series

36

1. To determine the relative strengths of oxidising and reducing agent.

With the help of the activity series, we can predict the relative strengths of oxidising and reducing agents. In this series, the various substances are arranged in an decreasing order of their reduction potential value. Therefore, the element placed on the top of activity series, possesses the maximum value of there reduction potential, thus have strong tendency to accept electrons while the element placed at the bottom of the activity series, possesses least value of there reduction potential, thus have strong tendency to lose electrons (Fig. 36).

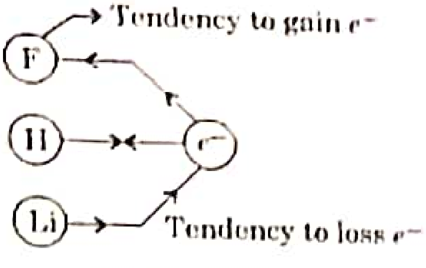


Fig. 36 : To compare oxidising and reducing power of an element

As given,

(i) electrode with high value of reduction potential *i.e.*, strong tendency to gain electron

(ii) electrode with low value of reduction potential *i.e.* less tendency to gain electron while possesses strong tendency to lose electron.

In the reactivity series, the reduction potential value of $F_2(g)$ is highest *i.e.*, + 2.87 V

∴ has strong tendency to accept electrons from the others. ∴ act as strongest oxidising agent or weakest reducing agent. On the other hand, the element lithium has least value of there reduction potential (–3.05 V). It means, element lithium has least tendency to accept electron, while it has strong tendency to lose electrons. ∴ *Li* act as strongest reducing agent than the others and act as weakest oxidising agent.

Conclusion : It has been concluded that a substance which has lower value of electrode potential are stronger reducing agent while which has higher value of electrode potential are stronger oxidising agent.

2. To compares the reactivity of metals : From the series it is clear that, the metal atom which having less value of their reduction potential than the other, have stronger tendency to give electrons than the others ∴ found to be more reactive. Thus, for a reactive metals, its reduction potential value should be low.

For example : The reduction potential values of four metals given as (fig. 37)

Zn^{2+}/Zn = – 0.76 V Ag^{+}/Ag = + 0.80 V

Cu^{2+}/Cu = + 0.34 V Mg^{2+}/Mg = – 2.36 V

The element Mg possesses least value of there reduction potential than others ∴ have strong tendency to loss electrons. Hence, found to be more reactive than others. Thus, from the reduction potential data of four elements, the decrasing order of reactivity given as

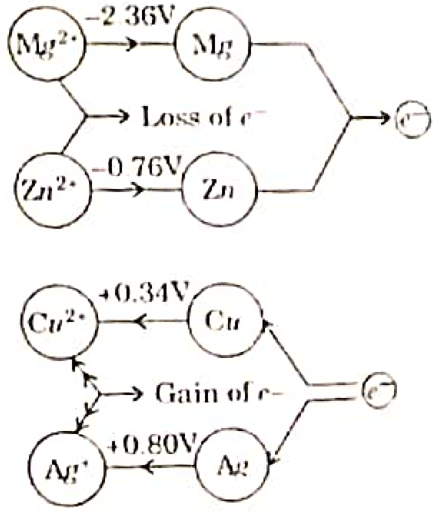


Fig. 37 : Reactivities of metals

$$Mg > Zn > Cu > Ag$$

Application of Electrochemical Series

36

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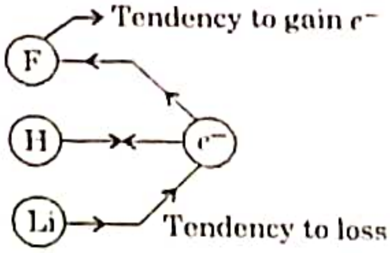

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$\therefore$ has strong tendency to accept electrons from the others, $\therefore$ act as strongest oxidising agent or weakest reducing agent. On the other hand, the element lithium has least value of there reduction potential (–3.05 V). It means, element lithium has least tendency to accept electron, while it has strong tendency to lose electrons. $\therefore$ *Li* act as strongest reducing agent than the others and act as weakest oxidising agent.

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Zn^{2+}/Zn = – 0.76 V Ag^{+}/Ag = + 0.80 V

Cu^{2+}/Cu = + 0.34 V Mg^{2+}/Mg = – 2.36 V

The element Mg possesses least value of there reduction potential than others $\therefore$ have strong tendency to loss electrons. Hence, found to be more reactive than others. Thus, from the reduction potential data of four elements, the decrasing order of reactivity given as

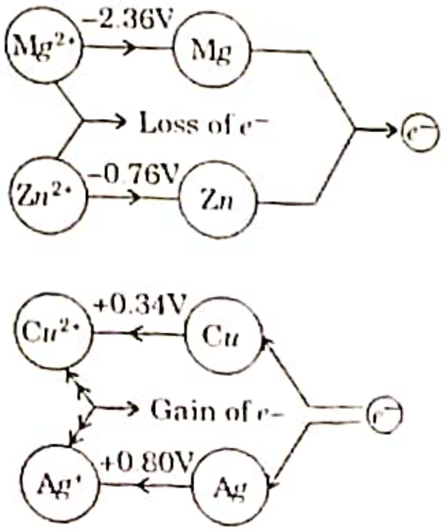

Fig. 37 : Reactivities of metals

Mg > Zn > Cu > Ag

Concept of activity and activity coefficient

It may be noted that when an electrolyte is dissolved in water, the effective concentration of ions in the solution is different than the actual concentration of ions. This is because of the fact, that the presence of large number of ions in the solution, the free movement of each ions get hindered. The situation is similar, if only one swimmer is swimming in a swimming pool, he has greater degree of freedom for movement than if a number of other swimmers are also swimming in the same swimming pool. (fig-42)

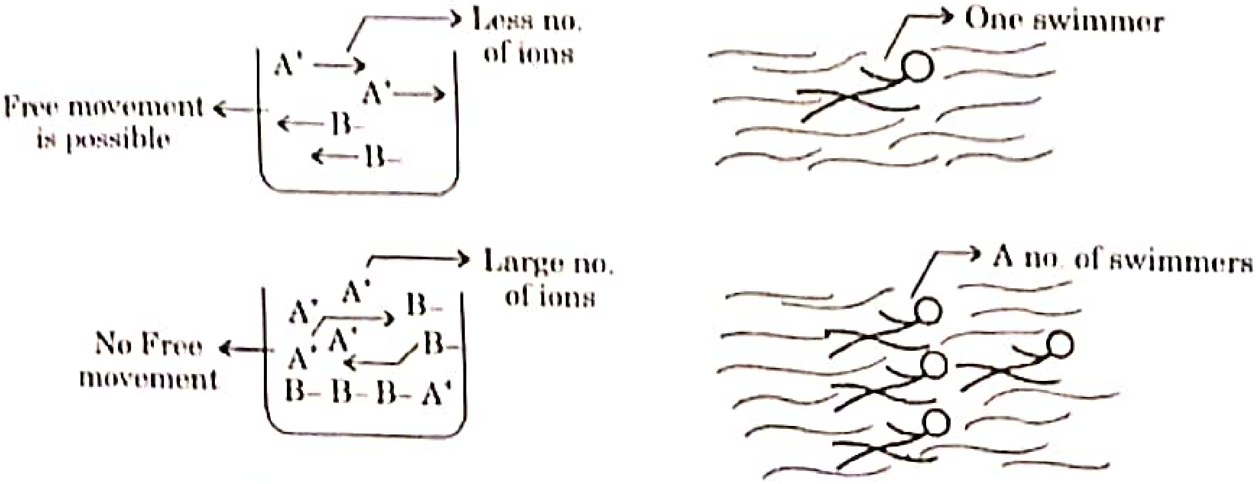

Fig. 42 : Movements of ions (swimmers) in solution

Thus, the effective concentration of an ion or the electrolyte in a solution is called its activity. The activity of an electrolyte represented by the letter 'a'. The term activity (a) related with the actual concentration by the equation

$$a = \gamma \times m$$

where

m – molality *i.e.* number of moles of solute dissolve in 1000 *g* of solvent

γ – activity coefficient

or

$$\gamma = \frac{a}{m} \text{ i.e., } \frac{\text{effective concentration of electrolyte}}{\text{actual concentration of an electrolyte}}$$

Thus, the activity coefficient (γ) is defined as,

It is the ratio of effective concentration to the actual concentration of the ion or electrolyte in solution. It can be determined experimentally if solution is real

$$a < m, \quad \therefore \gamma < 1$$

the less value of, γ due to formation of ion pairs between cations and anions due to electrostatic force of attraction. As a result the effective concentration of ions become less than the actual concentration (fig. 43.)

Nernst Equation for EMF of a Cell

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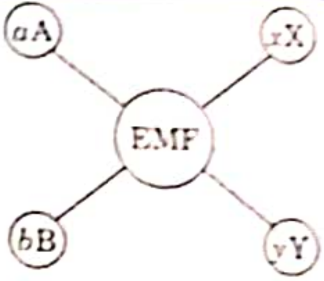

Fig. 44 : Relation of EMF with the activity of species

Nernst equation related with the standard state value of EMF of the cell and activity of the species taking part in cell reaction (Fig. 44).

Consider, a general reversible cell reaction

$$aA + bB \rightleftharpoons xX + yY \quad ...(1)$$

For an electro chemical cell, the change in free energy (ΔG) is related as

$$\Delta G = -nFE \quad ...(2)$$

where

n – number of moles of electrons

F – Faradays of electricity

E – EMF of the cell

Also, change in free energy related as

$$\Delta G^\circ = \Delta G^\circ + RT\, ln\, Q \quad ...(3)$$

where, ($\Delta G^\circ = -nFE^\circ$, E° standard state EMF of cell)

where Q is the quotient of activities on comparing equation (2) and (3) we have

$$-nFE = -nFE^\circ + RT\, ln\, Q \quad ...(4)$$

Dividing both side of equation by nF

$$\frac{-nFE}{nF} = \frac{-\cancel{nF}E}{\cancel{nF}} + \frac{RT}{nF} ln\, Q$$

$$-E = -E^\circ + \frac{RT}{nF} ln\, Q$$

or

$$E = E_0 - \frac{RT}{nF} ln\, Q \quad ...(5)$$

where, Q is the quotient of activity.

IRREVERSIBLE ELECTRODE PROCESSES

It is the process of measurement of EMF of the cell when electric current flowing through the circuit. The most important irreversible processes are

1. Polarisation
2. Over voltage

1. **Polarisation** :- In a cell containing two reversible electrodes, as the cell operates the rate of discharge of ions from the solution and rate of their formation are equal i.e. electrodes are in state of equilibrium. Hence there is no net flow of current if equilibrium is disturbed, then current may flow through the cell.

This disturbance of equilibrium associated with the flow of current is called electrode polarization and the disturbed electrode is said to be polarized. The polarised electrode behave as irreversible electrode. During polarisation rate of discharge of ions is greater than the rate of formation of ions or vice versa. Therefore concentration near the electrodes changes, it is called as concentration polarisation. The phenomenon of concentration polarisation explained as consider, a reversible electrode which is formed by dipping a rod of metal in the solution of its ions i.e. (M^{n+}/M). The reversible electrode possesses a definite value of electrode potential depending upon the concentration of ions in solution. If electrode generally act as cathode, and a potential greater than the reversible electrode potential is applied, then reduction occur at the cathode.

$$Mn^{+} + ne^{-} \longrightarrow M$$

∴ M – discharge on the cathode. As a result conc. near the electrode got decreased. If the ions from the bulk of solution do not migrate towards the electrode, there is fall in conc. of ions around the electrode and the value of electrode potential got decreases as shown in the Nernst equation

4-0

$$E_{M^{n+}/M} = E_{M^{n+}/M} + \frac{RT}{nF} ln \frac{[M^{n+}]}{[M]}$$

But the conc. of [M] = 1

∴ We have $$E_{M^{n+}/M} = E_{M^{n+}/M} + \frac{RT}{nF} ln [M^{n+}]$$

Similarly, consider that electrode act as anode, and a potential greater than its reversible electrode is applied then oxidation occur at the anode. i.e.,

$$M \longrightarrow M^{n+} + ne^-$$

Here, M is dissolve and to give metal ions. As a result conc. of metal ions near the electrode increases, if excess of these ions do not migrate away from the electrode, then the conc. of metal ions increases near the electrode as shown by the Nernst equation

$$E_{M/M^{n+}} = E^{\circ}_{M/M^{n+}} + \frac{RT}{nF} ln \frac{[M]}{[M^{n+}]}$$

or $$E^{\circ}_{M/M^{n+}} = E_{M/M^{n+}} + \frac{RT}{nF} ln \frac{[M]}{[M^{n+}]}$$

$$E_{M/M^{n+}} = E^{\circ}_{M/M^{n+}} + \frac{RT}{nF} ln \frac{1}{[M^{n+}]}$$

Thus, the change in concentration of metal ions around the electrode (*i.e.*, decrease or increase in conc. of ions) during electrolysis resulting into change in value of electrode potential (decrease or increase) than the reversible electrode potential value is called **concentration polarization**. The concenration poLarisation, is due to slow migration of ions from solution to the electrode or from electrode towards the solution. This is supported by the fact that if the solution is stirred during the electrolysis concentration polarisation almost reduce to zero. This is because on stirring the movements of ions increases.

OXYGEN OVER VOLTAGE

Oxygen overvoltage is the voltage observed when the evolution of oxygen gas start at the surface of anode in the electrolytic cell. It is also called as anodic overvoltage.

It is observed that at anode, oxygen is evolved at higher potential than the theoretical value of reversible electrode potential. The value of oxygen over voltage for a few different anodic material at 25°C are given below in table 5.

Table 5 : Oxygen overvoltages at 25°C at low current density ($1 mA/Cm^2$)

Anode	Overvoltage (volts)	Anode	Overvoltage (volts)
Platinized Pt	0.40	Copper	0.42
Smooth *Pt*	0.72	Silver	0.58
Gold	0.67	Nickel	0.35
Graphite	0.53		

Applications of Overvoltage

1. Deposition of metal at the cathode : Consider, the electrolysis of a solution of 1M $ZnSO_4$ and 1M H_2SO_4. The electrode potential of Zinc and hydrogen electrodes is –0.76V and 0.00V. Thus the discharge potential value for hydrogen greater than the discharge potential value of zinc, so hydrogen discharged first as compared to zinc. However in actual practice, the liberation of hydrogen and zinc take place simultaneously, because hydrogen show a overvoltage of 0.70V which is very close to the reversible potential of zinc electrode.

2. Seperation of metals : Consider, one molar solution of each of the following sample i.e. *Cu*, *Ag* and *Cd*, their reduction potential values given as + 0.34V, + 0.80V and – 0.40V respectively. The deposition of metals on the basis of there reduction potential, value follow the order *Ag* > *Cu* > *Cd*.

If there is no deposition of metals, the overvoltage taken into consideration. Overvoltage can be adjusted by changing the temperature so that metals have sufficient difference in there deposition potential.

For example : On electrolysis of ammonical solution of Ni and Zn at 20°C, deposition of both the metals occur simultaneously. However, when temperature is 90°C. *Ni* deposits first completely.

3. Dissolution and corrosion of metals : Generally a metal liberates H_2, on reaction with acid, if its oxidation potential greater than hydrogen.

For example – the oxidation potential of lead and zinc is greater than hydrogen i.e. + 0.13 V for Pb, + 0.76V for *Zn* and 0.00V for H_2. But actually when these two metals dissolve in HCl, they do not give H_2 gas, due to overvoltage of hydrogen *i.e.* 0.64V for *Pb* and 0.70V for *Zn*.

Explaination : Connect a strip of pure zinc with a piece of copper and immerge, both the strips in a solution of dilute acid, the rate of dissolution of zinc increases at the anode. Whereas rate of discharging of H_2 at the cathode (copper), because of overvoltage of *Cu* which is 0.2V Similar result is obtained when Zinc containing copper as an impurity comes in contact with a solution of dilute acid.

Generally, it has been observed, when zinc contains as an impurity of any noble metal whose hydrogen overvoltage is low. Zinc will dissolve and hydrogen gas will be liberated at the noble metal. ∴ corrosion of zinc takes place.

Similarly, when the less noble metals such as Fe and Pb contains impurity of nobler metals having low hydrogen overvoltage, the metals such as Fe and Pb will dissolve in acid while H_2 will be evolved in the nobler metal present as an impurity. The type of corrosion also called as **hydrogen evolution.**

molalities

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Liquid Junction Potontial and its Calculation

In a cell, when two solution of an electrolytes of different concentration are in contact with each other, the more concentrated solution tend to diffuse into the dilute solution *i.e.* there is diffusion of ions across the boundary between the two solution of an electrolyte of different concentrations. In general, the ions move across the boundary between the two solution of an electrolyte with different speeds. As a result an electrical double layer is produced at the junction of two layers. This seperation of charge produces a potential difference at the boundary known as liquid junction potential.

It can also be defined as the difference in potential set up at the junction of two solutions due to difference in speed of ions moving across the boundary. (Fig-62)

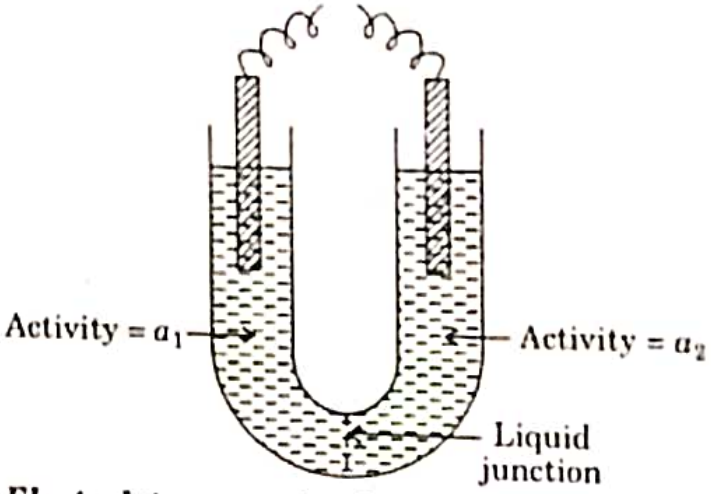

Fig. 62 : Electrolyte concentration cell with a liquid junction

The E_{cell} is equal to sum of the E_1 and E_2 and E_J

$$E_{cell} = E_1 + E_2 + E_J \quad ...(1)$$

Where E_1 and E_2 are the electrode potentials of two electrodes

Calculation : Consider the following cell

H_2 (1 atm) | HCl (a_1) | HCl (a_2) | H_2 (*1* atm)

The sum of the electrode reactions for the cell given as

$$H^+(a_2) \longrightarrow H^+(a_1)$$

The sum of two electrode potential ($E_1 + E_2$) from Nernst equation is

$$E_1 + E_2 = -\frac{RT}{F} ln \frac{(a_{H^+})_1}{(a_{H^+})_2} \quad ...(2)$$

$$= \frac{RT}{F} ln \frac{(a_{H^+})_2}{(a_{H^+})_1}$$

$$\therefore \quad E_1 + E_2 = \frac{RT}{F} ln \frac{(m_{H^+} \gamma_{H^+})_2}{(m_{H^+} \gamma_{H^+})_1} \quad ...(3)$$

The EMF of such cell given as

$$E = 2t \frac{RT}{F} ln \frac{m_2\gamma_2}{m_1\gamma_1} \qquad ...(4)$$

$$(E = E_1 + E_2 + E_J)$$

The equation (1) can be written as

$$E_J = E - (E_1 + E_2) \qquad ...(5)$$

Substitute the value of E from equation (4) and value of $E_1 + E_2$ from equation (3) into equation (5)

We obtain $$\boxed{E_J = 2t_- \frac{RT}{F} ln \frac{m_2\gamma_2}{m_1\gamma_1} - \frac{RT}{F} ln \frac{\left(m_{H^+}\gamma_{H^+}\right)_2}{\left(m_{H^+}\gamma_{H^+}\right)_1}} \qquad ...(6)$$

But where $\left(m_{H^+}\right)_1 = m_1$ and $\left(m_{H^+}\right)_2 = m_2$

and $\left(\gamma_{H^+}\right)_2 = \gamma_2$ and $\left(\gamma_{H^+}\right)_1 = \gamma_1$

Hence equation (1) becomes

$$\boxed{E_J = 2t_- \frac{RT}{F} ln \frac{m_2\gamma_2}{m_1\gamma_1} - \frac{RT}{F} ln \frac{m_2\gamma_2}{m_1\gamma_1}}$$

or

$$= (2t_- - 1) \frac{RT}{F} ln \frac{m_2\gamma_2}{m_1\gamma_1} \qquad ...(7)$$

Since

$$\begin{aligned} t_+ + t_- &= 1 \\ 2t_- - 1 &= t_- + (t_- - 1) \\ &= t_- + (-t_+) = t - t_+ \end{aligned}$$

∴ equation (7) takes the form

$$\boxed{E_J = (t_- - t_+) \frac{RT}{F} ln \frac{m_2\gamma_2}{m_1\gamma_1}} \qquad ...(8)$$

The equation (8) gives the liquid junction potential of the cell with transference. The liquid junction potentials depends on the (i) the difference between transport number of an electrolytes (ii) and the activity of two solutions.

> **Note :** When speed of cations and anions are same ($t_+ = t_-$) then liquid junction potential is equal to zero.
>
> For similar reason, we use the saturated solutions of KCl and NH_4Cl in the salt bridge.

Applications :

1. In determination of Activity and Activity coefficient: Consider a cell, without transference

$$H_2 (1\ atm) \mid HCl (a), AgCl(s)/Ag$$

Here in this cell the electrode of hydrogen and electrode of silver dipped in HCl solution of activity, *a*.

The activity coefficient of HCl calculated as the cell reaction given as

$$\frac{1}{2}H_2\,(1\text{ atm}) + AgCl\,(s) \longrightarrow Ag(s) + H^+\left(a_{H^+}\right) + Cl^-\,(a_{Cl^-})$$ where $(n = 1)$

The Nernst equation for EMF of the cell is

$$E = E^\circ_{Ag/AgCl} + \frac{RT}{F} ln \frac{1}{a_{H^+} a_{Cl^-}}$$

or

$$E^\circ_{Ag/AgCl} + \frac{RT}{F} ln \frac{1}{a}$$ $(a = a_{H^+} = a_{Cl^-})$

The activity (a) and molality (m) are related as

$$a = m^2 \gamma_\pm^2 \qquad \text{...(3)}$$

Putting the value of 'a' in equation (2) we obtain

$$E = E^\circ_{Ag/Ag\,Cl} + \frac{RT}{F} ln \frac{1}{m^2 \gamma_\pm^2}$$

or

$$E = E^\circ_{Ag/Ag\,Cl} + \frac{RT}{F} \qquad \left[ln\,1 - 2\,ln\,m\gamma_\pm\right]$$

$$= E^\circ_{Ag/Ag\,Cl} - \frac{2RT}{F} ln\,m\gamma_\pm$$

$$= E^\circ_{Ag/Ag\,Cl} - \frac{2RT}{F} ln\,m - \frac{2RT}{F} ln\,\gamma_\pm$$

On rearranging, we get the equation

$$\left(E + \frac{2RT}{F} ln\,m\right) - E^\circ_{Ag/AgCl} = -\frac{2RT}{F} ln\,\gamma_\pm \qquad \text{...(5)}$$

where

$\gamma_\pm$ – mean activity coefficient for H^+ and Cl^- ions in solution

5. **What are the difference between electrolytic and galvanic cells. Give examples.**

Ans.

Galvanic cell	Electrolytic cell
1. Electricity is produced because of indirect redox reaction.	1. Electricity is used to bring about chemical reaction.
2. The reaction is of spontaneous nature.	2. The chemical reaction is not spontaneous.
3. A salt bridge is used to connect two half cells.	3. No salt bridge is required.
4. In electrochemical cell anode is negative and cathode is positive.	4. In electrolytic cell anode is positive and cathode is negative.
5. In external circuit electrons flow from anode to cathode.	5. In electrolytic cell electrons enter through cathode and leave through anode.
6. In this cell oxidation and reduction reactions take place in two separate containers. *e.g.* $Zn - Cu$/Cell	6. In this cell oxidation and reduction reactions are carried out in single container. *e.g.* Electrolysis of $NaCl(aq)$

Give difference between electrochemical cell and electrolytic cell. 47

s.

Electrochemical cell	Electrolytic cell
1. Electricity is produced because of indirect redox reaction.	1. Electricity is used to bring about chemical reaction.
2. The reaction is of spontaneous nature.	2. The chemical reaction is not spontaneous.
3. A salt bridge is used to connect two half cells.	3. No salt bridge is required.
4. In electrochemical cell anode is negative and cathode is positive.	4. In electrolytic cell anode is positive and cathode is negative.
5. In external circuit electrons flow from anode to cathode.	5. In electrolytic cell electrons enter through cathode and leave through anode.
6. In this cell oxidation and reduction reactions take place in two separate containers.	6. In this cell oxidation and reduction reactions are carried out in single container.

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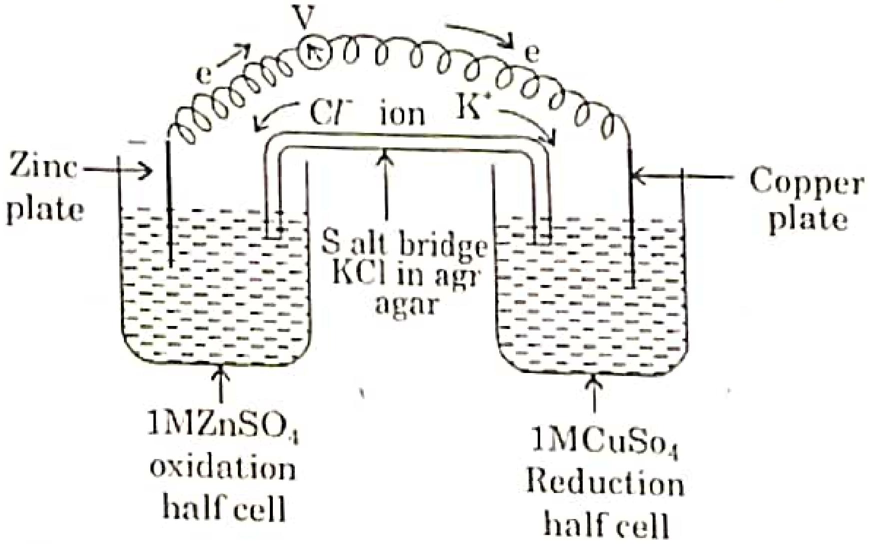
5. What is Galvenic cell? Explain its construction and operation by taking example of Daniel cell.

ns. Galvenic cell : It is a device in which chemical energy is converted to electrical energy and that chemical energy is obtained by indirect redox reaction.

A Daniel cell is an example of electrochemical cell e.g. Zn-Cu cell



A zinc plate is dipped in a 1M solution of zinc sulphate and a copper plate is dipped in 1M solution of copper sulphate taken in two different beakers. The solutions are connected by a salt bridge as in the diagram. The circuit is completed using copper wire and a voltmeter

Working : (i) Zn atom gets oxidised after losing electrons

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^- \qquad \text{Oxidation}$$

(ii) The electrons given by Zn are accepted by $Cu^{2+}(aq)$ in the other container.

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \qquad \text{reduction}$$

By adding the above equations, the net cell reaction is

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

It is an example of indirect redox reaction.

Function of salt bridge :

(1) It completes the electric circuit.

(2) It maintains electrical neutrality.

The salt bridge provides cations and anions to overcome the accumalation of positive and negative ions produced in the two half cells.

The galvenic cells works till the electrical neutrality is maintained by salt bridge.