

### Basic Concepts

System : A system may be defined as that part of universe which is under consideration. It possess fixed boundaries.

System is classified into 3 types :-

① Open System : The system which allows the exchange of both matter and energy with the surrounding.

Example : open cup of tea.

② Closed System : The system which allows only the exchange of energy (and not matter) with the surroundings is called a closed system.

Example : A cup of tea with lid.

③ Isolated System : The system which can neither exchange nor matter nor energy with the surrounding is called an Isolated system.

Example : Tea in thermos-flask.

Intensive Properties : The properties which do not depend upon the quantity of matter present in the system are called intensive properties.

Example : Melting Point, Boiling Point, Density, Viscosity etc.

Extensive Properties : The properties which depends upon the quantity of matter present in the system are called extensive properties.

Example : Mass, Volume, Internal Energy, Entropy etc.

## Types of Processes

- ① Isothermal Process :- A process is said to be isothermal if, in each step of process, temperature remains constant.
- ② Isochoric Process :- The process is said to be isochoric if volume remains constant in each step of the process.
- ③ Isobaric Process :- A process is said to be isobaric if the pressure remains constant.
- ④ Adiabatic Process :- It is a process in which heat remains constant means, heat change is zero.  
 $\Delta H = 0$

## Concept of Heat and Work

Heat :- The form of energy exchanged between a system and its surrounding, when the two are at different temperatures is commonly known as Heat.

It is represented by  $q$ .

Heat absorbed by the system  $\therefore q$  is positive

Heat lost by the system  $\therefore q$  is negative.

Units of Heat :- The SI unit of heat is Joule.

Work :- Work is usually referred to mechanical work if the point of application of a force is displaced in the direction of the force.

Work = Force applied  $\times$  Displacement

$$W = F \times d$$

## Sign convention for work

Work done on the system =  $w$  is positive

Work done by the system =  $w$  is negative

Units of work :- ergs, joules or Kilojoules

SI unit  $\therefore$  Joule.

## Some other type of work

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① Electrical work: This type of work is involved in the reactions involving ions.

It is defined as equal to product of EMF and the quantity of electricity. Thus

$$\text{Electrical work} = \text{E.M.F.} \times \text{Quantity of Electricity}$$

② Pressure-Volume work (Work of Expansion)

Let us consider a gas enclosed in a cylinder fitted with a movable piston as shown in figure.

Suppose the volume of the gas enclosed in the cylinder is  $V$  and the area of cross-section of the piston is  $A$ .

Suppose the piston moves a very small distance  $dl$ .

The change in volume  $dV$  is given by

$$dV = A \times dl$$

As Pressure =  $\frac{\text{Force}}{\text{Area}}$

or Force = Pressure  $\times$  Area

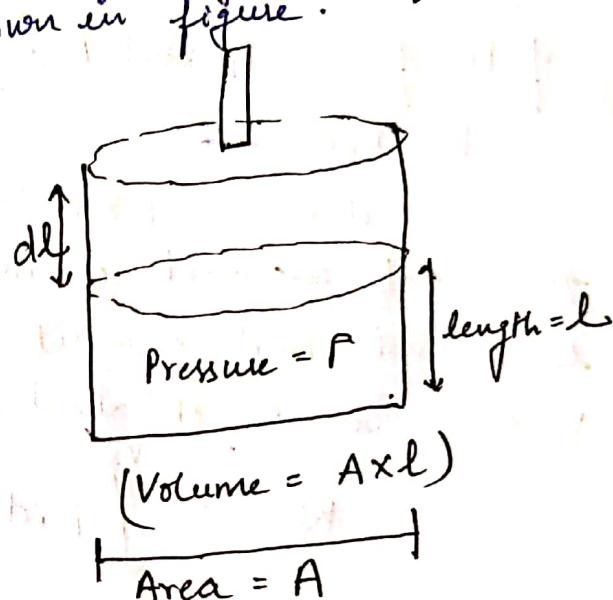
If the work done by the small movement of the piston is  $dw$ , we have

$$dw = -P \times A \times dl$$

$$= -P dV \quad (\text{By the system})$$

If Pressure is constant, the total work done,  $w$ , is given by.

$$w = - \int_{V_1}^{V_2} P dV = -P(V_2 - V_1) = -P\Delta V$$



# Work done in Isothermal and Reversible Expansion of an Ideal gas

Suppose an Ideal gas is taken at temperature  $T$  in a cylinder which is filled with frictionless and weightless piston. Let the initial volume of the gas be  $V_1$  and pressure  $P_1$ . Suppose the gas expands reversibly and isothermally (at fixed temperature  $T$ ) from volume  $V_1$  to  $V_2$ . Due to expansion, the pressure of gas falls from  $P_1$  and  $P_2$ .

We know . . .

$$dW = -P \times dV \quad (\text{in infinite small step})$$

The total amount of work done by the gas during isothermal and reversible expansion from volume  $V_1$  to  $V_2$  can be obtained by integrating the above eq.

$$W = - \int_{V_1}^{V_2} P \cdot dV$$

$$\text{For Ideal gas } PV = nRT$$

$$W_{rev} = - \int_{V_1}^{V_2} \frac{nRT}{V} \cdot dV$$

$$= -nRT \int_{V_1}^{V_2} \frac{1}{V} dV = -nRT \ln \frac{V_2}{V_1}$$

$$W_{rev} = -2.303 nRT \log_{10} \frac{V_2}{V_1}$$

Q-11 10g of Argon gas are expanded isothermally and reversibly at a temperature of 27°C from 10 ltr to 20 ltr. Find the work done in the process.  
 (Atomic Mass of Ar = 40 g mol<sup>-1</sup>) 3

Answer → Work done in Isothermal and reversible expansion of a gas is given by

$$W = -2.303 nRT \log \frac{V_2}{V_1}$$

In above question

$$n = \frac{10}{40} = 0.25 \quad (\text{Argon is monoatomic, its molecular mass = atomic mass})$$

$$T = 27^\circ\text{C} = 300\text{ K}$$

$$V_1 = 10\text{ L}, V_2 = 20\text{ L}$$

$$R = 8.31 \text{ J K}^{-1}\text{mol}^{-1}$$

Substituting the values

$$\begin{aligned} W &= -2.303 \times 0.25 \times 8.314 \times 300 \times \log \frac{20}{10} \\ &= -432.29 \text{ J} \end{aligned}$$

Q-2 :- 5 moles of an Ideal gas are expanded isothermally and reversibly at  $25^{\circ}\text{C}$  from a pressure of 100 atm to 1 atm. Calculate the work done in the process.

Answer :- Work done by a gas during isothermal reversible expansion is given by

$$W = -2.303 nRT \log \frac{P_1}{P_2}$$

$$n = 5 \text{ moles.}$$

$$T = 25^{\circ}\text{C} = 298 \text{ K}$$

$$P_1 = 100 \text{ atm}$$

$$P_2 = 1 \text{ atm.}$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$W = -2.303 \times 5 \times 8.314 \times 298 \times \log \frac{100}{1}$$

$$= -5.70 \times 10^4 \text{ J}$$

$$= \underline{-57.0 \text{ KJ}}$$

## Internal Energy

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Every system that has some quantity of matter is associated with definite amount of energy is called Internal Energy.

$$E = E_{\text{Electronic}} + E_{\text{Vibrational}} + E_{\text{Rotational}} + E_{\text{Translational}}$$

## Characteristics of Internal Energy

- ① Internal Energy is a state property
- ② The change in Internal energy does not depends on the path by which final state is reached.
- ③ Internal Energy of an Ideal gas is a function of temperature only.
- ④ Internal energy of a system depends upon the quantity of substance, its chemical nature, temperature, pressure and volume.
- ⑤ The unit of Internal Energy is ergs in CGS and Joule in SI

$$1 \text{ Joule} = 10^7 \text{ ergs}$$

- ⑥ Change in internal energy ( $\Delta E$ )  $\rightarrow$  It is neither possible nor necessary to calculate the absolute value of Internal Energy of a system

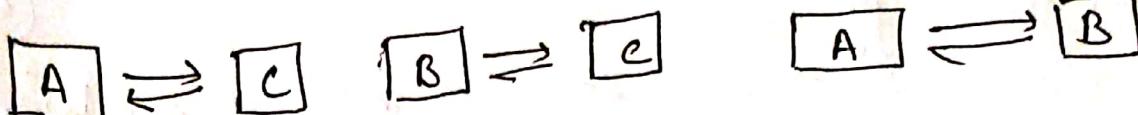
So, we calculate  $\Delta E = E_2 - E_1$

if  $E_2 > E_1$ , then  $\Delta E$  is positive

if  $E_1 > E_2$  then  $\Delta E$  is negative

## Zeroth law of Thermodynamics

If a system A is in thermal equilibrium with system C and if B is also in thermal equilibrium with system C, then A and B are in thermal equilibrium with each other whatever the composition of the system.



### First law of Thermodynamics

- ① Energy can neither be created nor be destroyed, although it can change from one form to another.
- ② The total Energy of the universe is constant

### Mathematical formulation of 1st law of Thermodynamics

The internal Energy of the system can be changed in two ways :-

(For increase in Internal Energy )

- ① Supply heat to the system

If an initial state Internal Energy is  $E_1$ , then after this step it becomes  $E_1 + q$

- ② By doing work on the system

$$E_1 + q + w = E_2$$

$$q + w = E_2 - E_1$$

$$\Delta E = q + w$$

### Some conclusions :-

- ① If  $w=0$ , then  $\Delta E = q$   
means if no work is done on the System, then change in Internal Energy is equal to heat absorbed by the system.
- ② If  $\Delta E = 0$  then  $q = -w$   
means if Internal Energy of system remains constant, then work done by the system is equal to heat absorbed.

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③ If the work done is work of expansion  
then  $w = -P\Delta V$

Substituting the value in equation

$$\Delta E = q + w$$

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

$$q = \Delta E + P\Delta V$$

If process is carried out at constant volume  $\Delta V = 0$

$$q_V = \Delta E$$

means under constant volume and constant temperature conditions, the change in Internal Energy of the system is equal to heat absorbed by the system.

Q-1 A system absorbs 400 J of heat and does work equivalent to 150 J on the surroundings.  
Calculate the change in Internal Energy.

Ans: Heat absorbed  $q = 400 \text{ J}$

Work done by the system  $w = -150 \text{ J}$

According to 1st law of Thermodynamics

$$\Delta E = q + w$$

$$= 400 + (-150)$$

$$= 250 \text{ J.}$$

## Enthalpy !

The sum of Internal Energy and Pressure-Volume energy of a system, under a particular set of conditions, is referred as Enthalpy of the system.

It is denoted by  $H$

$$H = E + PV$$

$$\text{and } \Delta H = \Delta E + P\Delta V \xrightarrow{\text{(If change takes place at Constant Pressure)}}$$

According to 1st law of Thermodynamics

$$\Delta E = q + w$$

If work is work of expansion, then  $w = -P\Delta V$

$$\text{we get } \Delta H = q \quad \Delta E = q - P\Delta V$$

Substitute this value of  $\Delta E$  in eq ①

$$\Delta H = q - P\cancel{\Delta V} + P\Delta V$$

$$\Delta H = q_p \quad (q_p \text{ refers to heat change at constant pressure})$$

## Heat Capacity !

The heat capacity of a system is the amount of heat required to raise the temperature of a substance by  $1^\circ C$  (or K)

## Molar Heat Capacity

The molar heat capacity of a system is defined as amount of heat required to raise the temperature of one mole of the substance by 1 K

①

$$C = \frac{q}{T_2 - T_1} = \frac{qV}{\Delta T}$$

Since the heat capacity varies with temperature, it would be more correct to define molar heat capacity in terms of following differential equation

$$C = \frac{dq}{dT}$$

where  $q$  is infinite small amount of heat absorbed by the system to raise its temperature by  $dT$ .

Units  $\therefore$  In CGS  $\pm$  cal  $K^{-1} mol^{-1}$   
SI  $= J K^{-1} mol^{-1}$

### Molar heat capacity at Constant Volume ( $C_V$ )

$$C_V = \frac{q_V}{dT}$$

We know  $q_V = \Delta E$

$$\cancel{C_V = q_V} \quad C_V = \left( \frac{\Delta E}{dT} \right)_V \text{ or } C_V = \left( \frac{\partial E}{\partial T} \right)_V$$

### At constant Pressure $C_P$

$$C_P = \frac{q_P}{dT}$$

$$q_P = \Delta H$$

$$C_P = \left( \frac{\Delta H}{dT} \right)_P = C_P = \left( \frac{\partial H}{\partial T} \right)_P$$

and  $\boxed{C_P - C_V = R}$

Entropy: Entropy is measure of randomness or disorder of molecules in a system. It is represented by  $S$ . It is state function i.e. it does not depend upon the path followed but depends upon the initial and final state of the system. It is extensive property.

$\text{Vapour} > \text{Liquid} > \text{Solid}$ .

Greater the randomness, higher is the entropy of the system. Solid substances have minimum randomness because the constituent particles are arranged in well-ordered fashion. Hence, solid substances having minimum entropy. Similarly, gaseous substance have maximum randomness due to arrangement of constituent particles in irregular fashion. Hence gaseous substances have maximum entropy.

Entropy is expressed in  $\text{JK}^{-1}\text{mole}^{-1}$   
A small differential change in entropy is given

$$\text{by } dS = \frac{dq}{T}$$

A finite change in entropy for a reversible process is given by

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

Note: All natural processes are spontaneous and irreversible and are accompanied by a net increase in entropy.

## Entropy change in Reversible process!

Suppose in an isothermal and reversible process, the system absorbs heat  $q_{rev}$  from surrounding at temperature  $T$ . This result in an increase in the entropy of the system given by

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

But the entropy of surrounding decreases because the surrounding lose the same amount of heat i.e  $-q_{rev}$  Hence  $\Delta S_{\text{surrounding}} = -\frac{q_{rev}}{T}$

Hence the net change in entropy is

$$\begin{aligned}\Delta S_{\text{net}} &= \Delta S_{\text{sys}} + \Delta S_{\text{sur}} \\ &= \frac{q_{rev}}{T} + \left( -\frac{q_{rev}}{T} \right) = 0\end{aligned}$$

This in a reversible process, the net entropy change for a combined system and surrounding is zero. (i.e there is no net change in entropy)

## Entropy change in a Irreversible process!

Suppose a system maintained at higher temperature  $T_1$ , passes  $q$  amount of heat irreversibly to its surrounding maintained at a lower temperature  $T_2$ , then

Decrease in entropy of system,

$$\Delta S_{\text{sys}} = -\frac{q}{T_1}$$

Increase in the entropy of surroundings

$$\Delta S_{\text{sur}} = \frac{+q}{T_2}$$

The net change in entropy is given by,

$$\Delta S_{\text{irr}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}}$$

$$= -\frac{q}{T_1} + \frac{q}{T_2}$$

$$= q \left( \frac{T_1 - T_2}{T_1 \cdot T_2} \right)$$

Since  $T_1 > T_2$ ,  $(T_1 - T_2)$  is positive

Hence  $\Delta S_{\text{irr}} > 0$

means entropy increases in irreversible process.

Entropy change for an Ideal gas

(a) In terms of  $T \delta V$ : Suppose  $n$  moles of an ideal gas occupy a volume  $V$  at temperature  $T$  and pressure  $P$ . If system absorbs infinite small amount of heat  $dq_{\text{rev}}$  reversibly at temperature  $T$ , the increase in entropy is given by

$$dS = \frac{dq_{\text{rev}}}{T} \quad \rightarrow (1)$$

According to 1st law of Thermodynamics

$$dE = dq_{\text{rev}} + dw$$

$$dq_{rev} = dE - dw \quad \textcircled{2}$$

If the work involved is due to expansion of gas,

$$\text{then } dw = -PdV$$

Then equation  $\textcircled{2}$  can be rewritten as

$$dq_{rev} = dE + PdV \quad \textcircled{3}$$

$$\text{We know } C_V = \frac{dE}{dT}$$

for  $n$  moles of ideal gas

$$dE = nC_VdT$$

Put value of  $dE$  in eq  $\textcircled{3}$

$$dq_{rev} = nC_VdT + PdV \quad \textcircled{4}$$

We know, for ideal gas

$$PV = nRT$$

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

Equation  $\textcircled{4}$  can be re-written as

$$dq_{rev} = nC_VdT + \frac{nRT}{V} \cdot dV \quad \textcircled{5}$$

Put this value of  $dq_{rev}$  in eq  $\textcircled{1}$  (Entropy formula)

$$ds = \frac{nC_VdT + \frac{nRT}{V} \cdot dV}{T}$$

$$ds = \frac{nC_VdT}{T} + nR \frac{dV}{V} \quad \textcircled{6}$$

For finite change of state of system, the entropy

change  $\Delta S$ , can be obtained by integrating equation ⑥

$$\int_{S_1}^{S_2} dS = nC_V \int_{T_1}^{T_2} \frac{dT}{T} + nR \int_{V_1}^{V_2} \frac{dV}{V}$$

$$\Delta S = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} - \textcircled{7}$$

$$\Delta S = 2.303 n C_V \log_{10} \frac{T_2}{T_1} + 2.303 n R \log_{10} \frac{V_2}{V_1} - \textcircled{8}$$

In terms of Temperature and Pressure

Let  $P_1$  be the pressure of the Ideal gas in initial state and  $P_2$  in final state. Then for  $n$  moles of an Ideal gas

$$P_1 V_1 = nRT_1 \quad \text{and}$$

$$\frac{P_1 V_1}{T_1}$$

$$P_2 V_2 = nRT_2$$

$$\frac{P_2 V_2}{T_2}$$

$$\text{or } \frac{V_2}{V_1} = \frac{P_1 \times T_2}{P_2 \times T_1}$$

Substitute this value of  $\frac{V_2}{V_1}$  in eq  $\textcircled{7}$

$$\Delta S = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{P_1 \times T_2}{P_2 \times T_1}$$

$$= nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2} - \textcircled{9}$$

As we know  $C_p - C_v = R$

$$\text{Therefore } C_V = (C_p - R)$$

Substitute value of  $C_V$  in eq ⑨

$$= n(C_p - R) \ln \frac{T_2}{T_1} + nR \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2}$$

$$= nC_p \ln \frac{T_2}{T_1} - nR \ln \cancel{\frac{T_2}{T_1}} + nR \ln \cancel{\frac{T_2}{T_1}} + nR \ln \cancel{\frac{P_1}{P_2}}$$

$$= nC_p \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2}$$

$$\Delta S = nC_p \ln \frac{T_2}{T_1} - nR \ln \frac{P_2}{P_1} \quad \textcircled{10}$$

$$\Delta S = 2.303 nC_p \log_{10} \frac{T_2}{T_1} - 2.303 nR \log_{10} \frac{P_2}{P_1} \quad \textcircled{11}$$

Entropy change of an Ideal gas in different processes.

① Isothermal process :- An isothermal process is carried out at constant temp,  $\Delta T = 0$

$$\text{So } \Delta T = T_2 - T_1 = 0$$

$$T_2 = T_1$$

Put value in eq  $\textcircled{10}$

$$\Delta S_T = nR \ln \frac{V_2}{V_1}$$

Put value in eq  $\textcircled{10}$

$$\Delta S_T = -nR \ln \frac{P_2}{P_1}$$

(2) Isobaric Process! - For Isobaric process

$$\Delta P = 0$$

$$\Delta P = P_2 - P_1 = 0.$$

$$P_2 = P_1$$

Put value in eq  $\textcircled{1}$

$$\Delta S_p = nC_p \ln \frac{T_2}{T_1}$$

(3) Isochoric Process! -  $\Delta V = 0$

$$\Delta V = V_2 - V_1 = 0$$

$$V_2 = V_1$$

Put value in eq  $\textcircled{2}$

$$\Delta S_v = nC_v \ln \frac{T_2}{T_1}.$$

Ques : The enthalpy change for transition of liquid water to steam  $\Delta H_{\text{vap}}$  is  $40.8 \text{ kJ mol}^{-1}$  at  $100^\circ\text{C}$ . Calculate the entropy change ( $\Delta S_{\text{vap}}$ ) for the process.

Ans :  $\Delta H_{\text{vap}} = 40.8 \text{ kJ/mol}$

$$T_b = 100^\circ\text{C} = 100 + 273 = 373 \text{ K}$$

Entropy of Vapourisation

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

$$\Delta S_{\text{vap}} = \frac{40.8}{373} = \underline{0.109 \text{ kJ mol}^{-1} \text{ K}^{-1}}$$

## Gibbs free Energy :

The maximum amount of energy available to a system during a process for doing useful work under constant temperature and pressure is called Gibbs free Energy.

Mathematically,  $G = H - TS$

## Free Energy change :

$$G_f = H - TS$$

$$H = E + PV$$

$$G_f = E + PV - TS$$

Differentiate this equation

$$\Delta G = \Delta E + P\Delta V + V\Delta P - T\Delta S - S\Delta T$$

If change is carried out at constant temp & Pressure  
 $\Delta T = 0$  and  $\Delta P = 0$

$$\Delta G = \Delta E + P\Delta V - T\Delta S$$

$$\Delta H = \Delta E + P\Delta V$$

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

Gibbs free Energy and spontaneity  
A process is spontaneous only when  $\Delta S_{total}$  is positive.  
i.e entropy of universe increases.

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

Suppose a reaction is carried out at constant temperature and pressure and  $q_p$  is heat transferred by the system to the surrounding. The heat taken by the surrounding will thus be equal to  $(-q_p)$  system.

$$q_{p\text{ surrounding}} = -q_{p\text{ system}} = -\Delta H_{system}$$

$$\Delta S_{sur} = \frac{-q_p}{T} = -\frac{\Delta H_{sys}}{T}$$

$$\begin{aligned}\Delta S_{total} &= \Delta S_{sys} + \Delta S_{sur} \\ &= \Delta S_{sys} - \frac{\Delta H_{sys}}{T}\end{aligned}$$

Omit the term system

$$\Delta S_{\text{total}} = \Delta S - \frac{\Delta H}{T}$$

Multiply whole equation by T

$$T\Delta S_{\text{total}} = T\Delta S - \Delta H$$

$$-T\Delta S_{\text{total}} = \Delta H - T\Delta S$$

$$\Delta G = -T\Delta S_{\text{total}}$$

when

$\Delta G = -ve$ , process is spontaneous

$\Delta G = 0$ , the process is in equilibrium

$\Delta G = +ve$ , the process is non-spontaneous

### Variation of Free Energy with Temperature and Pressure

$$G = H - TS$$

$$H = E + PV$$

$$G = E + PV - TS$$

Differentiate the above equation

$$dG = dE + PdV + VdP - TdS - SdT \quad \text{--- (1)}$$

According to 1st law of Thermodynamics

$$dE = dq + dw$$

$$dq = dE - dw \quad \text{--- (2)}$$

If work is done by the system and its pressure-

Volume work, then

$$dw = -PdV$$

Put value of dw in eq (2)

$$dq = dE + PdV \quad \text{--- (3)}$$

We know as per Entropy formulae

$$dS = \frac{dq}{T} \quad !. \quad TdS = dq$$

and eq (3) can be rewritten as

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$$TdS = dE + PdV$$

Substitute value in eq ①

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

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

If pressure remains constant

$$dP = 0$$

$$(dG)_p = - SdT \quad \text{--- (5)}$$

$$\boxed{\left(\frac{dG}{dT}\right)_p = -S}$$

If temperature remains constant

$$dT = 0$$

$$(dG)_T = VdP \quad \text{--- (6)}$$

$$\boxed{\left(\frac{dG}{dP}\right)_T = V}$$

### Variation of free Energy at constant Temperature

From equation ⑥

$$dG = VdP \quad (\text{At constant Temperature})$$

$$\int_{G_1}^{G_2} dG = \int_{P_1}^{P_2} VdP \quad PV = nRT \quad \left[ V = \frac{nRT}{P} \right]$$

$$\int_{G_1}^{G_2} dG = \int_{P_1}^{P_2} \frac{nRT}{P} dP$$

$$\int_{G_1}^{G_2} dG = nRT \int_{P_1}^{P_2} \frac{dP}{P}$$

$$G_2 - G_1 = nRT \ln \frac{P_2}{P_1}$$

$$\Delta G = 2.303 nRT \log_{10} \frac{P_2}{P_1}$$

The Helmholtz energy or Work function (A) (13)

It is denoted by A

and represented by

$$A = E - TS \rightarrow \begin{matrix} \text{Entropy} \\ \downarrow \\ \text{Internal Energy} \end{matrix}$$

$$\Delta A = \Delta E - T\Delta S \rightarrow (1)$$

We know.

$$\Delta E = q + w$$

For Reversible process

$$\Delta E = q_{rev} + w_{rev}$$

If work is done by the system

$$\Delta E = q_{rev} - w_{rev} \rightarrow (2)$$

$$\Delta S = \frac{q_{rev}}{T} \quad \therefore q_{rev} = T\Delta S$$

Substitute value of  $q_{rev}$  in equation (2)

$$\Delta E = T\Delta S - w_{rev}$$

$$\Delta E - T\Delta S = -w_{rev} \rightarrow (3)$$

We know.

$$\Delta A = \Delta E - T\Delta S$$

So, equation (3) can be rewritten as

$$\Delta A = -w_{rev}$$

$$\therefore \Delta A = w_{rev}$$

So decrease in work function A, in any process, at constant

## Free Energy and EMF of the cell :-

Gibbs free energy is defined as the thermodynamic potential that signifies the maximum or reversible work performed by a thermodynamic system at constant temp and pressure. Work done by electrical power in one second is given as the product of emf of the cell and total charge passed.

$$\text{Therefore } W = nFE_{cell}$$

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where  $w$  = work done,  $nF$  = total charge passed.

$w = \text{work done}$

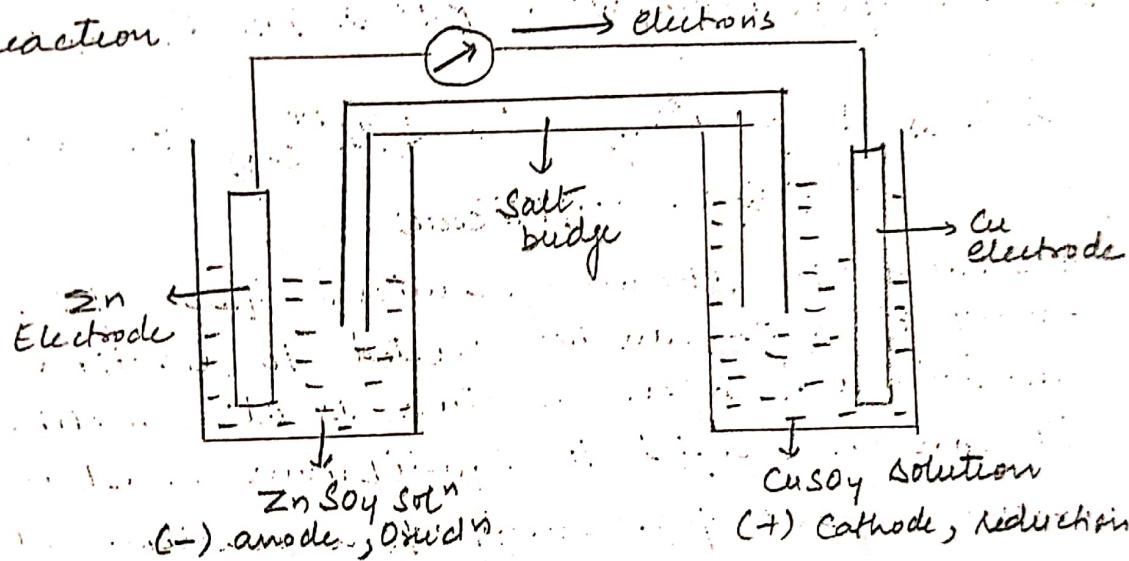
$nF = \text{total charge passed}$  through cell.

$E_{\text{cell}}$  = emf of the cell.

when the charge is passed reversibly through the galvanic cell, it is observed that.

maximum work is done by the galvanic cell.

This reversible work done by the galvanic cell is related to decrease in Gibbs energy of the reaction.



$$\Delta G = \pm w$$

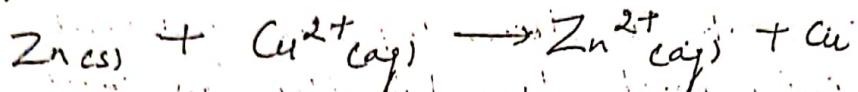
$$\Delta G = -nFE_{\text{cell}}$$

where  $w$  = work done,  $nF$  = total charge passed and  $E_{\text{cell}}$  = emf of the cell.

The above equation can also be used to calculate the standard cell potential when concentration of all the reacting species is unity. Then  $E_{\text{cell}} = E^{\circ}_{\text{cell}}$  (emf of the cell is equal to standard cell potential)

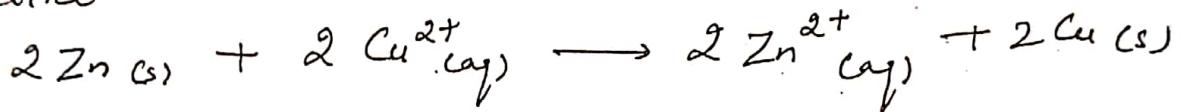
$$\Delta G^{\circ} = -nFE^{\circ}_{\text{cell}}$$

Gibbs energy of a reaction is an Extensive thermodynamic property means its value depends on  $n$ . Thus for two cell reactions involving different values of  $n$ , we observe different values of Gibbs free energy of the Rx.



$$\Delta G = -2FE_{(cell)}$$

whereas after multiplying RHS & LHS by 2, we notice



$$\Delta G = -4FE_{(cell)}$$

According to thermodynamics, Gibbs free energy of a Rx can be related to reaction quotient and when reaction is at equilibrium it can be related to equilibrium constant.

Since Gibbs free energy of a reaction also depends upon the emf of the cell, we can relate the equilibrium constant of a cell Rx with standard cell potential

$$\Delta G^\circ = -nFE^\circ_{(cell)}$$

$$\Delta G^\circ = -RT \ln K$$

$$-nFE^\circ_{(cell)} = -RT \ln K$$

$$E^\circ_{(cell)} = \frac{-T}{nF} \ln K$$

(7)

### Nernst Equation

(Dependence of EMF on Concentration and temperature)

In study of the electrochemical cells, the electrode potential of the electrodes as well as EMF of the cell is determined under standard conditions i.e. electrolyte conc. of each half cell is 1M and temp is 298 K. However these values will not hold good in case of concentration of electrolyte in two half cells are different from 1M and if temp is also not 298 K. Under these conditions, the electrode potential of an electrode as well as the EMF of the cell is determined with the help of Nernst Equation.

For a general Reduction Rx-



The Nernst Equation may be written as

$$E = E^{\circ} - \frac{RT}{nF} \ln \frac{[M(s)]}{[M^{n+} \text{ (aq)}]}$$

$$E = E^{\circ} - \frac{2.303 RT}{nF} \log \frac{[M(s)]}{[M^{n+} \text{ (aq)}]}$$

E = Electrode potential under given conditions

$E^{\circ}$  = Electrode potential under standard conditions

R = Gas Constant ( $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ )

$T$  = Temp. in Kelvin

$n$  = no. of electrons involved in the Rx

$F = 1 \text{ f araday } (96500 \text{ C mol}^{-1})$

$[M_{Cs}]$  = Molar conc. of metal = 1

$[M^{n+}]$  = Molar conc. of ions in soln

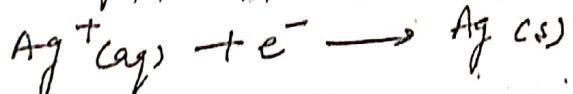
Substituting values of  $R$ ,  $F$  and  $T$  (298 K)

$$E = E^{\circ} - \frac{2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}}{F \times n \times 96500 \text{ C mol}^{-1}} \log \frac{1}{[M^{n+}]}$$

$$E = E^{\circ} - \frac{0.0591}{n} \log \frac{1}{[M^{n+}]}$$

$$\text{or } E = E^{\circ} + \frac{0.0591}{n} \log [M^{n+}]$$

Ques :- Calculate the reduction potential for the following half cell Rx at 298 K



Given that  $[\text{Ag}^{+}] = 0.1 \text{ M}$  and  $E^{\circ} = +0.80 \text{ V}$

Ans :- According to Nernst Equation

$$E = E^{\circ} - \frac{0.0591}{n} \log \frac{1}{[M^{n+}]}$$

$$E = E^{\circ} - \frac{0.0591}{n} \log \frac{1}{[\text{Ag}^{+}]}$$

$$E^{\circ} = +0.80 \text{ V}, n=1, [\text{Ag}^{+}] = 0.1 \text{ M}$$

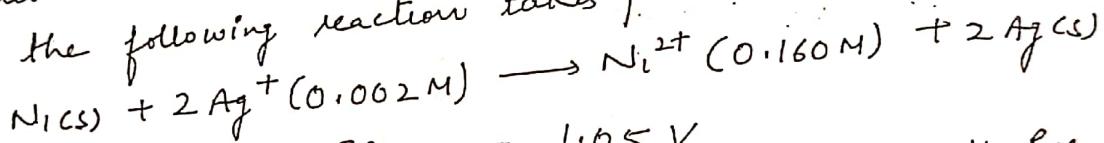
By substituting values in equation

$$E = 0.80 - \frac{0.0591}{1} \log \frac{1}{0.1} = 0.80 - 0.0591 \\ [as \log \frac{1}{0.1} = 1] = 0.741 V.$$

Applications  
Calculation of EMF of the cell with the help of  
 Nernst Equation

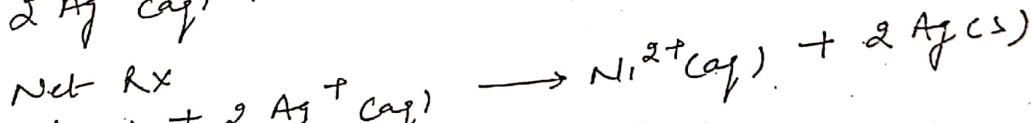
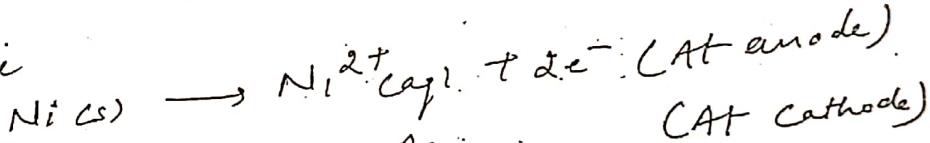
$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{n} \log \frac{[\text{Anode}]}{[\text{Cathode}]}$$

Ques! Calculate the e.m.f of the cell in which  
 the following reaction takes place:



$$\text{Given } E^{\circ}_{\text{cell}} = 1.05 V$$

Answer! The Oxidation and reduction half Rx



According to Nernst Eq:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{n} \log \frac{[\text{Anode}]}{[\text{Cathode}]}$$

$$E_{\text{cell}} = [E^{\circ}_{\text{Ag}^+/Ag} - E^{\circ}_{\text{Ni}^{2+}/\text{Ni}}] - \frac{0.0591}{2} \log \frac{[\text{Ni}^{2+}]}{[\text{Ag}^+]^2}$$

$$= 1.05 - \frac{0.0591}{2} \log \frac{0.16}{(0.002)^2}$$

$$= 1.05 - \frac{0.0591}{2} \log (4 \times 10^4) = 1.05 - \frac{0.0591}{2} (\log 4 + \log 10)$$

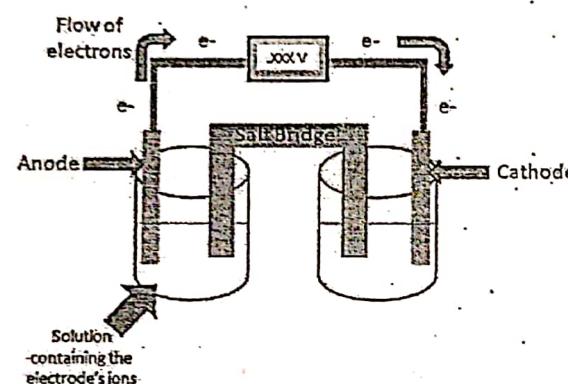
$$= 1.05 - \frac{0.0591}{2} \times 4.6020 = 1.05 - 0.1360 = 0.914 V$$

## CELL POTENTIAL

### Introduction

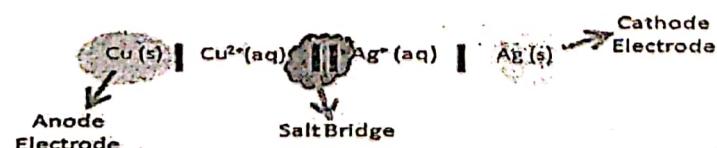
The cell potential,  $E_{cell}$ , is the measure of the potential difference between two half cells in an electrochemical cell. The potential difference is caused by the ability of electrons to flow from one half cell to the other. Electrons are able to move between electrodes because the chemical reaction is a redox reaction. A redox reaction occurs when a certain substance is oxidized, while another is reduced. During oxidation, the substance loses one or more electrons, and thus becomes positively charged. Conversely, during reduction, the substance gains electrons and becomes negatively charged. This relates to the measurement of the cell potential because the difference between the potential for the reducing agent to become oxidized and the oxidizing agent to become reduced will determine the cell potential. The cell potential ( $E_{cell}$ ) is measured in voltage (V), which allows us to give a certain value to the cell potential.

### How to measure the cell potential?



The image above is an electrochemical cell. The voltmeter at the very top in the gold color is what measures the cell voltage, or the amount of energy being produced by the electrodes. This reading from the voltmeter is called the voltage of the electrochemical cell. This can also be called the potential difference between the half cells,  $E_{cell}$ . Volts are the amount of energy for each electrical charge;  $1V=1J/C$ : V= voltage, J=joules, C=coulomb. The voltage is basically what propels the electrons to move. If there is a high voltage, that means there is high movement of electrons. The voltmeter reads the transfer of electrons from the anode to the cathode in Joules per Coulomb.

### Cell Diagram



## Standard Cell Potential

The standard cell potential ( $E^{\circ}_{\text{cell}}$ ) is the difference of the two electrodes, which forms the voltage of that cell. To find the difference of the two half cells, the following equation is used:

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{Red,Cathode}} - E^{\circ}_{\text{Red,Anode}} \quad (1a)$$

with

- $E^{\circ}_{\text{cell}}$  is the standard cell potential (under 1M, 1 Barr and 298 K).
- $E^{\circ}_{\text{Red,Cathode}}$  is the standard reduction potential for the reduction half reaction occurring at the cathode
- $E^{\circ}_{\text{Red,Anode}}$  is the standard reduction potential for the oxidation half reaction occurring at the anode

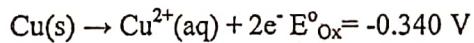
The units of the potentials are typically measured in volts (V). Note that this equation can also be written as a sum rather than a difference

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{Red,Cathode}} + E^{\circ}_{\text{Ox,Anode}} \quad (1b)$$

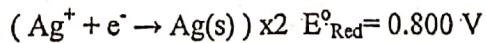
where we have switched our strategy from taking the difference between two reduction potentials (which are traditionally what one finds in reference tables) to taking the sum of the oxidation potential and the reduction potential (which are the reactions that actually occur). Since  $E^{\circ}_{\text{o}}\{\text{Red}\} = -E^{\circ}_{\text{o}}\{\text{Ox}\}$ , the two approaches are equivalent.

### Standard Cell Potential Example

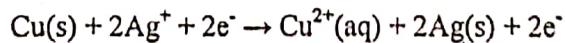
The example will be using the picture of the Copper and Silver cell diagram. The oxidation half cell of the redox equation is:



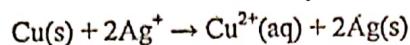
where we have negated the reduction potential  $E^{\circ}_{\text{Red}} = 0.340 \text{ V}$ , which is the quantity we found from a list of standard reduction potentials, to find the oxidation potential  $E^{\circ}_{\text{Ox}}$ . The reduction half cell is:



where we have multiplied the reduction chemical equation by two in order to balance the electron count but we have not doubled  $E^{\circ}_{\text{Red}}$  since  $E^{\circ}$  values are given in units of voltage. Voltage is energy per charge, not energy per reaction, so it does not need to account for the number of reactions required to produce or consume the quantity of charge you are using to balance the equation. The chemical equations can be summed to find:



and simplified to find the overall reaction:



where the potentials of the half-cell reactions can be summed

$$E^\circ_{\text{Cell}} = E^\circ_{\text{Red,Cathode}} + E^\circ_{\text{Ox,Anode}}$$

$$E^\circ_{\text{Cell}} = 0.800 \text{ V} + (-0.340 \text{ V})$$

$$E^\circ_{\text{Cell}} = 0.460 \text{ V}$$

to find that the standard cell potential of this cell is 0.460 V. We are done.

Note that since  $E^\circ_{\text{o,Red}} = -E^\circ_{\text{o,Ox}}$  we could have accomplished the same thing by taking the difference of the reduction potentials, where the absent or doubled negation accounts for the fact that the reverse of the reduction reaction is what actually occurs.

$$E^\circ_{\text{Cell}} = E^\circ_{\text{Red,Cathode}} - E^\circ_{\text{Red,Anode}}$$

$$E^\circ_{\text{Cell}} = 0.800 \text{ V} - 0.340 \text{ V}$$

$$E^\circ_{\text{Cell}} = 0.460 \text{ V}$$