

- from hot object to cold object and in case of reverse process, some work must be expanded.

Concept of Entropy: →

For each Carnot cycle

$$\frac{\Phi_2 - \Phi_1}{\Phi_2} = \frac{T_2 - T_1}{T_2}$$

(12R)

$$1 - \frac{\Phi_1}{\Phi_2} = 1 - \frac{T_1}{T_2}$$

$$\frac{\Phi_1}{\Phi_2} = \frac{T_1}{T_2}$$

$$\frac{\Phi_1}{T_1} = \frac{\Phi_2}{T_2}$$

$$\therefore \boxed{\frac{\Phi}{T} = \text{constant}}$$

The quantity where heat absorbed or lost divided by absolute temperature is a constant quantity.

If we use +ve sign for heat absorbed and -ve sign for heat lost

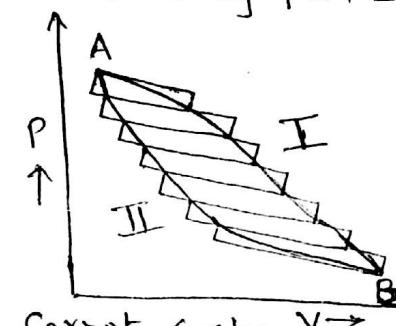
$$\frac{\Phi_2}{T_2} = -\frac{\Phi_1}{T_1}$$

$$\frac{\Phi_2}{T_2} + \frac{\Phi_1}{T_1} = 0$$

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

For all the isothermal and adiabatic process carried out infinitesimally or reversibly, the sum of  $\Phi/T$  terms is zero.

Any reversible cyclic process if carried out reversibly is shown to consist of infinite number of Carnot cycles. Consider a reversible cyclic process, where in the system at state A moves to state B along path I and this in turn moves to state A along path II.



The closed part ABCA consists of infinite no of Carnot cycles.

Starting from A and moving successively along these Carnot cycles, the system reaches the state B leaving the outer zig-zag path. This outer path closely corresponds to the continuous curve of ABA. From this it is clear that any reversible cyclic process will contain infinite number of Carnot cycles. For each Carnot cycle

$$+\frac{Q_2}{T_2} = -\frac{Q_1}{T_1}$$

$$\frac{Q_2}{T_2} + \frac{Q_1}{T_1} = 0$$

$$\sum \frac{\delta Q}{T} = 0$$

For infinitesimal changes  $\sum \frac{\delta Q}{T} = 0$

For the above reversible cyclic process

$$\sum \frac{\delta Q}{T} = \int_A^B \frac{\delta Q}{T} + \int_B^A \frac{\delta Q}{T} = 0$$

$\int_A^B \frac{\delta Q}{T}$  is a summation of all the  $\frac{\delta Q}{T}$  terms when system moves from A  $\rightarrow$  B along path I.

$\int_B^A \frac{\delta Q}{T}$  is a summation of  $\frac{\delta Q}{T}$  terms along path II.

$$\int_A^B \frac{\delta Q}{T} = \int_B^A -\frac{\delta Q}{T}$$

$$\int_A^B \frac{\delta Q}{T} = \int_A^B \frac{\delta Q}{T}$$

This indicates that  $\frac{\delta Q}{T}$  is a definite quantity which is independent of the path followed. Its value depends on the same functions at states A and B. This function is known as entropy function.

If  $S_A$  and  $S_B$  are the entropy values in initial(A) and final states(B) respectively, the change in entropy is given as  $S_B - S_A = \frac{\delta Q}{T}$

For an infinitesimal change, it is given as  $dS = \frac{\delta Q}{T}$   
For a finite process

$$\Delta S = \frac{Q}{T}$$

Therefore, entropy is defined as the change in entropy ( $\Delta S$ ), but not as entropy itself.

Entropy Change  $\Delta S$  is defined as "the amount of heat absorbed or lost isothermally and reversibly divided by the absolute temperature at which heat is absorbed or lost".

Since the heat changes in Carnot cycle are reversible the above equations can be written as,

$$\therefore \Delta S = \frac{Q_{rev}}{T}$$

Units of Entropy:-

Since entropy is equal to heat energy divided by absolute temperature therefore it is measured in entropy units (eu) which are cal.deg<sup>-1</sup>.mol<sup>-1</sup>.(or) cal.k<sup>-1</sup>.mol<sup>-1</sup>.

In the SI system, the units are J.mol<sup>-1</sup>.deg<sup>-1</sup> or J.mol<sup>-1</sup>.K<sup>-1</sup>. These are represented by EU.

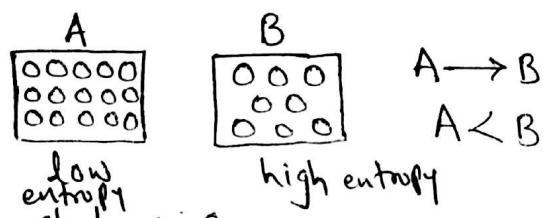
$$1 \text{ eu} = 4.184 \text{ EU}$$

Physical significance of Entropy:-

Entropy is a measure of disorder or randomness of a system. More is the disorder of the system, greater will be its entropy. An increase in disorderness during a physical or chemical process indicates increase of entropy.

Consider a molecular system existing in two states A and B. In the state A the molecules are regularly arranged in an orderly fashion and its entropy is low.

While in state B the molecules are randomly arranged and its entropy is high.



Change of state A (regular arrangement) to state B (disorder) leads to increase of entropy.

According to law of probability state A is less probable than state B. As a result of state A changing to state B is spontaneous. On this basis it can be stated that 'Any change which can be accompanied by increase of entropy tends to be spontaneous'.

Entropy change of a reversible process:-

A reversible process is the one, when heat is absorbed by the system reversibly and at the same time heat is lost by the surroundings also reversibly.

In a reversible process

$$\Delta S_{sys} = \frac{Q_{rev}}{T}$$

$$\Delta S_{surr} = -\frac{Q_{rev}}{T}$$

Net change of entropy  $\rightarrow$

$$\Delta S_{sys} + \Delta S_{surr} = \frac{Q_{rev}}{T} - \frac{Q_{rev}}{T} = 0$$

$$\therefore \Delta S_{sys} + \Delta S_{surr} = 0$$

For a thermodynamically reversible process, the net entropy change of the combined system and surroundings taken together is zero.

Entropy change of an irreversible process:

If any small part of a reversible process is carried out rapidly then the entire process becomes irreversible.

Even in such irreversible process,  $\Delta S$  of system will depend on the heat absorbed reversibly.

$$+ \Delta S_{sys} = \frac{Q_{rev}}{T} \quad \text{---(i)}$$

If  $-Q_{irrev}$  is the heat lost by the surroundings at temp T, then  $\Delta S$  of the surroundings in an irreversible process is given as,

$$\Delta S_{surr} = -\frac{Q_{irrev}}{T} \quad \text{---(ii)}$$

Net change of entropy

$$\Delta S_{sys} + \Delta S_{surr} = \frac{Q_{rev}}{T} - \frac{Q_{irrev}}{T} \quad \text{---(iii)}$$

It is known that the work done in a reversible process is greater than irreversible process.

$$W_{rev} > W_{irrev} \quad \text{---(iv)}$$

According to 1st law of thermodynamics

$$W \propto Q \quad \text{---(v)}$$

$$Q_{rev} > Q_{irrev} \quad \text{---(vi)}$$

Divide both sides with temperature

$$\frac{Q_{rev}}{T} > \frac{Q_{irrev}}{T}$$

$$\frac{Q_{rev}}{T} - \frac{Q_{irrev}}{T} > 0 \quad \text{---(vii)}$$

$$\therefore \Delta S_{sys} + \Delta S_{surr} > 0. \quad (\text{From eq (iii)})$$

For a thermodynamically irreversible process, the net entropy change for the combined system and surroundings together always  $> 0$ .  
 For a irreversible process, the total entropy always increases.  
 The combined equation for entropy change is,

$$\Delta S_{sys} + \Delta S_{surr} \geq 0$$

$$\Delta S_{sys} + \Delta S_{surr} = 0 \text{ (For reversible process)}$$

$$\Delta S_{sys} + \Delta S_{surr} > 0 \text{ (For irreversible process)}$$

Based on this another statement for second law given as,  
 "All spontaneous processes are accompanied by increase of entropy".

### Entropy Change in universe:-

Most of the processes occurring in nature are spontaneous and irreversible due to which the entropy of the universe is continuously increasing".

The essentials of 1st and 2nd law of thermodynamics were combined by Clausius and is stated as, "Energy of the universe remains constant - but entropy of universe is continuously increasing and it tends to maximum".

Problems:-

(1) A Carnot engine is operating between  $110^\circ\text{C}$  and  $25^\circ\text{C}$ . Calculate the efficiency of this heat engine. What would be the efficiency of heat-engine if the boiler temp is raised to  $140^\circ\text{C}$  and temperature of sink remaining same.

Sol:  $T_2 = 110^\circ\text{C} = 383\text{K}; T_1 = 25^\circ\text{C} = 298\text{K}$

$$\eta = \frac{T_2 - T_1}{T_2} = \frac{383 - 298}{383} = 0.222 = 22.2\%$$

$$T_2 = 140^\circ\text{C} = 413\text{K}$$

$$T_1 = 25^\circ\text{C} = 298\text{K}$$

$$\eta = \frac{T_2 - T_1}{T_2} = \frac{413 - 298}{413} = 0.278 = 27.8\%$$

(2) An engine operating at temps of ~~373~~ <sup>333</sup> ~~100~~ <sup>100</sup> ~~0~~ <sup>0</sup>  $100^\circ\text{C}$  and  $0^\circ\text{C}$  takes 453.6 kilocal. of heat. How much useful work can be done by it.

Sol:  $\frac{W}{Q_2} = \frac{T_2 - T_1}{T_2}$

$$W = \frac{373 - 273}{373} \times 453.6$$

$$W = 121.6 \text{ k.r.l} \Rightarrow 121.6 \times 4.184 \text{ kJ} \Rightarrow 508.8 \text{ kJ}$$

(3) Calculate the amount of heat supplied to Carnot cycle working between  $95^{\circ}\text{C}$  and  $15^{\circ}\text{C}$  if the maximum work obtained is 214 cal.

$$\text{Soln: } W = 214 \text{ cal} \quad T_1 = 15^{\circ}\text{C} \quad T_2 = 95^{\circ}\text{C} \quad (368\text{K}) \quad (288\text{K})$$

$$\frac{W}{Q_2} = \frac{T_2 - T_1}{T_2}$$

$$\frac{214}{Q_2} = \frac{368 - 288}{368}$$

$$Q_2 = \frac{214 \times 368}{80} = 984.4 \text{ cal.}$$

(4) An heat engine working b/w  $227^{\circ}\text{C}$  and  $27^{\circ}\text{C}$  absorbs 1 k.cal of heat from  $227^{\circ}\text{C}$  reservoir per cycle. Calculate amount of heat discharged into low temp reservoir, amount of work done,  $\eta$  of cycle.

$$\text{Sol: } T_2 = 227^{\circ}\text{C} = 500\text{K}$$

$$T_1 = 27^{\circ}\text{C} = 300\text{K}$$

$$\eta = \frac{500 - 300}{500} = \underline{\underline{0.4}} = 40\%$$

$$\eta = \frac{W}{Q_2}$$

$$W = \eta \times Q_2 = 0.4 \times 1 = \underline{\underline{0.4 \text{ Kcal}}}$$

$$\eta = \frac{Q_2 - Q_1}{Q_2} = \frac{1 - Q_1}{1} = 0.4$$

$$0.4 = 1 - Q_1$$

$$\therefore \boxed{Q_1 = \underline{\underline{0.6 \text{ K.cal.}}}}$$

(5) A heat engine working between  $0^{\circ}\text{C}$  and  $100^{\circ}\text{C}$  takes up 840 Joules from the high temperature reservoir. calculate the work done and the efficiency?

$$\eta = 26.4\%$$

$$+ \quad \quad \quad W = 225.20 \text{ Joules}$$

### Entropy Change - Phase Change:-

Change of phase occurs during the following processes.

(1) When solid melts to liquid (or) when liquid freezes to solid.

Solid melting  $\rightarrow$  liquid ; Liquid freezing  $\rightarrow$  solid

(2) Change in phase also occurs when liquid evaporates to vapour or when vapour condenses to liquid,

Liquid vapourisation  $\rightarrow$  Vapour ; Vapour condensation  $\rightarrow$  liquid

Temperature remains constant as long as the phase changes completely. Phase change occurs at constant temperature. The heat evolved or absorbed during phase change at constant temperature is called Latent heat ( $\Delta H$ )

Entropy Change ( $\Delta S$ ) for any process is

$$\Delta S = \frac{\Delta H_L}{T}$$

Entropy Change for melting

$$\Delta S_m = \frac{\Delta H_{Lm}}{T}$$

Entropy Change for vapourization

$$\Delta S_v = \frac{\Delta H_{Lv}}{T}$$

The process of melting and vapourization involve absorption of heat. They show increase in entropy and hence  $\Delta S$  for these processes is +ve.

The process of freezing and condensation involve evolution of heat therefore they show decrease of entropy and hence  $\Delta S$  is -ve.

Work function (A) and Free energy function (G):-

Apart from thermodynamics quantities like heat ( $Q$ ), internal energy ( $E$ ), enthalpy ( $H$ ), entropy ( $S$ ), two other thermodynamic quantities are of great significance. They are,

- (1) Helmholtz free energy function (or) work function (A)
- (2) Gibbs free energy function (G)

i) Work function (A):- It is defined as (Not in syllabus)

$$A = E - TS \quad \dots \textcircled{1}$$

In this internal energy ( $E$ ), entropy ( $S$ ) are state functions. Then function  $A$  where values depends on  $E$  &  $S$  values is also a state function.

Inorder to understand the physical significance of function  $A$ , we are considering an isothermal change from initial to final state. The values of  $A, E, S$  in initial and final states are represented by subscripts 1 & 2 respectively.

On applying equation  $\textcircled{1}$  to both initial and final states, we get

$$A_1 = E_1 - TS_1 ; A_2 = E_2 - TS_2$$

Then, the change of function  $\Delta A$  is given as,

$$\Delta A = A_2 - A_1$$

On substituting the above equations,

$$\Delta A = (E_2 - TS_2) - (E_1 - TS_1)$$

$$= (E_2 - E_1) - T(S_2 - S_1)$$

$$\Delta A = \Delta E - T \Delta S \quad \dots \textcircled{2}$$

From definition of Change of ~~entropy~~<sup>entropy</sup>

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

$$\therefore Q_{\text{rev}} = T \Delta S \quad \dots \text{(i)}$$

Consider the eqn of 1<sup>st</sup> law of thermodynamics

$$\Delta E = Q - W$$

Applying this equation to a reversible process

$$\Delta E = Q_{\text{rev}} - W_{\text{max}} \quad \dots \text{(ii)}$$

On substituting relationship (i) & (ii) in eqn  $\textcircled{2}$

$$\Delta A = Q_{\text{rev}} - W_{\text{max}} - Q_{\text{rev}}$$

$$\therefore \boxed{\Delta A = -W_{\text{max}}} \quad (\text{or}) \quad \boxed{-\Delta A = W_{\text{max}}}$$

For a process carried out at constant temperature, the decrease in function  $A$  gives the maximum work obtained from the system. (It is for this reason, function  $A$  which was earlier called as Helmholtz free energy is now said to be Work function.)

Gibb's Free energy function:  $\rightarrow (G_f)$

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Function  $G_f$  is defined as,

$$G_f = H - TS \quad \text{--- (1)}$$

Enthalpy ( $H$ ), Entropy ( $S$ ) are state functions, therefore function  $G_f$  is also a state function.

On applying eqn ① to initial and final states, we get

$$G_{f1} = H_1 - TS_1$$

$$G_{f2} = H_2 - TS_2$$

The change in the free energy ( $\Delta G$ ) on moving from initial state to final state under isothermal conditions,

$$\Delta G = G_{f2} - G_{f1}$$

On substituting above equations,

$$\Delta G = (H_2 - TS_2) - (H_1 - TS_1)$$

$$\Delta G = (H_2 - H_1) - T(S_2 - S_1)$$

$$\therefore \boxed{\Delta G = \Delta H - T\Delta S} \quad \text{--- (2)}$$

From definition of entropy

$$T\Delta S = Q_{rev} \quad \text{--- (i)}$$

From definition of enthalpy

$$\Delta H = \Delta E + P\Delta V \quad \text{--- (ii)}$$

Substitute (i) and (ii) in eqn ②

$$\Delta G = \Delta E + P\Delta V - Q_{rev} \quad \text{--- (3)}$$

Considering the equation of 1st law

$$\Delta E = Q - W$$

Applying this equation to a reversible process, we get

$$\Delta E = Q_{rev} - W_{max}$$

$$\Delta E - Q_{rev} = -W_{max} \quad \text{--- (iii)}$$

Substituting (iii) in equation ③

$$\Delta G = -W_{max} + P\Delta V$$

$$-\Delta G = W_{max} - P\Delta V$$

$$\therefore \boxed{-\Delta G = \text{Net work}}$$

For a process carried out at constant pressure, the decrease of function ( $G_f$ ) gives the maximum work obtained from the system other than pressure-volume work.

(In other words the decrease of function ( $G_f$ ) gives the net work obtained from the system which can be electrical work or chemical work.

Variation of free energy ( $G_f$ ) with temperature ( $T$ ) & pressure ( $P$ ):-

By definition of free energy function ( $G_f$ ),

$$G_f = H - TS \quad \text{--- (1)}$$

By definition of enthalpy the equation (1) can be written as,

$$G_f = E + PV - TS \quad \text{--- (2)}$$

On complete differentiation of (2)

$$dG_f = dE + Pdv + vdp - dT \cdot ds - SdT \quad \text{--- (3)}$$

For an infinitesimal change in a reversible process, entropy change is given as,

$$ds = \frac{\delta Q_{rev}}{T}$$

From 1st law,

$$\delta Q_{rev} = dE + Pdv \quad (\because dE = \delta Q - Pdv)$$

$$\therefore ds = \frac{dE + Pdv}{T}$$

$$Td\delta s = dE + Pdv$$

on substituting the above eqn in eqn (3)

$$dG_f = dE + Pdv + vdp - (dE + Pdv) - SdT$$

$$\therefore \boxed{dG_f = vdp - SdT} \quad \text{--- (I)}$$

The above eqn gives change of free energy with pressure and with temp.

$$dG_f = vdp - SdT$$

at constant temperature,  $dT = 0$

$$(dG_f)_T = vdp$$

$$\boxed{\left(\frac{\partial G_f}{\partial P}\right)_T = V} \quad \text{--- (II)}$$

Equation II represents the change of free energy with pressure at constant temperature.

$$dG = Vdp - SdT$$

At constant pressure  $dp = 0$ ,

$$(dG)_p = -SdT$$

$$\left( \frac{\partial G}{\partial T} \right)_p = -S \quad (\text{III})$$

Eqn (III) gives variation of free energy with temp at constant pressure

For an isothermal process, the change in free energy with pressure can be determined as follows:

Let  $G_1$  and  $G_2$  by values of free energy in initial and final state  
Let values of pressure by  $P_1$  and  $P_2$  in initial and final states.

Under isothermal Conditions,

$$(dG)_T = Vdp$$

on integration of above eqn within  $G_1$  to  $G_2$  and  $P_1$  and  $P_2$

$$\int_{G_1}^{G_2} dG = \int_{P_1}^{P_2} Vdp$$

From ideal gas equation  $PV = nRT$

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

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

$n, R, T$  are constants,

$$\frac{G_2 - G_1}{T} = nRT \ln \frac{P_2}{P_1} \quad \text{I}$$

$$P_1 V_1 = P_2 V_2$$

$$\frac{P_2}{P_1} = \frac{V_1}{V_2}$$

$$\frac{(dG)}{T} = nRT \ln \frac{V_1}{V_2} \quad \text{II}$$

Equation I and II give change of free energy with pressure at Constant temperature for a finite process.

## Criteria for Feasibility (or) Spontaneity of a Process:

The net entropy change of the system and surroundings taken together can be considered as criteria for determining the spontaneity or feasibility of a process.

(i)  $\Delta S_{sys} + \Delta S_{surr} > 0$

If net entropy of the combined system and surroundings is greater than zero, the process is irreversible, spontaneous and feasible.

(ii)  $\Delta S_{sys} + \Delta S_{surr} = 0$

If the net entropy remains constant, the process is reversible and the system is in the state of equilibrium.

The criteria of entropy change of the combined system and surroundings cannot be considered as a convenient criteria to find whether a given process is spontaneous or not. This is because it requires the knowledge of  $\Delta S$  values of both system and surroundings.

Other thermodynamic quantities like internal energy (E), enthalpy (H) work function (A), free energy function (G) are considered to be most convenient criteria for finding spontaneity of a process. This is because in these thermodynamic quantities, only the knowledge of change of these quantities i.e.,  $\Delta E$ ,  $\Delta H$ ,  $\Delta A$ ,  $\Delta G$  of the system is sufficient to determine whether the given process is spontaneous or not.

$$\Delta S_{sys} + \Delta S_{surr} \geq 0$$

For an infinitesimal change of a reversible process the above combined equation can be written as,

$$dS_{sys} + dS_{surr} \geq 0$$

If  $\delta Q_{rev}$  is the heat lost by the surroundings at temp T, then

$$dS_{surr} = -\frac{\delta Q_{rev}}{T}$$

From 1st law,

$$\delta Q_{rev} = dE + PdV$$

$$\therefore dS_{surr} = \frac{-(dE + PdV)}{T}$$

Substitute this eqn in the eqn of  $dS_{sys} + dS_{surr} \geq 0$

$$dS_{sys} + \left( -\frac{dE + PdV}{T} \right) \geq 0 \quad \left[ \frac{TdS - dE - PdV}{T} \geq 0 \right]$$

$$TdS - dE - PdV \geq 0$$

For convenience,  $dS_{sys}$  is written as  $dS$ .

$$Tds \geq dE + pdv$$

This equation is basic equation from which the criteria for spontaneity in terms of all quantities can be obtained.

### ① Criteria for spontaneity in terms of entropy: $\rightarrow x$

Considering basic equation

$$Tds \geq dE + pdv$$

If internal energy is constant,  $dE = 0$

If volume is constant,  $dv = 0$

Under these conditions, the above equation changes to  $Tds \geq 0$

$$\therefore (\Delta s)_{E,V} \geq 0$$

For a process carried out at constant E and V,

- (i) If there is increase in entropy ( $\Delta s > 0$ ) or  $\Delta s$  is +ve, it is irreversible, spontaneous and feasible.
- (ii) If there is no change in entropy ( $\Delta s = 0$ ), process is reversible and it is in equilibrium state.
- (iii) If  $\Delta s < 0$  (-ve), process is not ~~spontaneous~~ <sup>feasible</sup> at all.

### ② Criteria for spontaneity in terms of Internal energy: $\rightarrow x$

$$Tds \geq dE + pdv$$

If entropy is constant  $ds = 0$

If volume is constant  $dv = 0$

The above equation becomes  $0 \geq dE$

$$\therefore (\Delta E)_{S,V} \leq 0$$

For a process carried out at constant entropy and constant volume

- (i) If there is decrease in internal energy  $\Delta E < 0$ , (-ve). Process is irreversible, spontaneous, feasible

(ii)  $\Delta E = 0$ , reversible process and is in equilibrium state

(iii)  $\Delta E > 0$  (+ve), process is ~~spontaneous~~ <sup>not</sup> feasible.

### ③ Criteria for spontaneity in terms of enthalpy: $\rightarrow x$

By definition of enthalpy

$$H = E + PV$$

On differentiation of this equation

$$dH = dE + PdV + VdP$$

$$dH - VdP = dE + PdV$$

Substitute the above eqn in  $TdS \geq dE + PdV$

$$TdS \geq dH - VdP$$

If entropy is constant  $dS = 0$

If pressure is constant  $dP = 0$

Therefore, above equation changes to  $0 \geq dH$

$$\therefore (\Delta H)_{S,P} \leq 0$$

For a process carried out at constant entropy and at constant pressure.

(i) If there is decrease in enthalpy  $\Delta H < 0$  (-ve), Process is irreversible, spontaneous, feasible

(ii) If  $\Delta H = 0$ , Process is reversible and is in equilibrium state

(iii) If  $\Delta H > 0$  (+ve), Process is not feasible

4) Criteria for spontaneity in terms of work function ( $A$ ):  $\rightarrow x$

Work function ( $A$ ) is defined as,  $A = E - TS$

on differentiation of this equation,

$$dA = dE - TdS - SdT$$

$$TdS = dE - dA - SdT$$

Substitute the above equation in  $TdS \geq dE + PdV$

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

$$-dA \geq PdV + SdT$$

If temp is constant,  $dT = 0$

If volume is constant,  $dV = 0$

$$-dA \geq 0 \text{ (or) } dA \leq 0$$

$$\therefore (\Delta A)_{T,V} \leq 0$$

For a process carried out at constant temp & volume,

(i) If there is decrease in work function,  $\Delta A < 0$  (-ve), the process is irreversible, spontaneous, feasible.

(ii) If  $\Delta A = 0$ , the process is reversible and is in equilibrium state.

(iii) If  $\Delta A > 0$  (+ve), the process is not feasible.

Criteria for spontaneity of free energy ( $G$ ):

By definition of free energy

$$G = H - TS$$

on complete differentiation,

$$dG = dH - Tds - SdT$$

$$dG = dE + Pdv + Vdp - Tds - SdT \quad (\because dH = dE + Pdv + Vdp)$$

$$dE + Pdv = dG - Vdp + Tds + SdT$$

on substituting the above equation in basic equation,

$$Tds \geq dE + Pdv$$

$$Tds \geq dG - Vdp + Tds + SdT$$

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

$$-dG \geq -Vdp + SdT$$

$$dG \leq Vdp - SdT$$

If pressure is constant,  $dP = 0$

If temperature is constant,  $dT = 0$

$$dG \leq 0$$

$$\therefore (\Delta G)_{P,T} \leq 0$$

For a process carried out at constant pressure and temp.

- (i) If there is decrease in free energy,  $\Delta G < 0$  (-ve), the process is irreversible, spontaneous, feasible.
- (ii) If  $\Delta G = 0$ , reversible and is in equilibrium state.
- (iii) If  $\Delta G > 0$  (+ve), the process is not feasible.

To summarize various criteria for spontaneity:

$$(i) (\Delta S)_{E,V} \geq 0$$

$$(ii) (\Delta E)_{S,V} \leq 0$$

$$(iii) (\Delta H)_{S,P} \leq 0$$

$$(iv) (\Delta A)_{T,V} \leq 0$$

$$(v) (\Delta G)_{T,P} \leq 0$$

Of all these, the most important one is  $\Delta G$  (free-energy change) for determining the spontaneity of a process. This is because most of the processes in nature occur at constant temperature.

\* Calculate entropy change involved in thermodynamic expansion of 2 mol of an ideal gas from a volume of 5 lit to a volume of 50 lit at 30°C.

Soln:-

$$\Delta S = \frac{Q}{T}$$

But  $Q = W$

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

$$\Delta S = \frac{W}{T} = \frac{nRT 2.303 \log \frac{V_2}{V_1}}{T}$$

$$\Delta S = \frac{2 \times 1.98 \times 303 \times 2.303 \log \frac{50}{5}}{303}$$

$$\Delta S = 9.11 \text{ cal/K/mol}$$

\* Calculate the entropy change involved in the conversion of 1 mole of liquid water at 100°C to vapour at the same temp.  $\Delta HL_v$ , Latent heat of vaporisation of water is 540 cal/gm.

Soln:-

$$\Delta S = \frac{\Delta HL_v}{T}$$

$$1 \text{ gm water} \longrightarrow 540 \text{ cal}$$

$$18 \text{ gm water} \longrightarrow ?$$

$$\Delta HL_v = 18 \times 540 = 9720 \text{ cal.}$$

$$\Delta S = \frac{9720}{373} = 26.05 \text{ cal/K/mol.}$$

## Gibb's - Helmholtz equation:

(26)

There are two forms of this equation. One form is in terms of  $G_f$  and enthalpy. This form of equation gives the rate of change of free energy with enthalpy change and it also gives the change of  $G_f$  with temp. Other form is in terms of A and E. This gives rate of change of work function (A) with  $\Delta H$  change and it also gives change of A with temperature. Internal energy ( $E$ )

## Gibb's - Helmholtz equation in terms of $G_f$ & H:

Free energy ( $G_f$ ) by its definition is given as

$$G_f = H - TS \quad \text{--- (1)}$$

Applying the above equation to initial and final states

$$G_1 = H_1 - TS_1$$

$$G_2 = H_2 - TS_2$$

$$\Delta G = \Delta H - TAS \quad \text{--- (2)}$$

The values of free energy  $G_f$ , enthalpy  $H$ , entropy  $S$ , in initial and final states are given subscripts of 1 and 2 respectively.

The variation of free energy ( $G_f$ ) with pressure and temp is given as,

$$dG = Vdp - SdT$$

$$(dG)_p = -SdT \quad (\text{at constant pressure})$$

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \quad \text{--- (3)}$$

On applying equation (3) to initial and final states,

$$\left(\frac{\partial G_1}{\partial T}\right)_p = -S_1 \quad \text{--- (i)}$$

$$\left(\frac{\partial G_2}{\partial T}\right)_p = -S_2 \quad \text{--- (ii)}$$

On subtracting (ii) - (i)

$$\left(\frac{\partial G_2}{\partial T}\right)_p - \left(\frac{\partial G_1}{\partial T}\right)_p = -S_2 - (-S_1)$$

$$\left(\frac{\partial G_2 - \partial G_1}{\partial T}\right)_p = - (S_2 - S_1)$$

$$-\Delta S = \left( \frac{\partial \Delta G}{\partial T} \right)_P$$

$$\therefore \Delta S = - \left( \frac{\partial \Delta G}{\partial T} \right)_P \quad (\text{iii})$$

Substitute (iii) in ②

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

$$\therefore \Delta G = \Delta H + T \left( \frac{\partial \Delta G}{\partial T} \right)_P \quad (\text{I})$$

Eqn (I) is known as Gibbs-Helmholtz eqn in terms of free energy ( $G$ ) and enthalpy ( $H$ ). This is applicable to all the processes at constant pressure.

Gibbs-Helmholtz eqn in terms of A and E:

Starting with  $A = E - TS$  and proceeding as same manner as above, we get,

$$\Delta A = \Delta E + T \left( \frac{\partial \Delta A}{\partial T} \right)_V \quad (\text{II})$$

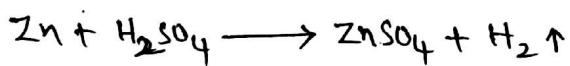
[Detailed derivation is in page no 28].

This is applicable to processes at constant volume.

Applications of Gibbs-Helmholtz equation:

One of the most important application of Gibbs-Helmholtz equation is in the study of galvanic cell.

When a reaction of



is allowed to take place in a simple beaker, heat is evolved. When the same above reaction occurs in an electrochemical cell it was believed that the electrical energy = the heat evolved.

However this latter statement was found to be incorrect and according to Gibbs and Helmholtz the electrical energy = decrease of free energy.

Let 'n' be no. of electrons given out or taken up by any electrode. quantity of electricity produced =  $nF$  coulombs

where  $F$  is 1 Faraday = 96500 Coulombs.

Let 'E' be the EMF of the cell in Volts. Therefore electrical energy produced =  $nFE$  Joules (or) Volts coulombs.

According to Gibbs and Helmholtz, decrease of free energy = Electrical energy,

$$-\Delta G = nFE$$

$$\therefore \boxed{\Delta G = -nFE}$$

On substituting this in Gibbs Helmholtz equation,

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

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

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

$\left( \frac{\partial E}{\partial T} \right)_P$  is the temp coefficient of EMF i.e., it gives change of EMF with temp at constant pressure.

Knowing the temp coefficient of the EMF and the EMF of the cell E, by using above eqn the decrease in enthalpy determined.

If the temp. coefficient  $\left( \frac{\partial E}{\partial T} \right)_P$  is zero, then the electrical energy

Produced =  $-\Delta H$  (decrease in enthalpy).

- ① Free energy  $\Delta G$  in a process was found to be  $-138$  Kilojoules at  $303K$  and  $-135$  Kilojoules at  $313K$ . Calculate change in enthalpy ( $\Delta H$ ) accompanying the process at  $308K$ .

Sol:-  $\Delta G_1 = -138 \text{ KJ}$        $T_1 = 303 \text{ K}$   
 $\Delta G_2 = -135 \text{ KJ}$        $T_2 = 313 \text{ K}$

$$\left( \frac{\partial \Delta G}{\partial T} \right)_P = \frac{\Delta G_2 - \Delta G_1}{T_2 - T_1} = \frac{-135 + 138}{313 - 303} = \frac{3}{10} = 0.3$$

Free energy change,  $\Delta G$  at  $308K$  is taken as average of  $\Delta G$  values at  $303K$  and  $313K$ .

$$-\Delta G \text{ at } 308K = \frac{\Delta G_2 + \Delta G_1}{2} = \frac{-135 - 138}{2} = -136.5 \text{ KJ.}$$

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

$$-136.5 = \Delta H + 298 (0.3)$$

$$\Delta H = -228.9 \text{ kJ}$$

② EMF of standard Weston cell, in which the cell reaction is,



EMF of cell is 1.0185 V at 25°C. calculate  $\Delta G$ ,  $\Delta S$ ,  $\Delta H$  for the cell reaction if  $\left( \frac{\partial E}{\partial T} \right)_P$  is  $5 \times 10^{-5} \text{ V/K}$  (in VK).

Sol:  $\Delta G = -nFE$   
 $= -(2) (96500) (1.0185)$

$$\Delta H = -196570 \text{ J}$$

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

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

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

~~$\approx 2.65 \text{ kJ}$~~

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

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

$$\Delta H = -196570 + (25)(9.65)$$

$$\Delta H = -193696 \text{ J}$$

$$\Delta S$$

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

$$-\Delta S = \frac{\Delta G - \Delta H}{T}$$

$$-\Delta S = \frac{-2.65 \text{ kJ}}{298 \text{ K}}$$

③ Enthalpy change  $\Delta H$  for a certain reaction at 298 K is  $-5 \text{ kJ/mol}$ . The entropy change under these condition is  $-7.2 \text{ cal/mol} \cdot \text{K}^{-1}$ . calculate the free energy change for the reaction

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

$$= -5 \times 1000 + (298)(-7.2)$$

$$= -28544 \text{ cal.} = -2.8544 \text{ kJ.}$$

④ At the Boiling point 308 K, the heat of vapourization of  $\text{MgF}_6$  is  $25.1 \text{ kJ/mol}$ . calculate  $\Delta S$  of vapourisation?

Sol:  $\Delta S = \frac{\Delta H_{\text{vap}}}{T} = \frac{25.1 \times 10^3}{308}$

$$\Delta S = 81.44 \text{ J/K/mol},$$