

T. D. C. Part II ; chem (Hons)
Paper IV (G-A)

Thermodynamics :-

GIBBS FREE ENERGY

OR

NET WORK FUNCTION (G_f)

OR

GIBBS POTENTIAL

OR

THERMODYNAMIC POTENTIAL (G)

The GIBBS free energy is defined as

$$G = H - TS$$

$$= E + PV - TS \quad (\because H = E + PV)$$

$$= (E - TS) + PV$$

$$= A + PV$$

where, H = Enthalpy of the system

and TS = isothermally unavailable energy

CHARACTERISTICS \rightarrow

(i) As H , T and S are thermodynamic properties G_f is a thermodynamic property.

(ii) Like E , H , T and S , G_f is a state function, and dG_f is independent of path i.e. a perfect differential.

(iii) G_f like H and S is an extensive property.

(iv) G_f is a measure of isothermally available energy enthalpy.

(v) G_f is a function of T and P . i.e.

$$G_f = f(T, P)$$

$$(vi) \quad \frac{\partial^2 G_f}{\partial T \partial P} = \frac{\partial^2 G_f}{\partial P \partial T}$$

(vii) G_f is used for the constant pressure process

Physical significance of G is \rightarrow

For a state of a system

$$G = H - TS$$

$$= E + PV - TS$$

For an infinitesimal change

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

$$= q_{rev} - W_{max} + PdV + VdP - TdS - SdT$$

For a process occurring at const. temp. and pressure

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

$$\therefore dG = q_{rev} - W_{max} + PdV - TdS$$

$$= TdS - W_{max} + PdV - TdS$$

$$= -W_{max} + PdV$$

$$= -(W_{max} - PdV)$$

$$= -(W_{max} - W)$$

$$= -W_{net}$$

Here, W_{max} refers to the maximum work as the process is occurring in thermodynamical reversible manner and, $PdV = W$, is the work wasted against the confining the pressure.

$$dG = -W_{net}$$

$$\text{or } -dG = W_{net} \text{ or } W_{useful}$$

Thus ΔG is a measure of net work (useful work done in the process).

From the above equation it means that decrease in free energy is equal to useful work from a reversible process at constant temp. and pressure. Hence by the above discussion the free energy is defined as -

"The function of total energy, which is so thermally available for converting into useful work, is called the free energy of the system."

Variation of free energy with pressure and temperature \rightarrow

Since,

$$G_f = H - TS$$
$$= E + PV - TS \quad [\because H = E + PV]$$

$$\therefore dG_f = dE + PdV + v dP - T ds - S dT$$

$$= q_{rev} - PdV + PdV + v dP - T ds - S dT$$

$$= T ds + v dP - T ds - S dT$$

$$dG_f = v dP - S dT$$

$$\text{or, } \left(\frac{\partial v}{\partial T} \right)_P = - \left(\frac{\partial S}{\partial P} \right)_T$$

Free energy change with temperature \rightarrow

since,

$$dG_f = v dP - S dT$$

$$\text{At const. } P, dP = 0 \therefore v dP = 0$$

$$\therefore dG_f = -S dT$$

$$\text{or, } \left(\frac{\partial G_f}{\partial T} \right)_P = -S$$

This equation defines the variation of free energy of the system with temp. at const. pressure.

Free energy change with pressure \Rightarrow

since $dG = v dP - S dT$

At constant temp. $dT = 0 \therefore S dT = 0$

$$\therefore dG = v dP$$

$$\text{or, } \left(\frac{\partial G}{\partial P} \right)_T = V$$

This equation shows the variation of free energy of the system with pressure at const. temp.

Isothermal change in free energy function \Rightarrow

(a) For an ideal gas \Rightarrow . For an isothermal process change in Gibb's free energy is given by.

$$dG = v dP$$

Change in free energy from a finite pressure change P_1 to P_2 of an ideal gas is given by.

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

$$\text{or, } G_2 - G_1 = RT \int_{P_1}^{P_2} \frac{dP}{P}$$

$$\Delta G = RT \ln \frac{P_2}{P_1}$$

for one mole of an ideal gas $PV = RT$ $\therefore V = \frac{RT}{P}$

(b) For a liquid or solid \Rightarrow . In case of liquids solids the volume remains constant for the pressure change from P_1 to P_2 . Hence

$$\Delta G = v \int_{P_1}^{P_2} dP = v [P]_{P_1}^{P_2}$$

$$\text{or, } \Delta G = V (P_2 - P_1)$$

This equation remains applicable to liquids and solids.

HELMHOLTZ FREE ENERGY

OR
WORK FUNCTION

OR
MAXIMUM WORK FUNCTION

OR
WORK CONTENT (A or F)

Ques :- What are Helmholtz and Gibbs function? Show how pressure and entropy are related to these functions.

Ans :->

Helmholtz's function :->

The Helmholtz function or Helmholtz's free energy is defined by

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

Where, U = The energy content of the system.

and, TS = isothermally unavailable energy

Since, U , T and S are characteristic functions of the state, so F is also a characteristic function of the state and dF is a perfect differential. This is sometimes called the 'work function'.

Differentiating equation (1)

$$dF = dU - Tds - SdT$$

Bwt, $dU = Tds - pdv$

$$\therefore dF = Tds - Tds + pdv - SdT$$

$$\text{or } \boxed{dF = -pdv - SdT} \quad \text{--- (2)}$$

This relation equation shows the relation of this function with pressure and entropy.

Taking partial differentials of F . Since, T and V are independent variables, we get

$\left(\frac{\partial F}{\partial T}\right)_V = -S$	(iii)
$\left(\frac{\partial F}{\partial V}\right)_T = -P$	(iv)

Equation (iii) shows the relation between this function and entropy and (iv) that between this function and pressure.

Properties \Rightarrow

$$(1) \quad dF = -SdT - PdV$$

For a reversible isothermal process, $dT=0$

$$\therefore dF = -PdV$$

$$\text{or } F_f - F_i = - \int_i^f PdV = -W$$

It means that the decrease of the function F in a reversible isothermal process is equal to the amount of work obtainable in that process. This is why the function is termed as the 'free-energy' of the system or more appropriately the 'work-function'.

(2) For an isothermal and reversible process,

$$dT = 0 \quad \text{and} \quad dP = 0$$

$$\therefore dF = 0$$

$$\text{or, } F = \text{constant}$$

(3) Since $dF = -SdT - PdV$

Taking partial derivatives, we get

$$\left(\frac{\partial F}{\partial T}\right)_V = -S$$

and

$$\left(\frac{\partial F}{\partial V}\right)_T = -P$$

(4) We can obtain one of the four thermodynamic relations using this functions.

$$dF = -SdT - PdV$$

$$\therefore \left(\frac{\partial F}{\partial T}\right)_V = -S \quad \text{and} \quad \left(\frac{\partial F}{\partial V}\right)_T = -P$$

since, dF is perfect differential

$$\frac{\partial}{\partial V} \left(\frac{\partial F}{\partial T}\right) = \frac{\partial}{\partial T} \left(\frac{\partial F}{\partial V}\right)$$

$$\text{or, } \boxed{\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V}$$