

T.D.C. Part II ; Chem. (Hons.)
Paper IV ; (Gr. A) Thermodynamics
GIBB'S - HELMHOLTZ EQUATION

OR
G-H EQUATION

The equation deals the variation of ΔG with T at constant P / ΔA with T at constant V for a process.

For any state of a system,

$$G = H - TS$$
$$= E + PV - TS$$

For an infinitesimal change in a process involving the system,

$$dG = dE + PdV + VdP - TdS - SdT$$
$$= q_{rev.} - PdV + PdV + VdP - TdS - SdT$$
$$= TdS + VdP - TdS - SdT$$
$$= VdP - SdT$$
$$= -SdT \quad (\text{at const. } P)$$

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

Using the above value of S in the equation

$$G = H - TS \quad \text{we have,}$$

$$G = H - T \left(- \frac{\partial G}{\partial T} \right)_P$$
$$= H + T \left(\frac{\partial G}{\partial T} \right)_P \quad \text{--- (1)}$$

Similarly,

for the process at constant V ,

$$A = E + T \left(\frac{\partial A}{\partial T} \right)_V \quad \text{--- (2)}$$

Equation (1) and (2) are useful form of G-H equation

Dividing equation (1) by T^2 , we have

$$\frac{G_1}{T^2} = \frac{H}{T^2} + \frac{1}{T} \left(\frac{\partial G_1}{\partial T} \right)_P$$

$$\text{or, } -\frac{H}{T^2} = -\frac{G_1}{T^2} + \frac{1}{T} \left(\frac{\partial G_1}{\partial T} \right)_P$$

$$= +G_1 \left(-\frac{1}{T^2} \right) + \frac{1}{T} \left(\frac{\partial G_1}{\partial T} \right)_P$$

$$= G_1 \left\{ \frac{\partial}{\partial T} \left(\frac{1}{T} \right) \right\}_P + \frac{1}{T} \left(\frac{\partial G_1}{\partial T} \right)_P$$

$$\text{or, } -\frac{H}{T^2} = \left\{ \frac{\partial (G_1/T)}{\partial T} \right\}_P \quad (3)$$

$$\text{or, } H \left\{ \frac{\partial (1/T)}{\partial T} \right\}_P = \left\{ \frac{\partial (G_1/T)}{\partial T} \right\}_P$$

$$\therefore H = \left\{ \frac{\partial (G_1/T)}{\partial T} \right\}_P$$

$$= \left\{ \frac{\partial (1/T)}{\partial T} \right\}_P$$

$$H = \left\{ \frac{\partial (G_1/T)}{\partial (1/T)} \right\}_P$$

Equation (3) and (4) are other forms of G_1 - H equation.

Similarly,

We have equations involving A and E

$$\frac{-E}{T^2} = \left\{ \frac{\partial A/T}{\partial T} \right\}_V \quad (5)$$

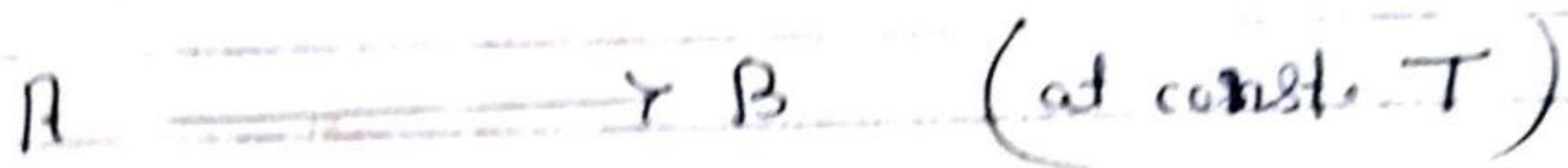
$$\text{or, } E = \left\{ \frac{\partial (A/T)}{\partial T} \right\}_V$$

$$= \left\{ \frac{\partial (A/T)}{\partial (1/T)} \right\}_V \quad (6)$$

Useful forms of G - H equations deals with change in free energy, heat content etc. accompanying an appreciable change.

The process may be physical and chemical in nature and occurs in closed system.

For the process



$$G_1 \qquad \qquad \qquad G_2 \qquad \Delta G = G_2 - G_1$$

$$H_1 \qquad \qquad \qquad H_2 \qquad \Delta H = H_2 - H_1$$

$$\therefore G_2 = H_2 - TS_2 = H_2 - T \left(- \frac{\partial G_2}{\partial T} \right)_P$$

$$G_1 = H_1 - TS_1 = H_1 - T \left(- \frac{\partial G_1}{\partial T} \right)_P$$

Substituting,

$$\Delta G = G_2 - G_1$$

$$= (H_2 - H_1) - T \left\{ \left(\frac{\partial G_2}{\partial T} \right)_P - \left(\frac{\partial G_1}{\partial T} \right)_P \right\}$$

$$= \Delta H + T \left\{ \frac{\partial (\Delta G)}{\partial T} \right\}_P \quad \text{--- (7)}$$

Similarly,

$$\Delta A = \Delta E + T \left\{ \frac{\partial (\Delta A)}{\partial T} \right\}_V \quad \text{--- (8)}$$

Since,

$$\Delta A = -W^{\text{max.}}$$

We have,

$$-W^{\text{max.}} = \Delta E + T \left\{ \frac{d(-W^{\text{max.}})}{dT} \right\}$$

$$= \Delta E - T \frac{dW}{dT}$$

$$\therefore -W^{\max} = \Delta E + W$$

$$\therefore \Delta E + W = T \frac{dW}{dT} \quad \text{--- (9)}$$

G-H equation is of general applicability. It holds for any change chemical, physical, reversible or irreversible in a closed system. The system must be in thermodynamic equilibrium in the initial and final state of the process.

from equation (7)

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

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

$$\text{or, } \frac{-\Delta H}{T^2} = \frac{-\Delta G}{T^2} + \frac{1}{T} \left\{ \frac{\partial (\Delta G)}{\partial T} \right\}_P$$

$$= \left\{ \frac{\partial (\Delta G/T)}{\partial T} \right\}_P \quad \text{--- (10)}$$

$$\text{or, } \Delta H \left\{ \frac{\partial (1/T)}{\partial T} \right\}_P = \left\{ \frac{\partial (\Delta G/T)}{\partial T} \right\}_P$$

$$\text{or, } \Delta H = \left\{ \frac{\partial (\Delta G/T)}{\partial T} \right\}_P \left\{ \frac{\partial (1/T)}{\partial T} \right\}_P$$

$$\text{or, } \Delta H = \left\{ \frac{\partial (\Delta G/T)}{\partial (1/T)} \right\}_P \quad \text{--- (11)}$$

Equations 7, 8, 9, 10 and 11 are different useful forms of G-H equation.

Relation between work function (A) and free energy (G) \rightarrow

Since

$$G = H - TS$$

$$= E + PV - TS$$

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

$$\boxed{G = A + PV} \quad \text{--- (1)}$$

for an infinitesimal change

$$dG = dA + PdV + VdP$$

$$= dA + PdV \quad (\text{at const } P)$$

For a finite change,

$$\Delta G = \Delta A + P\Delta V$$

$$\text{or, } -W_{\text{net}} = -W_{\text{max}} + P\Delta V \quad \text{--- (2)}$$

Equation (1) gives the relation between the thermodynamic function A and G

Equation (2) ~~gives~~ describes the relation between ΔA and ΔG . i.e

net work and maximum work function.