

## Thermodynamic Potentials.

### or Thermodynamic functions

For the complete knowledge of the system, we introduce some functions of the variables  $P, V, T$  and  $S$  known as thermodynamical potentials or the thermodynamic functions.

There are four principal thermodynamical potentials —

(i) Internal Helmholtz's function (F) →

From first law of thermodynamics

$$dQ = dU + dW$$

From second law of thermodynamics

$$dQ = Tds$$

Combining the two laws, we have

$$Tds = dU + dW$$

$$dU = Tds - dW \quad \text{--- (1)}$$

If we consider the process in which the system exchanges heat with the surrounding and maintain a constant temperature  $T$  then

$$Tds = d(Ts)$$

then from (1)

$$dU = d(Ts) - dW$$

$$\text{or } dU - d(Ts) = -dW$$

$$\text{or } d(U - Ts) = -dW$$

$$\text{or } dF = -dW$$

where  $F = U - Ts$  is

known as the Helmholtz free energy or more appropriately the work-function.

The value of  $F$  depends only on the state of the substance and  $dF$  is a perfect differential. ⊛

$$\text{Now } dF = dU - d(TS)$$

$$= dU - Tds - SdT$$

$$\text{But } dU = Tds - PdV$$

$$\therefore dF = \cancel{Tds} - PdV - \cancel{Tds} - SdT$$

$$dF = -PdV - SdT$$

Here  $T$  and  $V$  are independent variables.

Taking partial differentials of  $F$

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

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

Since  $dF$  is a perfect differential

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

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

This is Maxwell's relation

(ii) Gibbs potential ( $G$ )  $\rightarrow$

(ii) Internal or Intrinsic energy

According to first law of thermodynamics, there is a certain function,  $U$ , of the variables which characterises the system and this function is called the intrinsic or internal energy. When the system passes from one state to another, the change in the internal energy is independent of the route followed between the two states. The internal energy of a system is defined by the equation,

$$dU = dQ - dW$$

Here,  $dW = PdV$

and  $dQ = Tds$  (from second law of thermodynamics)

$$dU = Tds - PdV$$

Differentiating w.r.t  $S$  taking  $V$  as constant

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

and Again Differentiating w.r.t  $V$  taking  $S$  constant.

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

These are the relations connecting the internal energy  $U$  with the thermodynamical variables  $S$ ,  $V$ ,  $T$  and  $P$ .

Now since  $dU$  is a perfect differential, we must have,

$$\frac{\partial}{\partial V} \left(\frac{\partial U}{\partial S}\right)_V = \frac{\partial}{\partial S} \left(\frac{\partial U}{\partial V}\right)_S$$

$$\text{or } \left(\frac{\partial T}{\partial V}\right)_S = - \left(\frac{\partial P}{\partial S}\right)_V$$

This is Maxwell's relation

(iii) Enthalpy or total heat (H)  $\rightarrow$  Enthalpy is an extensive thermodynamical property and is of particular significance. It is mathematically defined as —

$$H = U + PV$$

The differentiation of which yields

$$dH = dU + d(PV)$$

$$= Tds - PdV + PdV + VdP$$

$$= Tds + VdP$$

At constant pressure

$$dp = 0$$

$dH = Tds = dQ$ , the quantity of heat given to the system from an extensive source. This explains the name of heat function given to it. It also shows that for an isobaric process, change in enthalpy is equal to the heat given to the system.

Now taking partial differentials of  $H$  treating  $s$  and  $p$  as independent variables.

$$\left(\frac{\partial H}{\partial s}\right)_p = T \text{ and } \left(\frac{\partial H}{\partial p}\right)_s = V$$

And since  $dH$  is a perfect differential

$$\frac{\partial}{\partial p} \left(\frac{\partial H}{\partial s}\right)_p = \frac{\partial}{\partial s} \left(\frac{\partial H}{\partial p}\right)_s$$

$$\left(\frac{\partial T}{\partial p}\right)_s = \left(\frac{\partial V}{\partial s}\right)_p$$

(iv) Gibb's potential (G)  $\rightarrow$

From the definition of enthalpy

$$H = U + PV$$

$$dH = dU + d(PV)$$

$$dH = dU + PdV + VdP$$

$$dU = Tds - PdV$$

$$dH = Tds - \cancel{PdV} + \cancel{PdV} + VdP$$

$$dH = Tds + VdP$$

If the process is an isothermal then  $Tds = d(TS)$

and if the process is an isobaric, then  $dP = 0$ , we get

$$dH = d(TS) + dU$$

$$dH - d(TS) = 0$$

$$d(H - TS) = 0$$

$$\text{or } dG_1 = 0$$

$$\text{i.e. } G_1 = H - TS = \text{constant}$$

$$\text{The function } G_1 = H - TS$$

$$= U + PV - TS$$

$$= U - TS + PV$$

$$G_1 = U - TS + PV$$

is known as thermodynamic potential at constant pressure or Gibbs's function.

It is obvious that the function  $G_1$  remains constant if a thermodynamic process remains isothermal as well as isobaric. Thus the fundamental equation defining the Gibbs's function  $G_1$  is

$$G_1 = U - TS + PV$$

$$dG_1 = dU - d(TS) + d(PV)$$

$$= TdS - PdV - TdS - SdT + PdV + vdp$$

$$dG_1 = vdp - SdT$$

Here  $T$  &  $P$  are independent variables

Take partial differentials

$$\left(\frac{\partial G_1}{\partial P}\right)_T = v \quad \text{and} \quad \left(\frac{\partial G_1}{\partial T}\right)_P = -S$$

Since  $dG_1$  is a perfect differential, then

$$\frac{\partial}{\partial T} \left(\frac{\partial G_1}{\partial P}\right)_T = \left(\frac{\partial v}{\partial T}\right)_P$$

$$\text{and } \frac{\partial}{\partial P} \left(\frac{\partial G_1}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$$

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