

### \* Thermodynamic potential:

Thermodynamic potential function is a quantity used to represent the state of a system.

There are four fundamental functions:-

#### (i) Internal energy ( $U$ ):

The first law of thermodynamics,

$$\boxed{dQ = du + dw} \quad | \quad dQ = Tds \\ \therefore du = Tds - Pdv \quad | \quad dw = - Pdv$$

This equation gives the change in internal energy of the system in terms of four thermodynamical variables  $P$ ,  $V$ ,  $T$  and  $S$ .

##### ① For an adiabatic process,

$$dQ = 0 \\ \therefore du = - Pdv$$

the work done by the system in an adiabatic process is at the expense of its internal energy.

##### ② For an isochoric, adiabatic process,

$$dv = 0 \text{ and } dQ = 0$$

$$\therefore du = 0 \text{ or } u = \text{a constant}$$

Internal energy of system remains constant in an isochoric adiabatic process.

(ii) <sup>Exam - 19</sup> Helmholtz free energy, F:

Helmholtz free energy is defined as,

$$F = U - TS$$

Differentiating,

$$dF = dU - TdS - SdT$$

$$= TdS - PdV - TdS - SdT \quad | \quad dU = TdS - PdV$$

$$\therefore dF = -PdV - SdT$$

This equation gives the change  $\rightarrow$  in Helmholtz free energy during an infinitesimal reversible process.

অবিস্থান অস্থায়ী

(a) For reversible isothermal process,

$$dT = 0$$

$$\therefore dF = -PdV \quad \text{or} \quad PdV = -dF$$

Thus, the work done in a reversible isothermal process is equal to the decreases in Helmholtz free energy.

(b) For isothermal isochoric process,

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

$$\therefore dF = 0 \quad \text{or}, \quad F = \text{a constant}$$

the Helmholtz free energy remains constant during isothermal isochoric process.

### (iii) Enthalpy, (H);

This is known as the total heat and is given by,

$$H = u + Pv$$

Differentiating,

$$dH = du + Pdv + vdp$$

$$= TdS - Pdv + vdp + Pdv$$

$$dH = TdS + vdp$$

(a) For reversible isobaric process,  
અસ્થપત્ર

$$dp = 0$$

$$\therefore dH = TdS = dq$$

for an isobaric process, the change in enthalpy is equal to the heat absorbed.

(b) For an isobaric adiabatic process,

અનુભવિત

$$dp = 0 \quad dq = 0$$

$$\therefore dH = 0 \quad \text{or} \quad H = \text{a constant}$$

Enthalpy remains constant in a reversible isobaric-adiabatic process.

(iv) Gibbs function (or) or Gibbs free energy:

The equation of Gibbs function is,

$$G_r = H - TS$$
$$G_r = U - TS + PV \quad | \quad H = U + PV$$

Differentiating,

$$\begin{aligned} dG_r &= du - TdS - SdT + pdv + vdp \\ &= TdS - pdv - TdS - SdT + pdv + vdp \\ dG_r &= vdp - SdT \end{aligned}$$

(a) For an isothermal process,

$$\begin{aligned} dT &= 0 \\ \therefore dG_r &= vdp \end{aligned}$$

(b) For isothermal-isobaric process,

$$\begin{aligned} dT &= 0 \quad \text{and} \quad dp = 0 \\ \therefore dG_r &= 0 \quad \text{or} \quad G_r = \text{a constant} \end{aligned}$$

Gibbs function or Gibbs free energy remains constant in an isothermal-isobaric process.

Ex Exam - 17

## Maxwell's thermodynamical relations

(10)

From the first and second law of thermodynamics, Maxwell able to derive four fundamental thermodynamical relations.

The state of a system can be specified by any pair of quantities, i.e., pressure ( $P$ ), volume ( $V$ ), temperature ( $T$ ) and entropy ( $S$ ).

∴ From the first law of thermodynamics,

$$dQ = dU + dW$$

$$\text{or, } du = dQ - dW$$

$$\therefore du = Tds - pdv \quad \text{--- (1)}$$

Second law of thermodynamics,  
 $ds = \frac{dQ}{T}$   
 $dQ = Tds$   
and,  $dW = pdv$

considering  $U$ ,  $S$  and  $V$  to be function of two independent variables  $x$  and  $y$ ,

$$\therefore du = \left(\frac{\partial U}{\partial x}\right)_y dx + \left(\frac{\partial U}{\partial y}\right)_x dy$$

$$ds = \left(\frac{\partial S}{\partial x}\right)_y dx + \left(\frac{\partial S}{\partial y}\right)_x dy$$

$$dv = \left(\frac{\partial V}{\partial x}\right)_y dx + \left(\frac{\partial V}{\partial y}\right)_x dy$$

Substituting these values in equation (1), we get,

$$\begin{aligned} \left(\frac{\partial U}{\partial x}\right)_y dx + \left(\frac{\partial U}{\partial y}\right)_x dy &= T \left[ \left(\frac{\partial S}{\partial x}\right)_y dx + \left(\frac{\partial S}{\partial y}\right)_x dy \right] \\ &\quad - P \left[ \left(\frac{\partial V}{\partial x}\right)_y dx + \left(\frac{\partial V}{\partial y}\right)_x dy \right] \end{aligned}$$

$$\therefore \left(\frac{\partial u}{\partial n}\right)_y du + \left(\frac{\partial u}{\partial y}\right)_n dy = \left[ T \left(\frac{\partial s}{\partial n}\right)_y - P \left(\frac{\partial v}{\partial n}\right)_y \right] dn - \left[ T \left(\frac{\partial s}{\partial y}\right)_n - P \left(\frac{\partial v}{\partial y}\right)_n \right] dy$$

Comparing the co-efficients of  $dn$  and  $dy$ , we get

$$\left(\frac{\partial u}{\partial n}\right)_y = T \left(\frac{\partial s}{\partial n}\right)_y - P \left(\frac{\partial v}{\partial n}\right)_y \quad \text{--- (2)}$$

$$\text{and } \left(\frac{\partial u}{\partial y}\right)_n = T \left(\frac{\partial s}{\partial y}\right)_n - P \left(\frac{\partial v}{\partial y}\right)_n \quad \text{--- (3)}$$

Differentiating equation (2) w.r.t  $y$  and equation (3) w.r.t  $n$ ,

$$\therefore \frac{\partial^2 u}{\partial y \cdot \partial n} = \left(\frac{\partial T}{\partial y}\right)_n \left(\frac{\partial s}{\partial n}\right)_y + T \frac{\partial^2 s}{\partial y \cdot \partial n} - \left(\frac{\partial P}{\partial y}\right)_n \left(\frac{\partial v}{\partial n}\right)_y - P \frac{\partial^2 v}{\partial y \cdot \partial n}$$

$$\text{and } \frac{\partial^2 u}{\partial n \cdot \partial y} = \left(\frac{\partial T}{\partial n}\right)_y \left(\frac{\partial s}{\partial y}\right)_n + T \frac{\partial^2 s}{\partial n \cdot \partial y} - \left(\frac{\partial P}{\partial n}\right)_y \left(\frac{\partial v}{\partial y}\right)_n - P \frac{\partial^2 v}{\partial n \cdot \partial y}$$

The change in internal energy brought about by changing  $V$  and  $T$ , whether  $V$  is changed by  $dv$  first and  $T$  by  $dT$  later or vice-versa is the same,

$$\therefore \frac{\partial^2 u}{\partial y \cdot \partial n} = \frac{\partial^2 u}{\partial n \cdot \partial y}$$

$$\begin{aligned} \left(\frac{\partial T}{\partial y}\right)_n \left(\frac{\partial s}{\partial n}\right)_y + T \frac{\partial^2 s}{\partial y \cdot \partial n} - \left(\frac{\partial P}{\partial y}\right)_n \left(\frac{\partial v}{\partial n}\right)_y - P \frac{\partial^2 v}{\partial y \cdot \partial n} &= \left(\frac{\partial T}{\partial n}\right)_y \left(\frac{\partial s}{\partial y}\right)_n + T \frac{\partial^2 s}{\partial n \cdot \partial y} \\ &\quad - \left(\frac{\partial P}{\partial n}\right)_y \left(\frac{\partial v}{\partial y}\right)_n - P \frac{\partial^2 v}{\partial n \cdot \partial y} \end{aligned}$$

$$\Rightarrow \left(\frac{\partial T}{\partial y}\right)_n \left(\frac{\partial s}{\partial n}\right)_y - \left(\frac{\partial P}{\partial y}\right)_n \left(\frac{\partial v}{\partial n}\right)_y = \left(\frac{\partial T}{\partial n}\right)_y \left(\frac{\partial s}{\partial y}\right)_n - \left(\frac{\partial P}{\partial n}\right)_y \left(\frac{\partial v}{\partial y}\right)_n \quad \text{--- (4)}$$

$$\text{whence, } \frac{\partial^2 S}{\partial y \cdot \partial n} = \frac{\partial^2 S}{Rc \cdot nc} \text{ and } \frac{\partial^2 V}{\partial n \cdot \partial c} = \frac{\partial^2 V}{n \cdot Rc}$$

This is the general expression for Maxwell's thermodynamical relations.

$$dn = \left(\frac{\partial T}{\partial n}\right)_y dy, \quad dy = \left(\frac{\partial T}{\partial c}\right)_n nc \Rightarrow \frac{\partial T}{\partial n} y = \frac{\partial T}{\partial c} n$$

There may be four sets of possible substitutions ( $S, V$ ); ( $T, V$ ); ( $S, P$ ) and ( $T, P$ ), providing the four Maxwell's thermodynamical relations.

(i) First relation: (internal energy) ( $U$ )

put,  $n=S$  and  $y=V$  in eqn. (4), so that

$$\frac{\partial S}{\partial n} = 1, \quad \frac{\partial V}{\partial c} = 1 \\ \Rightarrow \frac{\partial S}{\partial y} = 0, \quad \Rightarrow \frac{\partial V}{\partial n} = 0$$

substituting in eqn. (4) we get,

$$\left(\frac{\partial T}{\partial c}\right)_n = -\left(\frac{\partial P}{\partial n}\right)_y$$

But,  $\partial y = \partial V$  (as  $y=V$ ) and  $\partial n = \partial S$  (as  $n=S$ ). Hence,

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

This is Maxwell's first thermodynamical relation.

(ii) Second relation: (Helmholtz energy) Exam - 19

put,  $n=T$  and  $y=V$  in eqn. (4),

$$\frac{\partial T}{\partial n} = 1, \quad \frac{\partial V}{\partial c} = 1$$

$$\frac{\partial T}{\partial c} = 0, \quad \frac{\partial V}{\partial n} = 0$$

Substituting in eqn. (4) we get,

$$\left(\frac{\partial \theta}{\partial y}\right)_u = \left(\frac{\partial P}{\partial u}\right)_y$$

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

This is Maxwell's Second thermodynamical relation.

(iii) Third relation: (Enthalpy)

put,

$$u = S \text{ and } y = P \text{ in eqn. (4)}$$

$$\frac{\partial S}{\partial u} = 1 \quad \frac{\partial P}{\partial y} = 1$$

$$\Rightarrow \frac{\partial S}{\partial y} = 0 \quad \frac{\partial P}{\partial u} = 0$$

substituting these in eqn. (4),

$$\left(\frac{\partial T}{\partial y}\right)_u = \left(\frac{\partial V}{\partial u}\right)_y$$

$$\Rightarrow \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

This is Maxwell's third thermodynamical relation.

(iv) Fourth relation: (Gibbs free)

put,  $u = T$  and  $y = P$ , in eqn. (4)

$$\frac{\partial T}{\partial u} = 1 \quad \frac{\partial P}{\partial y} = 1$$

$$\Rightarrow \frac{\partial T}{\partial y} = 0 \quad \frac{\partial P}{\partial u} = 0$$

Substituting these values in eqn. (4) we get,

$$\left(\frac{\partial S}{\partial y}\right)_u = \left(-\frac{\partial V}{\partial u}\right)_y$$

$$\Rightarrow \left(\frac{\partial S}{\partial P}\right)_u = -\left(\frac{\partial V}{\partial T}\right)_P$$

This is Maxwell's fourth thermodynamical relation.

## Ques. 19. Joule - Thomson effect $\rightarrow$ definition (Enam 2018)

Statement:

If the gas at constant high pressure is forced through a porous plug to a region of constant low pressure, the temperature of escaping gas changes. This is called Joule - Thomson effect.

Mathematical terms:

Due to throttling, the gas suffers expansion. संतोषन

Although there is a pressure difference in two sides of the porous plug, the enthalpy  $H$  of the gas remains constant.

$$H = u + Pv = \text{Constant}$$

Differentiating,

$$dH = du + pdv + vdp = 0 \quad \text{--- (1)}$$

From, first law of thermodynamics we get,

$$dQ = du + dw$$

$$dQ = du + pdv$$

$$du = dQ - Pdv \quad \text{--- (2)}$$

Second law of thermodynamics,

$$ds = \frac{dQ}{T}$$

$$\therefore dQ = Tds$$

putting this value in eqn. (2),

$$\therefore du = Tds - Pdv$$

Substituting this value in eqn. ①

$$dS = TdS - Pdv + Pdv + vdp = 0$$

$$\therefore dS = TdS + vdp = 0 \quad \text{--- } ③$$

Now  $dS$  being a perfect differential and  $S$  is a function of  $P$  and  $T$  i.e.,  $S = f(P, T)$ , we have

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

Substituting in eqn. ③,

$$T \left[ \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP \right] + vdp = 0$$

$$\text{OR, } T \left(\frac{\partial S}{\partial T}\right)_P dT + \left[ T \left(\frac{\partial S}{\partial P}\right)_T + v \right] dp = 0 \quad \text{--- } ④$$

Now,  $\frac{C_p}{C_p}$

$C_p$  is specific heat at constant pressure.

$$\therefore C_p = \left(\frac{\partial Q}{\partial T}\right)_P = T \left(\frac{\partial S}{\partial T}\right)_P$$

Putting this value in eqn. ④,

$$C_p dT + \left[ T \left(\frac{\partial S}{\partial P}\right)_T + v \right] dp = 0$$

$$\text{OR, } C_p dT = - \left[ T \left(\frac{\partial S}{\partial P}\right)_T + v \right] dp \quad \text{--- } ⑤$$

According to Maxwell's fourth thermodynamical relation.

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

Substituting this value in eqn. ⑤,

$$C_p dT = \left[ T \left(\frac{\partial v}{\partial T}\right)_P - v \right] dp$$

$$dT = \frac{1}{C_p} \cdot \left[ T \left(\frac{\partial v}{\partial T}\right)_P - v \right] dp$$

This is the equation of Joule-thomson effect.

## Q) Joule-thomson co-efficient ( $\mu$ )

The Joule-thomson co-efficient is given by:

$$\begin{aligned}\mu &= \left( \frac{\partial T}{\partial P} \right)_H \\ &= \frac{1}{C_p} \left[ T \left( \frac{\partial V}{\partial T} \right)_P - V \right]\end{aligned}$$

Now,

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

where,  $\alpha$  is the co-efficient of increase of volume at constant pressure.

Substituting this value in Joule-Thomson effect,

$$dT = \frac{1}{C_p} [T \cdot \alpha V - V]$$

$$\text{OR, } dT = \frac{V}{C_p} [\alpha T - 1]$$

This equation gives the change in temperature due to Joule-Thomson effect.

Here,  $dP$  represents a fall in pressure in porous plug experiment and it is always negative quantity. All other are +ve. Hence

(i) There is cooling effect, i.e.,  $dT$  is negative if  $(\alpha T - 1)$  is negative or  $\alpha T > 1$ .

(ii) There is neither a cooling nor a heating effect i.e.  $dT = 0$  when  $(\alpha T - 1) = 0$  or  $\alpha T = 1$

(iii) There is heating effect i.e.,  $dT$  is positive if  $(\alpha T - 1)$  is positive or  $\alpha T < 1$ .

## Thermodynamical treatment of heating and cooling a to a ideal gas

According to the ideal gas equation,

$$PV = RT \Rightarrow V = \frac{RT}{P}$$

at constant pressure,

$$P \frac{\partial V}{\partial T} = R$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$$

The equation of Joule-Thomson effect is,

$$dT = \frac{1}{C_p} \left[ T \left( \frac{\partial V}{\partial T} \right)_P - v \right] dP \quad \text{--- (1)}$$

Putting these values,  $v = \frac{RT}{P}$  and  $\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$  in eqn. (1),

$$dT = \frac{1}{C_p} \left( \frac{RT}{P} - \frac{RT}{P} \right) dP$$

$$\text{or, } dT = 0$$

There is no Joule-Thomson effect for a ideal gas,

For a ideal gas,

the Joule-thomson co-efficient ( $\mu$ ) is zero.

$$\therefore \mu = \left(\frac{\partial T}{\partial P}\right)_H - \frac{1}{C_p} \left[ T \left( \frac{\partial V}{\partial T} \right)_P - v \right] = 0$$

Q The thermodynamical treatment of heating and cooling effect for van der waals gas

T

Vander waals equation for a real gas is given by,

$$(P + \frac{a}{V^2})(V - b) = RT \quad \text{--- (1)}$$

OR,  $PV - Pb + \frac{a}{V} - \frac{ab}{V^2} = RT$

Since, both the vander waals constants  $a$  and  $b$  are both very small quantities, their product  $ab$  is very small as compared to  $V^2$  and hence  $\frac{ab}{V^2}$  can be neglected,

$$\therefore Pv - Pb + \frac{a}{V} = RT$$

Differentiating both sides w.r.t.  $T$ , keeping  $P$  constant we get,

$$P\left(\frac{dV}{dT}\right)_P - \frac{a}{V^2}\left(\frac{dV}{dT}\right)_P = R$$

OR,  $\left(\frac{dV}{dT}\right)_P \left(P - \frac{a}{V^2}\right) = R$

$$\therefore \left(\frac{dV}{dT}\right)_P = \frac{R}{P - \frac{a}{V^2}} \quad \text{--- (2)}$$

From eqn. (1),

$$P = \frac{RT}{V-a} - \frac{a}{V^2}$$

Substituting for  $P$  in eqn. (2),

$$\begin{aligned} \left(\frac{dV}{dT}\right)_P &= \frac{R}{\left(\frac{RT}{V-a} - \frac{a}{V^2}\right) - \frac{a}{V^2}} \\ &= \frac{R}{\frac{RT}{V-a} - \frac{2a}{V^2}} \end{aligned}$$

$$= \frac{R(v-b)}{RT - \frac{2a(v-b)}{\sqrt{v^2}}}$$

$$\left( \frac{dv}{dT} \right)_P = \frac{R(v-b)}{RT - \frac{2a}{v}} \quad [ \text{as } b \text{ is very small, } v-b=v ]$$

$$T \cdot \left( \frac{dv}{dT} \right)_P = \frac{RT(v-b)}{RT - \frac{2a}{v}}$$

$$= \frac{RT(v-b)}{RT \left( 1 - \frac{2a}{vRT} \right)}$$

$$= \frac{v-b}{1 - \frac{2a}{vRT}}$$

$$= (v-b) \left( 1 - \frac{2a}{vRT} \right)^{-1}$$

$$= (v-b) \left( 1 + \frac{2a}{vRT} \right)$$

$$= (v-b) + \frac{2a(v-b)}{vRT}$$

Neglecting squares and  
 higher powers of  
 $\frac{2a}{vRT}$  as  $\frac{2a}{vRT} \ll 1$

$$T \cdot \left( \frac{dv}{dT} \right)_P = v-b + \frac{2a}{RT}$$

$$T \left( \frac{dv}{dT} \right)_V - v = \frac{2a}{RT} - b$$

$b$  is very small  
 $v-b=v$

According to Joule-Thomson effect, the change in temperature,

$$dT = \frac{1}{C_P} \left[ T \left( \frac{dv}{dT} \right)_P - v \right] dp \quad \text{--- (3)}$$

Substituting the value of  $[T\left(\frac{dv}{dT}\right)_P - v]$  in eqn. ③

$$dT = \frac{1}{C_P} \left[ \frac{2a}{RT} - b \right] dP$$

This equation gives the change in temperature for van der Waals gas i.e., real gas due to Joule-Thomson effect.

① If  $\frac{2a}{RT} > b$  i.e.,  $T$  is less than  $\frac{2a}{Rb}$ , then  $dT$  is positive

Since,  $dP$  is  $-ve$ ,  $dT$  will be  $-ve$ . Hence there will be a cooling effect.

② If  $\frac{2a}{RT} < b$  i.e.,  $T$  is greater than  $\frac{2a}{Rb}$ , then  $dT$  is negative.

Since,  $dP$  is  $-ve$ ,  $dT$  will be  $+ve$ . Hence, there will be a cooling effect.

③ If  $\frac{2a}{RT} = b$  or  $T = \frac{2a}{Rb}$ , then  $dT = 0$ .

there will be no change of temperature.

#### Temperature of inversion — zero

The temperature at which Joule-Thomson effect is zero and changes sign is known as temperature of inversion.

$$T_i = \frac{2a}{Rb}$$

If  $T < \frac{2a}{Rb}$ , there will be cooling.

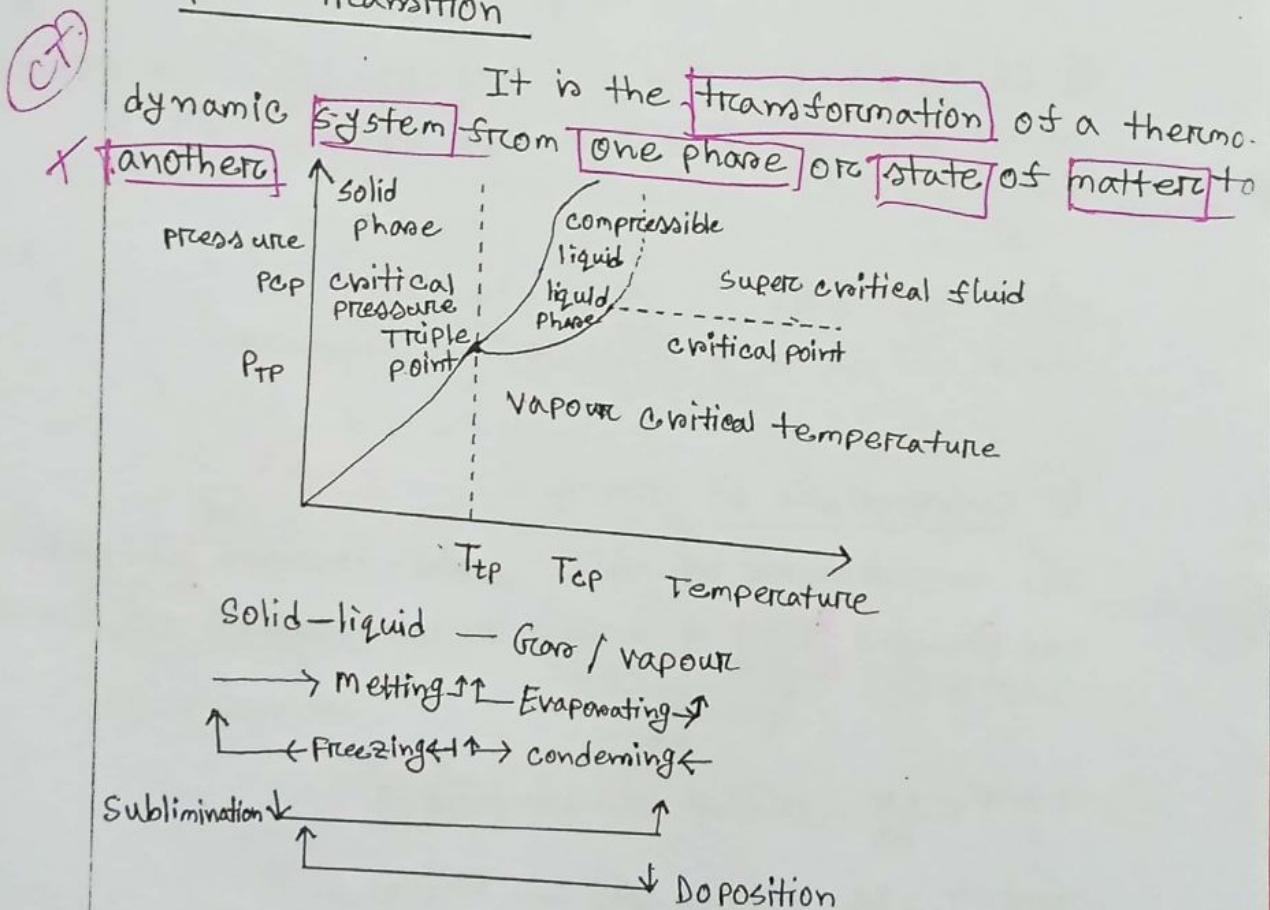
and  $T > \frac{2a}{Rb}$ , there will be heating.

## Q1 Phase:

A phase is a form of matter that is homogeneous and heterogeneous or uniform and chemically and physically.

The three fundamental phases are - solid, liquid and gas.

## Q2 Phase transition



## Gibbs free energy

The Gibbs free energy of a system at any moment in time is defined as the enthalpy of the system minus the product of the temperature times the entropy of the system.

$$G_c = H - TS$$

$$\begin{aligned} dG_c &= Tds + vdp - Tds - sdt \\ &= vdp - sdt \end{aligned}$$

The Gibbs function is,  $dG_c = vdp - sdt$

- ① For isothermal process,  $dT = 0$       ② For isobaric process,  $dp = 0$   
 $\therefore dG_c = vdp$                            $dG_c = 0$

<sup>Exam-18</sup>  
18) Clausius- Clapeyron latent heat equation

OR,

T First order phase transitions  $\rightarrow$  definition + Exam (2017 - cnm)

The changes of phase which take place at constant temperature and pressure and in which heat is either absorbed or evolved during change of phase are called first order phase transitions.

In first order phase transitions, the entropy and density change. The Gibbs function  $G_c$  remains constant in both sides phases, while its derivative with respect to temperature and pressure is discontinuous at a transition point.

consider an enclosure containing a liquid and its <sup>NH<sub>3</sub></sup> sat vapour in equilibrium. If this system undergoes an isothermal, isobaric change, then

$$g_1 = g_2 \quad \text{--- (i)}$$

Let the temperature of the system be increased from  $T$  to  $T+dt$ . For equilibrium,

$$g_1 + dg_1 = g_2 + dg_2 \quad \text{--- (ii)}$$

$$dg_1 = dg_2 \quad \text{--- (iii)}$$

If the condition of saturation is satisfied,

$$\left(\frac{\partial g_1}{\partial T}\right)_{\text{sat}} = \left(\frac{\partial g_2}{\partial T}\right)_{\text{sat}} \quad \text{--- (iv)}$$

The pressure also changes from  $p$  to  $p+dp$ .

$$dg_1 = \left(\frac{\partial g_1}{\partial T}\right)_P dT + \left(\frac{\partial g_1}{\partial P}\right)_T dp \quad \text{--- (v)}$$

$$\text{or, } \left(\frac{\partial g_1}{\partial T}\right) = \left(\frac{\partial g_1}{\partial T}\right)_P + \left(\frac{\partial g_1}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right) \quad \text{--- (vi)}$$

In Gibbs free energy, Gibbs function is,

$$dg = vdp - sdT$$

$$\therefore \left(\frac{\partial g}{\partial T}\right)_P = v$$

$$\text{and } \left(\frac{\partial g}{\partial P}\right)_T = -s$$

Substituting these values in eqn. (VI),

$$\left(\frac{\partial g_1}{\partial T}\right)_{\text{sat}} = -s_1 + v_1 \left(\frac{\partial P}{\partial T}\right)_{\text{sat}}$$

Similarly,

$$\left(\frac{\partial g_2}{\partial T}\right)_{\text{sat}} = -s_2 + v_2 \left(\frac{\partial P}{\partial T}\right)_{\text{sat}}$$

Substituting these values in eqn. (V),

$$-s_1 + v_1 \left(\frac{\partial P}{\partial T}\right)_{\text{sat}} = -s_2 + v_2 \left(\frac{\partial P}{\partial T}\right)_{\text{sat}}$$

$$\text{OR, } \left(\frac{\partial P}{\partial T}\right)_{\text{sat}} = \frac{s_2 - s_1}{v_2 - v_1} \quad \text{--- (VII)}$$

The equation of entropy,

$$dS = s_2 - s_1 = \frac{dQ}{T} = \frac{L}{T} \quad | L = \text{latent heat of vaporization}$$

Substituting this value in eqn. (VII),

$$\frac{dP}{dT} = \frac{L}{T(v_2 - v_1)}$$

This is Clausius-Clapeyron latent heat equation,

OR,

this equation is first order phase transition.

It can be defined as that one in which the Gibbs function with respect to pressure and temperature change discontinuously at the transition point.

However, the value of the Gibbs function is the same in both the phases of equilibrium.

⇒ In Graphically —

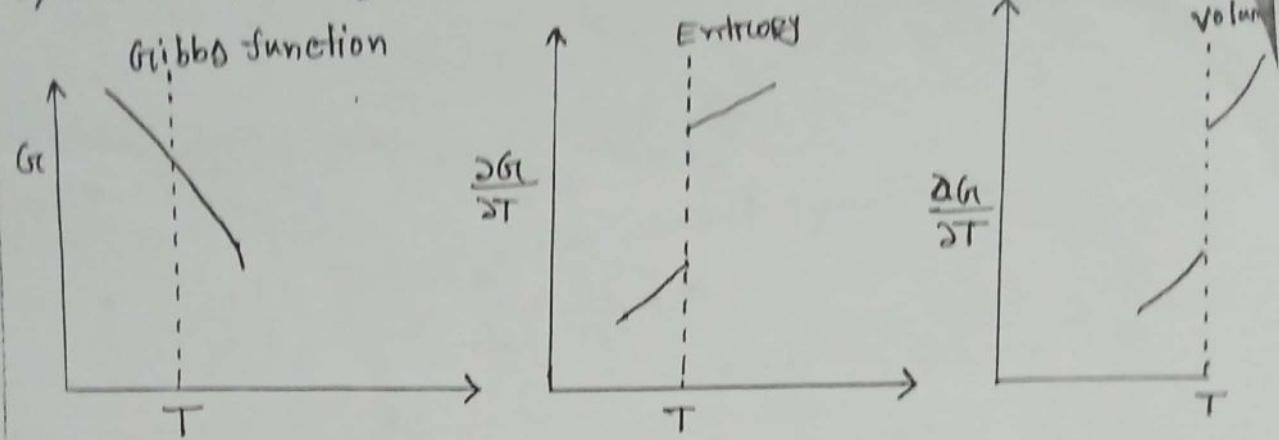


Fig. 1. First order phase transition.

✳ \* Second order Phase transitions → Definition + Example (20) OR (17)

✳ Ehrenfest's equation

Second order phase transitions can be defined as the phenomenon that takes place with no change in enthalpy and volume at constant temperature and pressure.

In case of, there is no discontinuity of  $(\frac{\partial G_f}{\partial T})_P$  and  $(\frac{\partial G_f}{\partial P})_T$ . For a phase transition,

$$g_1 = g_2$$

$$\text{OR, } g_2 - g_1 = 0 \quad \text{--- (1)}$$

$$\therefore -(\frac{\partial g_2}{\partial T})_P + (\frac{\partial g_1}{\partial T})_P = s_2 - s_1 = 0 \quad \text{--- (2)}$$

$$\text{and, } (\frac{\partial g_2}{\partial P})_T - (\frac{\partial g_1}{\partial P})_T = v_2 - v_1 = 0 \quad \text{--- (3)}$$

∴ The specific heat at constant pressure,

$$C_p = T \left( \frac{\partial g}{\partial T} \right)_P$$

$$\text{or, } \frac{C_p}{T} = \left( \frac{\partial g}{\partial T} \right)_P = \frac{\partial}{\partial T} \left[ \left( \frac{\partial g}{\partial T} \right)_P \right]_P = - \left( \frac{\partial^2 g}{\partial T^2} \right)_P \quad \text{--- (4)}$$

Similarly,

From equation (4)

$$\frac{C_{p1}}{T} = - \left( \frac{\partial^2 g_1}{\partial T^2} \right)_P \quad \text{--- (5)}$$

$$\frac{C_{p2}}{T} = - \left( \frac{\partial^2 g_2}{\partial T^2} \right)_P \quad \text{--- (6)}$$

Subtracting equations (6) from (5)

$$\left( \frac{\partial^2 g_2}{\partial T^2} \right)_P - \left( \frac{\partial^2 g_1}{\partial T^2} \right)_P = \frac{C_{p1} - C_{p2}}{T} \quad \text{--- (7)}$$

K is the isothermal compressibility,

$$K = - \frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$$

$$KV = - \left( \frac{\partial V}{\partial P} \right)_T = - \frac{\partial}{\partial P} \left[ \left( \frac{\partial g}{\partial P} \right)_T \right]$$

$$KV = - \left( \frac{\partial^2 g}{\partial P^2} \right)_T \quad \text{--- (8)}$$

Similarly, the equation (8)

$$K_1 V = - \left( \frac{\partial^2 g_1}{\partial P^2} \right)_T \quad \text{--- (9)}$$

$$\text{and } K_2 V = - \left( \frac{\partial^2 g_2}{\partial P^2} \right)_T \quad \text{--- (10)}$$

Subtracting from equation (10) from (9)

$$\left(\frac{\partial^2 g_2}{\partial P^2}\right)_T - \left(\frac{\partial^2 g_1}{\partial P^2}\right)_T = v(k_1 - k_2)$$

Again,

$\alpha$  is the volume-coefficient of expansion.

$$\therefore \alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$$

$$\alpha_V = \left( \frac{\partial V}{\partial T} \right)_P = \frac{\partial}{\partial T} \left[ \left( \frac{\partial g}{\partial P} \right)_T \right]_P$$

$$\alpha_V = \frac{\partial^2 g}{\partial T \partial P}$$

Similarly,

$$\alpha_1 V = \frac{\partial^2 g_1}{\partial T \partial P} \quad (11)$$

$$\text{and, } \alpha_2 V = \frac{\partial^2 g_2}{\partial T \partial P} \quad (12)$$

Subtracting from eqn. (11) from (12)

$$\frac{\partial^2 g_2}{\partial T \partial P} - \frac{\partial^2 g_1}{\partial T \partial P} = v(\alpha_1 - \alpha_2)$$

For second order phase transitions,  
the entropy and volume remains constant.  
So, for a change of phase at Temperature (T) and  
pressure (P),

$$S_1 = S_2$$

for a change of phase at  $T + dT$  and  $P + dP$ .

$$S_1 + dS_1 = S_2 + dS_2$$

$$\therefore dS_1 = dS_2$$

If the  $T$  and  $P$  are independent variables,

$$S = S(T, P)$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

Multiplying  $T$  both sides,

$$TdS = T\left(\frac{\partial S}{\partial T}\right)_P dT + T\left(\frac{\partial S}{\partial P}\right)_T dP$$

$$\text{OR, } TdS = C_P dT + T\left(\frac{\partial S}{\partial P}\right)_T dP \quad | \quad C_P = T\left(\frac{\partial S}{\partial T}\right)_P$$

$$\text{OR, } TdS = C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP$$

$$\text{OR, } dS = C_P \cdot \frac{dT}{T} - \left(\frac{\partial V}{\partial T}\right)_P dP$$

$$\therefore dS = C_P \frac{dT}{T} - V\alpha dP$$

$$\left| \begin{array}{l} \text{2nd Maxwell's} \\ \text{relation} \end{array} \right| \quad \left( \frac{\partial S}{\partial P} \right)_T = -\left( \frac{\partial V}{\partial T} \right)_P$$

$$\left| \begin{array}{l} \alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \\ V\alpha = \left( \frac{\partial V}{\partial T} \right)_P \end{array} \right.$$

Similarly,

$$dS_1 = C_{P_1} \cdot \frac{dT}{T} - V\alpha_1 dP$$

$$\text{and } dS_2 = C_{P_2} \cdot \frac{dT}{T} - V\alpha_2 dP$$

$$\text{As, } dS_1 = dS_2$$

$$C_{P_1} \frac{dT}{T} - V\alpha_1 dP = C_{P_2} \frac{dT}{T} - V\alpha_2 dP$$

$$\therefore \frac{dP}{dT} = \frac{C_{P_2} - C_{P_1}}{T V (\alpha_2 - \alpha_1)}$$

This equation known as Ehrenfest equation for first order

Again, for second order phase transitions, the volume remain constant.

So, for a change of phase at temperature ( $T$ ) and pressure ( $P$ ) is

$$V_1 = V_2$$

for a change of phase at  $T + dT$  and  $P + dP$ ,

$$V_1 + dV_1 = V_2 + dV_2$$

$$dV_1 = dV_2$$

If,

$T$  and  $P$  are independent variables,

$$V = V(T, P)$$

OR,  $dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP$

$$\therefore dV = V\alpha dT - VK dP$$

Similarly,

$$dV_1 = V\alpha_1 dT - VK_1 dP$$

and,  $dV_2 = V\alpha_2 dT - VK_2 dP$

$$\therefore V\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P$$
$$\text{and } VK = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$$
$$\therefore VK = -\left(\frac{\partial V}{\partial P}\right)_T$$

As,

$$dV_1 = dV_2$$

OR,  $V\alpha_1 dT - VK_1 dP = V\alpha_2 dT - VK_2 dP$

$$\therefore \frac{dP}{dT} = \frac{\alpha_2 - \alpha_1}{K_2 - K_1}$$

; this equation is known as  
Ehrenfest equation for 2nd  
order.

These equations represents the condition of equilibrium between the two phases.

⇒ In Graphically -

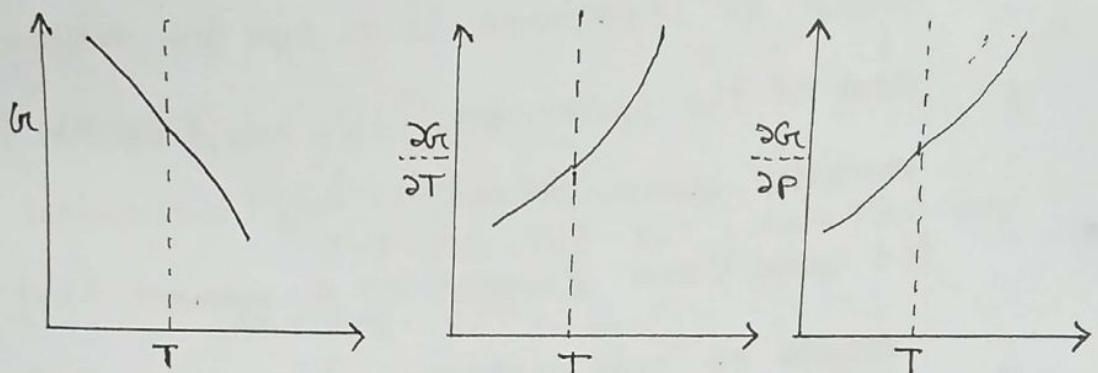


Fig.1. Second order phase transition

Chemical potential:

In thermodynamics, chemical potential of a species is energy that can be absorbed or released due to a change of the particle number of the given species, e.g. in a chemical reaction or phase transition.

(1) Chemical potential and internal energy,  $\mu$ :

The thermodynamic identity is,

$$d\mu = Tds - Pdv \quad \text{--- (1)}$$

to allow for the extra energy brought into the system by the additional particles. This extra energy is clearly of importance if it can be released to the rest of the system and this could be the case if the particles were involved in, say, a chemical reaction of some form. Suppose for a moment that the system consists of only one type of particle and  $dN$  particles are added.

Then the equation ① can be modified as,

$$du = Tds - pdv + \mu dN$$

where  $\mu$  is called the chemical potential, defined as the increase in the internal energy per ~~cycle~~ particle added under conditions of constant  $S$  and  $V$ . That is,

$$\mu = \left( \frac{\partial U}{\partial N} \right)_{S,V} \quad \text{--- ②}$$

If there is more than one type of particle, equation ① has to be modified,

$$du = Tds - pdv + \sum_i \mu_i dN_i$$

## (ii) Chemical potential and Helmholtz function, F:

Chemical potential,  $\mu$  can be given in terms of the Helmholtz function,  $F$ .  $F$  is related to  $u$  and  $S$  by.

$$F = u - TS$$

Differentiating,

$$\begin{aligned} dF &= du - TdS - SdT \\ &= TdS - PdV - TdS - SdT \quad \Big| \quad du = TdS - PdV \\ dF &= -PdV - SdT \quad \text{--- (3)} \end{aligned}$$

Let, for a moment that the system consists of only one type of particle and  $dN$  particles are added. Then,

$$dF = -PdV$$

Therefore,

$$\mu = \left( \frac{\partial F}{\partial N} \right)_{V,T} \quad \text{--- (4)}$$

That is,  $\mu$  is the increase of the Helmholtz free energy upon the addition of one particle under conditions of constant  $T$  and  $V$ .

The connection between  $\mu$  and  $F$  may be expanded using the relationship between  $F$  and the statistical partition function  $Z$ :

$$F = -Nk_B T \ln Z$$

Using this form  $F$  in the expression for  $\mu$  in eqn. (4)

$$\mu = -k_B T \left[ \frac{\partial}{\partial N} (N \ln Z) \right]_{V,T}$$

### (III) Chemical Potential and Gibbs function, $G_c$ ;

Chemical potential can be linked to the Gibbs function,  $G_c$ . The equation is,

$$G_c = H - TS$$

$$\text{or, } G_c = U + PV - TS \quad \text{--- (5)}$$

Differentiating,

$$\begin{aligned} dG_c &= du + pdv + vdp - Tds - SdT \\ &= Tds - pdv + pdv + vdp - Tds - SdT \\ dG_c &= vdp - SdT \quad \text{--- (6)} \end{aligned}$$

Let, for a moment that the system consists of only one type of particle and  $dN$  particles are added. Then

$$dG_c = vdp - SdT + \mu dN$$

Therefore,

$$\mu = \left( \frac{\partial G_c}{\partial N} \right)_{T, P} \quad \text{--- (7)}$$

That is,  $\mu$  is the increase of the Gibbs free energy upon the addition of one particle under conditions of constant  $T$  and  $P$ .

Equation (2), (3) and (7) give three independent way to define chemical potential.

For this system, the number of degrees of freedom are given by,

$$F = \text{Total number of variable} - \text{Number of fixed variable}$$

(i) Total number of variable:

For any system, there is only one pressure and one temperature.

Hence, there are 2 variables.

For a system having 'c' components, there are  $(c-1)$  concentration terms in each phase.

∴ Number of concentration terms in 'p' phase is,

$$= p(c-1)$$

So, total number of variable is,

$$= p(c-1) + 2$$

(ii) Number of fixed variable:

For a system having three phases A, B and C in equilibrium and  $\mu_A$ ,  $\mu_B$  and  $\mu_C$  are the chemical potentials of these components in the three phases.

$$\therefore \mu_A = \mu_B = \mu_C$$

Mathematically,

$$\mu_A = \mu_B \text{ and } \mu_B = \mu_C$$

For one component, p phase have variable =  $p-1$

∴ For c component, p phase have variable =  $c(p-1)$

Number of fixed variable is =  $c(p-1)$

Degree of freedom is given by,

$$F = [p(c-1)+2] - [c(p-1)]$$

$$= pc - p + 2 - cp + c$$

$$\therefore F = c - p + 2$$

This equation is known as Gibbs phase rule.

### Example-1

\* At the triple point, at liquid-solid curve and at liquid of  $H_2O$  what is D.O.F?

Soln:

By the phase rule equation we get,

$$F = c - p + 2$$

(1) At the triple point:

Phase,  $p = 3$  (solid, liquid and gas)

Component,  $c = 1$

From eqn. ①,

$$F = 1 - 3 + 2$$

$$= 0$$

At the triple point of  $\text{H}_2\text{O}$  have no degrees of freedom

(ii) At liquid-solid curve:

$$P = 2$$

$$C = 1$$

From eqn. (1),

$$F = 1 - 2 + 2$$

$$= 1$$

(iii) At liquid:

$$P = 1$$

$$C = 1$$

From equation (1)

$$F = 1 - 1 + 2$$

$$= 2$$

### ④ Third law of thermodynamics

According to Nernst,

3<sup>rd</sup> law of thermodynamics state that as the temperature of a system approaches absolute zero, its entropy become constant or the entropy is zero.

∴ The entropy of any systems vanishes in the state for which,

$$\left(\frac{\partial V}{\partial S}\right)_{N_1, N_2, \dots, N_R} = 0 \quad | \quad S = \int_0^T \frac{dq}{T} + S_0$$

that is, at zero of temperature.

### Planck statement:

The entropy of all perfect crystals is the same at absolute zero and may be taken as zero

$$\left(\frac{\partial V}{\partial S}\right)_{V, N_1, \dots, N_R} = 0 \quad | \quad S = \int_0^T \frac{dq}{T} + S_0$$

T<sub>0</sub> -