

## 4th chapter

### ■ Legendre transformation :

The transformation which transforms Lagrangian formulation variables  $(q, q', t)$  into Hamiltonian formulation variables  $(q, p, t)$  is called Legendre transformation.

Consider a function of two variables. i.e.,  $f = f(x, y)$

The differential of this function is,

$$df = \frac{\partial f}{\partial x} dx + \frac{\partial f}{\partial y} dy \quad \dots (1)$$

Let,  $\frac{\partial f}{\partial x} = u$  and  $\frac{\partial f}{\partial y} = v$

From equation (1),

$$df = u dx + v dy \quad \dots (2)$$

We wish now to change the basis of description from  $x, y$  to other independent variables  $u, v$  so that differential quantities are expressed in terms of differential  $du$  and  $dv$ . This type of transformation is called Legendre transformation.

Let  $g$  be the function of  $u$  and  $v$  defined by the equation

$$g = f - ux \quad \dots (3) \quad [ \because f = g + ux ]$$

Differential of  $g$  is given by,

$$\begin{aligned} dg &= df - u dx - x du \\ &= u dx + v dy - u dx - x du \end{aligned}$$

$$\therefore dg = v dy - x du \quad \text{--- (4)}$$

Which is exactly in the desired form. In equation (4)  $dg$  is expressed in terms of  $dy$  and  $du$  which means that  $g$  is a function of  $y$  and  $u$ .

$$g = g(y, u) \quad \text{--- (5)}$$

The differential form of  $g$ ,

$$dg = \frac{\partial g}{\partial y} dy + \frac{\partial g}{\partial u} du \quad \text{--- (6)}$$

Comparing equation (6) and equation (4), the quantities  $x$  and  $v$  are now functions of the variables  $u$  and  $y$  given by the relation,

$$x = -\frac{\partial g}{\partial u} \quad \text{and} \quad v = \frac{\partial g}{\partial y} \quad \text{--- (7)}$$

Actually equation (7) is the converse of equations,

$$u = \frac{\partial f}{\partial x} \quad \text{and} \quad v = \frac{\partial f}{\partial y}$$

Transformation  $x, y \rightarrow u, y$  is called the Legendre transformation.

## Thermodynamic potential :

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

There are four thermodynamic potential functions —

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

The internal energy or the intrinsic energy is the total energy of a system. According to 1st law of thermodynamics,

$$dQ = dU + dW$$

$$\Rightarrow dU = dQ - PdV \quad [ \because dW = PdV ]$$

and from second law of thermodynamics,

$$dQ = TdS$$

$$\therefore dU = TdS - PdV \quad \text{--- (1)}$$

This equation gives the change in internal energy of the system in terms of four thermodynamic variables  $P, V, T$  and  $S$ . Internal energy ( $U$ ) is called the first thermodynamical potential.

#### (a) For an adiabatic process :

$$dQ = 0$$

$$\therefore dU = -PdV$$

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

(b) For an isochoric adiabatic process :

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

$$\therefore dU=0$$

$$\Rightarrow U = \text{constant}$$

i.e; the internal energy of system remains constant in an isochoric adiabatic process.

(ii) Helmholtz Free energy ( $F$ ) :

Helmholtz free energy is defined as,

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

As  $U, T, S$  are state variables,  $F$  is also a state variable.

According to first and second law of thermodynamics,

$$dU = TdS - dW$$

$$\Rightarrow dU = TdS - PdV \quad \text{--- (2)}$$

Differentiating equation (1)

$$dF = dU - TdS - SdT$$

$$\Rightarrow dF = TdS - PdV - TdS - SdT$$

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

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

(a) For reversible isothermal process :

$$\begin{aligned}dT &= 0 \\dF &\doteq -PdV \\ \Rightarrow PdV &= -dF\end{aligned}$$

$$\begin{aligned}dU &= TdS - PdV \\&\quad + dQ - dW \\F &= U - TS \\H &= U + PV \\G &= H - TS \\&= U + PV - TS\end{aligned}$$

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

(b) For isothermal isochoeric process :

$$\begin{aligned}dT &= 0 \text{ and } dV = 0 \\ \therefore dF &= 0 \\ \Rightarrow F &= \text{constant}\end{aligned}$$

i.e; Helmholtz free energy remains constant during isothermal isochoeric process.

(iii) Enthalpy (H) :

This is known as total heat and is given by,

$$H = U + PV \quad \text{--- (1)}$$

As  $U, P, V$  are state function,  $H$  is also state function.  
According to first and 2nd law of thermodynamics,

$$dU = TdS - PdV \quad \text{--- (2)}$$

Differentiating (1),

$$dH = dU + PdV + VdP$$

$$= TdS - PdV + PdV + VdP$$

$$\therefore dH = TdS + VdP$$

(a) For reversible isobaric process,

$$dP = 0$$

$$dH = TdS = dQ$$

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

(b) For an isobaric adiabatic process :

$$dP = 0 ; dQ = 0$$

$$\therefore dH = 0$$

$$\Rightarrow H = \text{constant}$$

i.e; the enthalpy remains constant in an isobaric adiabatic process .

(iv) Gibbs Function  $G_f$  or Gibbs Free Energy :

The equation of Gibbs free energy is ,

$$G_f = H - TS$$

$$\Rightarrow G_f = U + PV - TS \quad \left[ \because H = U + PV \right] \\ \longrightarrow (1)$$

According to first and 2nd law of thermodynamics,

$$dU = TdS - PdV \quad \text{---(2)}$$

Differentiating (1),

$$dG_c = dU - TdS - SdT + PdV + VdP$$

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

$$\therefore dG_c = VdP - SdT$$

(a) For an isothermal process:

$$dT = 0$$

$$\therefore dG_c = VdP$$

(b) For an isothermal-isobaric process:

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

$$\therefore dG_c = 0$$

$$\Rightarrow G_c = \text{constant}$$

i.e.; Gibbs function or gibbs free energy remains constant in an isothermal isobaric process.



## ■ Significance of thermodynamic potentials :

A mechanical system is said to be in stable equilibrium when the potential energy of the system is minimum. It means that the system must be proceed in such a direction so as to acquire minimum potential energy. This what we observe in nature, water flows from higher level to lower level, electric current flows from higher to lower potential, heat flows from higher to lower temperature, a body falls from higher to lower potential due to gravitational field and so on.

In thermodynamics, the behaviour of internal energy ( $U$ ), Helmholtz free energy ( $F$ ), enthalpy ( $H$ ), Gibbs free energy ( $G$ ), is similar to potential energy in mechanics. As we have seen, the direction of isothermal-isochoric process is to make Helmholtz free energy ( $F$ ) minimum. In isothermal-isobaric process, Gibbs free energy ( $G$ ) tends to be minimum. In an isobaric-adiabatic process, the enthalpy tends to be minimum.

Since the four functions  $U, F, H$  and  $G$  play in thermodynamics the same role as played by potential energy in mechanics, they are called thermodynamic potentials.

## ~~Maxwell's Thermodynamical Relations :~~

~~Q~~ The general expression for Maxwell's thermodynamical relations :

→ From the first and second law of thermodynamics , Maxwell was able to derive four fundamental thermodynamical relations . The state of a system can be specified by any pair of quantities pressure ( $P$ ) , volume ( $V$ ) , temperature ( $T$ ) and ~~enthalpy (S)~~ ~~entropy~~

From the first law of thermodynamics ,

$$dQ = dU + dW$$

$$\Rightarrow dU = dQ - PdV \quad \text{--- (1)}$$

For the second law of thermodynamics ,

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

$$\Rightarrow dQ = TdS$$

Substituting the value of  $dQ$  ,

$$dU = TdS - PdV \quad \text{--- (2)}$$

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

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

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

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

Substituting these value in equation (2), we get,

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

Comparing the coefficients of  $dx$  and  $dy$ , we get

$$\left(\frac{\partial U}{\partial x}\right)_y = T \left(\frac{\partial S}{\partial x}\right)_y - P \left(\frac{\partial V}{\partial x}\right)_y \quad \text{--- (3)}$$

$$\left(\frac{\partial U}{\partial y}\right)_x = T \left(\frac{\partial S}{\partial y}\right)_x - P \left(\frac{\partial V}{\partial y}\right)_x \quad \text{--- (4)}$$

Differentiating equation (3) with respect to  $y$  and equation (4) with respect to  $x$ ,

$$\frac{\partial^2 U}{\partial y \partial x} = \left(\frac{\partial T}{\partial y}\right)_x \left(\frac{\partial S}{\partial x}\right)_y + T \frac{\partial^2 S}{\partial y \partial x} - \left(\frac{\partial P}{\partial y}\right)_x \left(\frac{\partial V}{\partial x}\right)_y - P \frac{\partial^2 V}{\partial y \partial x}$$

and

$$\frac{\partial^2 U}{\partial x \partial y} = \left(\frac{\partial T}{\partial x}\right)_y \left(\frac{\partial S}{\partial y}\right)_x + T \frac{\partial^2 S}{\partial x \partial y} - \left(\frac{\partial P}{\partial x}\right)_y \left(\frac{\partial V}{\partial y}\right)_x - P \frac{\partial^2 V}{\partial x \partial y}$$

The change in internal energy brought about by changing  $V$  and  $T$  wheather  $V$  is changed by  $dV$  first and  $T$  by  $dT$  later or vice versa is the same.

It means  $dU$  is a perfect differential.

$$\frac{\partial^2 U}{\partial y \partial x} = \frac{\partial^2 U}{\partial x \partial y} \text{ and}$$

$$\left(\frac{\partial T}{\partial y}\right)_x \left(\frac{\partial S}{\partial x}\right)_y + T \frac{\partial^2 S}{\partial y \partial x} - \left(\frac{\partial P}{\partial y}\right)_x \left(\frac{\partial V}{\partial x}\right)_y - P \frac{\partial^2 V}{\partial y \partial x} = \\ \left(\frac{\partial T}{\partial x}\right)_y \left(\frac{\partial S}{\partial y}\right)_x + T \frac{\partial^2 S}{\partial x \partial y} - \left(\frac{\partial P}{\partial x}\right)_y \left(\frac{\partial V}{\partial y}\right)_x - P \frac{\partial^2 V}{\partial x \partial y} \quad (5)$$

Since  $ds$  and  $dv$  are also perfect differentials, we have

$$\frac{\partial^2 S}{\partial x \partial y} = \frac{\partial^2 S}{\partial y \partial x} \text{ and } \frac{\partial V}{\partial x \partial y} = \frac{\partial V}{\partial y \partial x}$$

Therefore equation (5) therefore reduces to

$$\left(\frac{\partial T}{\partial y}\right)_x \left(\frac{\partial S}{\partial x}\right)_y - \left(\frac{\partial P}{\partial y}\right)_x \left(\frac{\partial V}{\partial x}\right)_y = \left(\frac{\partial T}{\partial x}\right)_y \left(\frac{\partial S}{\partial y}\right)_x - \left(\frac{\partial P}{\partial x}\right)_y \left(\frac{\partial V}{\partial y}\right)_x$$

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

In place of  $x$  and  $y$  any two of the four variable  $S, T, P, V$  can be substituted to get four Maxwell's thermodynamical relations.

Relations:

We have the general expression for Maxwell's thermodynamical relation,

$$\left(\frac{\partial T}{\partial y}\right)_x \left(\frac{\partial S}{\partial x}\right)_y - \left(\frac{\partial P}{\partial y}\right)_x \left(\frac{\partial V}{\partial x}\right)_y = \left(\frac{\partial T}{\partial x}\right)_y \left(\frac{\partial S}{\partial y}\right)_x - \left(\frac{\partial P}{\partial x}\right)_y \left(\frac{\partial V}{\partial y}\right)_x \quad (1)$$

First relation:

Put  $x=S$  and  $y=V$  in equation (1)

$$\frac{\partial S}{\partial x} = 1, \quad -\frac{\partial V}{\partial y} = 1$$

$$\text{and } \frac{\partial S}{\partial y} = 0, \quad -\frac{\partial V}{\partial x} = 0$$

Substituting in equation (1) we get,

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

But  $\partial y = \partial V$  as  $y=V$  and

$$\partial x = \partial S \text{ as } x=S$$

Hence,

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

This is the 1st thermodynamical relation.

### By second relation :

Put  $x=T$  and  $y=v$  in equation (1)

$$\frac{\partial T}{\partial x} = 1 , \quad \frac{\partial v}{\partial y} = 1$$

$$\text{and } \frac{\partial T}{\partial y} = 0 , \quad \frac{\partial v}{\partial x} = 0$$

Substituting in equation (1) and putting  $x=T$  and  $y=v$

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

This is Maxwell's second thermodynamical relation.

### By Third relation :

Put  $x=s$  and  $y=p$  in equation (1)

$$\frac{\partial s}{\partial x} = 1 , \quad \frac{\partial p}{\partial y} = 1$$

$$\text{and } \frac{\partial s}{\partial y} = 0 , \quad \frac{\partial p}{\partial x} = 0$$

Substituting in equation (1) and putting  $x=s$  and  $y=p$

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

This is the Maxwell's third thermodynamical relation.

#### 4) Fourth Relation:

Put  $x=T$  and  $y=P$  in equation (1) we get,

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

and  $\frac{\partial T}{\partial y} = 0, \quad , \quad \frac{\partial P}{\partial x} = 0$

Substituting those value in equation (1) and putting  $x=T$  and  $y=P$  we get,

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

This is the fourth Maxwell's thermodynamical relation.

### Q First T.dS Equation :

The entropy  $S$  of a pure substance can be taken as a function of temperature and volume,

$$S = S(T, V)$$

Differentiating,

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \quad \text{--- (1)}$$

Multiplying both side by  $T$ ,

$$TdS = T \left(\frac{\partial S}{\partial T}\right)_V dT + T \left(\frac{\partial S}{\partial V}\right)_T dV \quad \text{--- (2)}$$

$$\therefore \text{But } C_V = T \left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{dQ}{dT}\right)_V \quad \left[\because dS = \frac{dQ}{T}\right]$$

and from Maxwell's relation,

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

Substituting these value in equation (2),

$$TdS = C_V dT + T \left(\frac{\partial P}{\partial T}\right)_V dV$$

This is called the first T.dS equation.

### ■ Second TdS Equation :

The entropy  $S$  of a pure substance can also be regarded as a function of temperature and pressure.

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

Differentiating,

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP \quad \text{--- (1)}$$

Multiplying both sides by  $T$ ,

$$TdS = T \left(\frac{\partial S}{\partial T}\right)_P dT + T \left(\frac{\partial S}{\partial P}\right)_T dP \quad \text{--- (2)}$$

But  $C_P = \left(\frac{\partial Q}{\partial T}\right)_P = T \left(\frac{\partial S}{\partial T}\right)_P$

and from Maxwell's relation,

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

Substituting those value in equation (2),

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

This is called the second TdS equation.

### ⇒ Third Tds Equation :

The entropy  $S$  of a pure substance can also be regarded as a function of pressure and volume.

$$S = S(P, V)$$

Differentiating,

$$dS = \left(\frac{\partial S}{\partial P}\right)_V dP + \left(\frac{\partial S}{\partial V}\right)_P dV \quad \dots (1)$$

Multiplying by  $T$ ,

$$TdS = T \left(\frac{\partial S}{\partial P}\right)_V dP + T \left(\frac{\partial S}{\partial V}\right)_P dV \quad \dots (2)$$

In constant volume,

$$dQ = TdS = C_V dT$$

$$\Rightarrow T \left(\frac{\partial S}{\partial P}\right)_V = C_V \left(\frac{\partial T}{\partial P}\right)_V \quad \dots (3)$$

Again in constant pressure,

$$dQ = TdS = C_P dT$$

$$\Rightarrow T \left(\frac{\partial S}{\partial V}\right)_P = C_P \left(\frac{\partial T}{\partial V}\right)_P \quad \dots (4)$$

Putting these value in equation (2) we get,

$$TdS = C_V \left(\frac{\partial T}{\partial P}\right)_V dP + C_P \left(\frac{\partial T}{\partial V}\right)_P dV$$

This is the third Tds equation .

■ Entropy for ideal gas using TdS equation:

⇒ We have the first TdS equation,

$$TdS = C_V dT + T \left( \frac{\partial P}{\partial T} \right)_V dV \quad \text{--- (1)}$$

For ideal gas,

$$PV = RT$$

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

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

Putting this in equation (1) and dividing by T,

$$dS = C_V \frac{dT}{T} + R \frac{dV}{V}$$

Integrating,

$$S = C_V \ln T + R \ln V + S_0$$

Here  $S_0$  is integrating constant.

This is the required entropy.

■ Entropy for real gas / Vander Waal's gas using TdS equation :

⇒ We have the first TdS equation,

$$TdS = C_V dT + T \left( \frac{\partial P}{\partial T} \right)_V dV \quad \text{--- (1)}$$

$$\Rightarrow dU = TdS - PdV$$

Dividing by  $dV$ ,

$$\frac{dU}{dV} = T \frac{dS}{dV} - P$$

If temperature is fixed,

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial S}{\partial V}\right)_T - P \quad \text{--- (Q)}$$

Using Maxwell's equation,

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

We get from (Q)

$$\begin{aligned} \left(\frac{\partial U}{\partial V}\right)_T &= T \left(\frac{\partial S}{\partial V}\right)_T - P \\ &= T \left(\frac{\partial P}{\partial T}\right)_V - P \end{aligned}$$

From equation (1) ,

$$dU = C_V dT + \left[ T \left(\frac{\partial P}{\partial T}\right)_V - P \right] dV \quad \text{--- (3)}$$

This is the internal energy equation and it

For ideal gas the internal energy —

For ideal gas,  $PV = RT$

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

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

Putting this in equation (3) ,

$$dU = C_V dT + \left[ \frac{RT}{V} - P \right] dV$$

For Vander Waal's gas,

$$(P + \frac{a}{v^2})(v - b) = RT$$

$$\Rightarrow P = \frac{RT}{(v-b)} - \frac{a}{v^2}$$

$$\Rightarrow (\frac{\partial P}{\partial T})_V = \frac{R}{(v-b)}$$

Now putting these in equation (1) and dividing by T

$$dS = C_V \frac{dT}{T} + \frac{R}{(v-b)} dv$$

Integrating ,

$$S = C_V \ln T + R \ln(v-b) + S_0$$

Here  $S_0$  is integrating constant.

This is the required entropy for Vander Waal's gas.

■ Internal energy equation :

Internal energy is the function of Temperature and volume,

$$U = U(T, v)$$

Differentiating ,  $dU = (\frac{\partial U}{\partial T})_V dT + (\frac{\partial U}{\partial v})_T dv$  — (1)

We know from 1st law of thermodynamics ,

$$dQ = dU + dW$$

$$\Rightarrow dU = dQ - dW$$

$$\Rightarrow dU = C_V dT + [P - P] dv$$

$$\Rightarrow dU = C_V dT$$

Integrating,

$$\int dU = \int C_V dT$$

$$\Rightarrow U - U_0 = C_V T$$

This is the required equation and it is only the function of temperature.

For real gas the internal energy —

For real gas,

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

Integrating in constant volume with respect to T,

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{v-b}$$

Putting this in equation (3),

$$\begin{aligned} dU &= C_V dT + \left[ T \left( \frac{\partial P}{\partial T} \right)_V - P \right] dv \\ &= C_V dT + \left[ \frac{RT}{v-b} - P \right] dv \\ &= C_V dT + \left[ \frac{RT}{v-b} - \frac{RT}{v-b} + \frac{a}{v^2} \right] dv \end{aligned}$$

$$\Rightarrow dU = C_V dT + \frac{a}{v^2} dv$$

$$\Rightarrow \int dU = \int C_V dT + a \int \frac{dv}{v^2}$$

$$\Rightarrow U - U_0 = C_V T - \frac{a}{v}$$

This is the required function and it is the function of temperature, ( $T$ ) and volume ( $v$ )

### Heat capacity Equation :

The specific heat at constant pressure is given by,

$$C_p = \left(\frac{\partial Q}{\partial T}\right)_p = T \left(\frac{\partial S}{\partial T}\right)_p \quad [ \because dQ = T dS ]$$

and the specific heat at constant volume is given by,

$$C_v = \left(\frac{\partial Q}{\partial T}\right)_v = T \left(\frac{\partial S}{\partial T}\right)_v$$

Now if entropy  $S$  is regarded as a function of  $T$  and  $v$  and since  $ds$  is a perfect differential,  $s = s(T, v)$

$$ds = \left(\frac{\partial S}{\partial T}\right)_v dT + \left(\frac{\partial S}{\partial v}\right)_T dv$$

$$\Rightarrow \left(\frac{\partial S}{\partial T}\right)_p = \left(\frac{\partial S}{\partial T}\right)_v \left(\frac{\partial T}{\partial T}\right)_p + \left(\frac{\partial S}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p$$

$$\Rightarrow T \left(\frac{\partial S}{\partial T}\right)_p = T \left(\frac{\partial S}{\partial T}\right)_v + T \left(\frac{\partial S}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p$$

$$\Rightarrow C_p - C_v = T \left(\frac{\partial S}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p \quad \text{---(1)}$$

We have,

$$\text{Maxwell's relation, } \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

From (1)

$$C_p - C_v = T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P \quad \dots \text{(2)}$$

And, we know cyclical rule:

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

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

Putting this in equation (2)

$$C_p - C_v = - T \left(\frac{\partial V}{\partial T}\right)_P^2 \left(\frac{\partial P}{\partial V}\right)_T \quad \dots \text{(3)}$$

In case of water at  $4^\circ\text{C}$

$$\left(\frac{\partial V}{\partial T}\right)_P = 0$$

$$C_p = C_v$$

Q) Show that for ideal gas heat capacity or specific heat equation is  $C_p - C_v = R$ .

$\Rightarrow$  We know,

Specific heat equation,

$$C_p - C_v = T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P \quad \dots \text{(4)}$$

The equation of state for ideal gas ,

$$PV = RT$$

When pressure is constant ,

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

When volume is constant ,

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

Putting these value in equation (1) ,

$$\begin{aligned}C_p - C_v &= T \cdot \frac{R}{V} \cdot \frac{R}{P} \\&= \frac{R^2 T}{PV} \\&= \frac{R^2 T}{RT} \\&= R\end{aligned}$$

$$\therefore C_p - C_v = R \quad [\text{Proved}]$$

For real gas the specific heat equation is  $C_p - C_v = R \left(1 + \frac{2a}{RTv}\right)$  shows that .

⇒ We have the specific heat equation ,

$$C_p - C_v = T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P \quad \dots \dots \dots (1)$$

For real gas ,

$$\left(P + \frac{a}{V^2}\right) (V - b) = RT$$

When pressure is constant,

$$\left(P + \frac{a}{V^2}\right) = \frac{RT}{V-b}$$

$$0 + \frac{-2a}{V^3} \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{V-b} + \frac{-RT}{(V-b)^2} \left(\frac{\partial V}{\partial T}\right)_P$$

$$\Rightarrow -\frac{2a}{V^3} \left(\frac{\partial V}{\partial T}\right)_P + \frac{RT}{(V-b)^2} \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{V-b}$$

$$\Rightarrow \left(\frac{\partial V}{\partial T}\right)_P \frac{RT}{(V-b)^2} \left[1 - \frac{2a(V-b)^2}{RTV^3}\right] = \frac{R}{(V-b)}$$

$$\Rightarrow \left(\frac{\partial V}{\partial T}\right)_P \frac{T}{(V-b)} \left[1 - \frac{2a(V-b)^2}{RTV^3}\right] = 1 \cancel{\frac{R}{(V-b)}}$$

$$\Rightarrow T \left(\frac{\partial V}{\partial T}\right)_P = \frac{(V-b)}{\left[1 - \frac{2a(V-b)^2}{RTV^3}\right]}$$

When volume is constant,

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

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{(V-b)}$$

Putting all these in equation (1) we get,

$$\alpha_{P-V} = \frac{(V-b)}{\left[1 - \frac{2a(V-b)^2}{RTV^3}\right]} \times \frac{R}{(V-b)}$$

$$\Rightarrow \rho_p - \rho_v = \frac{R}{\left[ 1 - \frac{2a(v-b)^2}{RTv^3} \right]}$$

When  $b$  is very small then it can be neglected in comparison to  $v$ ,

$$\rho_p - \rho_v = \frac{R}{\left[ 1 - \frac{2a v^2}{RTv^3} \right]}$$

$$\Rightarrow \rho_p - \rho_v = \frac{R}{\left( 1 - \frac{2a}{RTv} \right)}$$

$$\Rightarrow \rho_p - \rho_v = R \left( 1 - \frac{2a}{RTv} \right)^{-1}$$

Expanding binomially and neglecting  $a$  in higher powers, as  $a$  is also small as compared to  $v$ , we have,

$$\rho_p - \rho_v = R \left( 1 + \frac{2a}{vRT} \right)$$

Hence  $R$  is in heat units

Q1 Derive the equation,  $\left(\frac{\partial \ell_v}{\partial v}\right)_T = T \left(\frac{\partial^2 P}{\partial T^2}\right)_V$

$\Rightarrow$  We know,

$$\ell_v = \left(\frac{\partial Q}{\partial T}\right)_V$$

$$\Rightarrow \left(\frac{\partial \ell_v}{\partial v}\right)_T = \left\{ \frac{\partial}{\partial v} \left(\frac{\partial Q}{\partial T}\right)_V \right\}_T$$

$$\Rightarrow \left(\frac{\partial \ell_v}{\partial v}\right)_T = \left\{ \frac{\partial}{\partial v} \left(\frac{T dS}{\partial T}\right)_V \right\}_T$$

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

$$\Rightarrow \left(\frac{\partial \ell_v}{\partial v}\right)_T = T \left\{ \frac{\partial}{\partial T} \left(\frac{\partial S}{\partial v}\right)_T \right\}_V \quad \text{--- (1)}$$

From Maxwell's relation,

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

Now from equation (1)

$$\left(\frac{\partial \ell_v}{\partial v}\right)_T = T \left\{ \frac{\partial}{\partial T} \left(\frac{\partial P}{\partial T}\right)_V \right\}_V$$

$$\therefore \left(\frac{\partial \ell_v}{\partial v}\right)_T = T \left(\frac{\partial^2 P}{\partial T^2}\right)_V$$

④ Derive the equation,

$$\left(\frac{\partial C_p}{\partial P}\right)_T = -T \left(\frac{\partial^2 V}{\partial T^2}\right)_P$$

⇒ We know,

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

$$\Rightarrow \left(\frac{\partial C_p}{\partial P}\right)_T = \left\{ \frac{\partial}{\partial P} \left(\frac{\partial Q}{\partial T}\right)_P \right\}_T$$

$$\Rightarrow \left(\frac{\partial C_p}{\partial P}\right)_T = \left\{ \frac{\partial}{\partial P} \left(\frac{T dS}{\partial T}\right)_P \right\}_T$$

$$\Rightarrow \left(\frac{\partial C_p}{\partial P}\right)_T = T \left\{ \frac{\partial}{\partial T} \left(\frac{\partial S}{\partial P}\right)_T \right\}_P \quad \text{--- (1)}$$

From Maxwell's relation,

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

Pulling this in equation (1),

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

$$\therefore \left(\frac{\partial C_p}{\partial P}\right)_P = -T \left(\frac{\partial^2 V}{\partial T^2}\right)_P$$

### Joule-Thomson effect:

In Joule-Thomson porous plug experiment, if a 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.

### Joule-Thomson coefficient ( $\mu$ ):

The Joule-Thomson coefficient is given by,

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

Now  $\left( \frac{\partial V}{\partial T} \right)_P = \alpha V$  where  $\alpha$  is the coefficient of increase of volume at constant pressure, because  $\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$

From equation (1),

$$\begin{aligned} \left( \frac{\partial T}{\partial P} \right)_H &= \frac{1}{C_p} \left[ T \alpha V - V \right] \\ \Rightarrow dT &= \frac{V}{C_p} \left[ \alpha T - 1 \right] dP \quad \text{--- (2)} \end{aligned}$$

Equation (2) 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 a negative quantity. All other quantities in equation (2) are positive. Hence

- (i) There is cooling effect i.e;  $dT$  is negative if  $(\alpha T - 1)$  positive 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 a heating effect i.e;  $dT$  is positive if  $(\alpha T - 1)$  is negative or  $\alpha T < 1$ .

Q) Thermodynamic equation for Joule-Thomson coefficients:

Q) Mathematical explanation of Joule Thomson effect:

Q) Thermodynamical treatment of heating and cooling effect:

Due to throttling the gas suffers expansion. Although there is a pressure difference on two sides of the porous plug, the enthalpy  $H$  of the gas remains constant. This is the necessary condition i.e;

$$H = U + PV = \text{constant}$$

$$\Rightarrow dH = dU + PdV + VdP = 0 \quad \text{---(1)}$$

From first and second law of thermodynamics,

$$dQ = dU + PdV$$

$$\text{and} \quad dQ = TdS$$

$$\therefore dU = TdS - PdV$$

From (1)  $dH = TdS - PdV + PdV + VdP = 0$

$$dH \Rightarrow TdS + VdP = 0 \quad \text{---(2)}$$

Now  $dS$  being a perfect differential and  $S$  is a function of Pressure and Temperature,

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

Differentiating,

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

Putting this in equation (2)

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

$$\Rightarrow T \left(\frac{\partial S}{\partial T}\right)_P dT + \left[T \left(\frac{\partial S}{\partial P}\right)_T + v\right] dP = 0 \quad \text{--- (3)}$$

Now, specific heat at constant pressure,

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

From (3),

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

According to Maxwell's thermodynamical relation

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

Therefore,

$$C_p dT + \left[-T \left(\frac{\partial v}{\partial T}\right)_P + v\right] dP = 0$$

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

$$\Rightarrow dT = \frac{1}{C_p} \left[T \left(\frac{\partial v}{\partial T}\right)_P - v\right] dP \quad \text{--- (4)}$$

This gives the change in temperature due to Joule-

Thomson effect.

Now the Joule-thomson coefficient is,

$$\mu = \left( \frac{\partial T}{\partial P} \right)_H$$

From equation (g) we get,

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

∴ Joule-thomson coefficient,

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

■ Thermodynamical Treatment of heating and cooling effect for ideal gas:

■ Joule-Thomson coefficient for a perfect gas:

According to ideal gas equation,

$$PV = RT$$

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

At constant pressure,

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

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 value in equation (1),

$$dT = \frac{1}{C_p} \left[ \frac{RT}{P} - \frac{RT}{P} \right] dP$$

$$\Rightarrow dT = 0$$

There is no Joule-Thomson effect for an ideal gas. For ideal gas Joule Thomson coefficient is zero,

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

■ Thermodynamical treatment of heating and cooling effect for real gas or Van der Waal's gas :

■ Joule Thomson coefficient for Van der Waal's gas :

According to Van der Waal's gas equation :

$$\left( P + \frac{a}{v^2} \right) (v-b) = RT$$

At constant pressure,

$$0 + \frac{-2a}{v^3} \left( \frac{\partial v}{\partial T} \right)_P = \frac{R}{(v-b)} + \frac{-RT}{(v-b)^2} \left( \frac{\partial v}{\partial T} \right)_P$$

$$\Rightarrow \frac{RT}{(v-b)^2} \left( \frac{\partial v}{\partial T} \right)_P - \frac{2a}{v^3} \left( \frac{\partial v}{\partial T} \right)_P = \frac{R}{v-b}$$

$$\Rightarrow \frac{RT}{(v-b)^2} \left( \frac{\partial v}{\partial T} \right)_P \left[ 1 - \frac{2a(v-b)^2}{Rv^3} \right] = \frac{R}{v-b}$$

$$\Rightarrow T \left( \frac{\partial V}{\partial T} \right)_P = \left[ 1 - \frac{2a(v-b)^2}{RTv^3} \right] = (v-b)$$

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

$$\therefore T \left( \frac{\partial V}{\partial T} \right)_P = \frac{(v-b)}{\left[ 1 - \frac{2av^2}{RTv^3} \right]}$$

$$\Rightarrow T \left( \frac{\partial V}{\partial T} \right)_P = \frac{(v-b) \left[ 1 + \frac{2a}{RTv} \right]}{\left[ 1 - \frac{2a}{RTv} \right] \left[ 1 + \frac{2a}{RTv} \right]}$$

$$\Rightarrow T \left( \frac{\partial V}{\partial T} \right)_P = \frac{(v-b) \left[ 1 + \frac{2a}{RTv} \right]}{\left[ 1 - \left( \frac{2a}{RTv} \right)^2 \right]}$$

Neglecting square and higher powers of  $\frac{2a}{VRT}$  as  $\frac{2a}{VRT} \ll 1$

$$\therefore T \left( \frac{\partial V}{\partial T} \right)_P = (v-b) \left[ 1 + \frac{2a}{VRT} \right]$$

$$\Rightarrow T \left( \frac{\partial V}{\partial T} \right)_P = v-b + \frac{2a(v-b)}{VRT}$$

Again  $b$  is very small,  $v-b=v$ , then,

$$T \left( \frac{\partial V}{\partial T} \right)_P - v = -b + \frac{2av}{VRT}$$

$$\Rightarrow \left[ T \left( \frac{\partial V}{\partial T} \right)_P - v \right] = -\frac{2a}{RT} - b \quad \text{--- (1)}$$

We have the Joule Thomson effect equation,

$$dT = \frac{1}{C_p} \left[ \left( \frac{\partial v}{\partial P} \right)_P - v \right] dP \quad \text{--- (2)}$$

From equation (1) and (2)

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

$$\therefore dT = \frac{dP}{C_p} \left[ \frac{2a}{RT} - b \right] \quad \text{--- (3)}$$

This equation gives the change in temperature of real gas due to Joule Thomson effect.

The Joule Thomson coefficient, for real gas,

$$\mu = \left( \frac{dT}{dP} \right)_H = \frac{1}{C_p} \left[ \frac{2a}{RT} - b \right] \quad \frac{2a}{Rb} = \cancel{b} T$$

Thus we conclude that,

(i) If  $\frac{2a}{RT} > b$  i.e;  $T$  is less than  $\frac{2a}{Rb}$ , then  $\delta T$  is positive since  $dP$  is negative  $dT$  will be negative. Hence there will be a cooling effect.

(ii) If  $\frac{2a}{RT} < b$  i.e;  $T$  is greater than  $\frac{2a}{Rb}$ , then  $\delta T$  is negative since  $dP$  is positive  $dT$  will be positive. Hence there will be a heating effect.

(iii) If  $\frac{2a}{RT} = 0$  then  $T = \frac{2a}{Rb}$  and  $dT = 0$  there will be no change of temperature.

~~Q~~ Joule Kelvin coefficient for throttling process -

The process of throttling involves utilizing a throttle valve to change a high-pressure fluid into a low pressure fluid.

Let the initial equilibrium state before throttling is the point  $i$  at  $(T_i, P_i)$ . With the gas in this initial state, the gas can be throttled to the lower pressure  $P_{f_1}$  and final temperature  $T_{f_1}$ , so that the final equilibrium state  $(T_{f_1}, P_{f_1})$ . This state will have the same enthalpy as  $i$ . If instead the gas were throttled from the same initial state to lower final pressure  $P_{f_2}$  the final equilibrium state will be  $(T_{f_2}, P_{f_2})$  with same enthalpy as  $i$ .

By repeating this experiment a series of points can be obtained all starting with same enthalpy as  $i$  and from same initial point. The curve joining these points is called an isenthalp because it is a line of constant enthalpy.

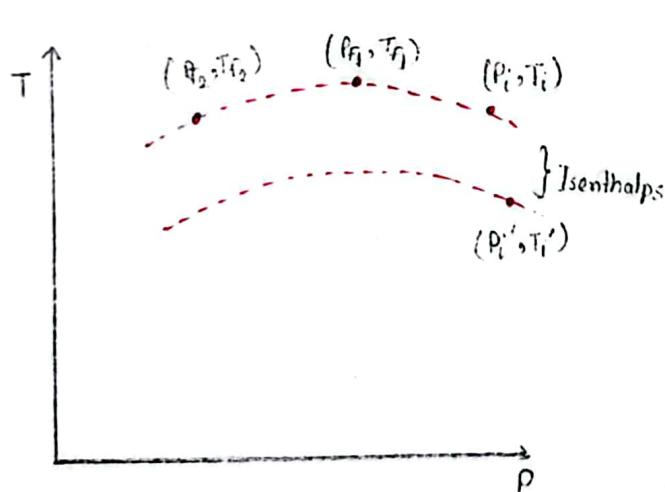


Fig.1. Isenthalps of a throttling process.

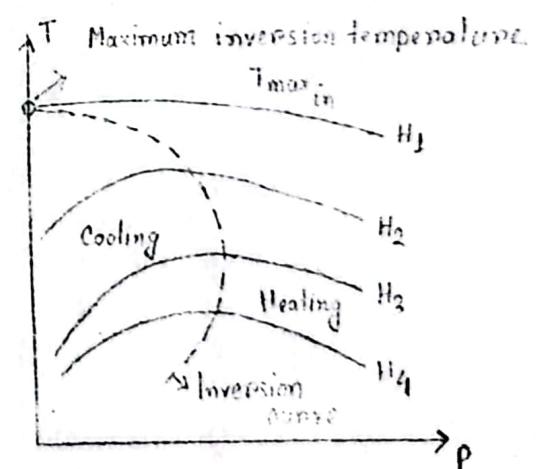


Fig.2. Inversion curve for a throttling process.

The inversion curve (Fig.2) separates the region of heating from the region of cooling. The maxima of the different isenthalps lie on the inversion curve. The greatest cooling effect, for a given pressure drop and starting temperature, will occur when the initial state is on the inversion curve. The temperature coordinate of a point on the inversion curve is called inversion temperature  $T_i$ . For there to be cooling effect, the initial temperature must be chosen to be less than the maximum inversion temperature.

### ④ Inversion Temperature :

The temperature at which Joule-Thomson effect is zero and changes sign is known as temperature of inversion and is denoted by  $T_i$ ,

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

When the room temperature is above the inversion temperature ( $T > T_i$ ) or  $\frac{2a}{RT} \geq b$  there will be heating effect.

Hence during the expansion of gas through a porous plug,

(i) cooling will take place when temperature of gas is less than its temperature of inversion  $[T < \frac{2a}{Rb}]$  and

(ii) heating will take place when temperature of gas is more than its temperature of inversion  $[T > \frac{2a}{Rb}]$

## E) Linde liquefaction process:

The most difficult gas to liquify is helium, which has the lowest boiling point at atmospheric temperature, pressure, a mere  $4.2\text{K}$ . This discussion involves using the Linde liquefier for helium, but of course it can be used for other gases.

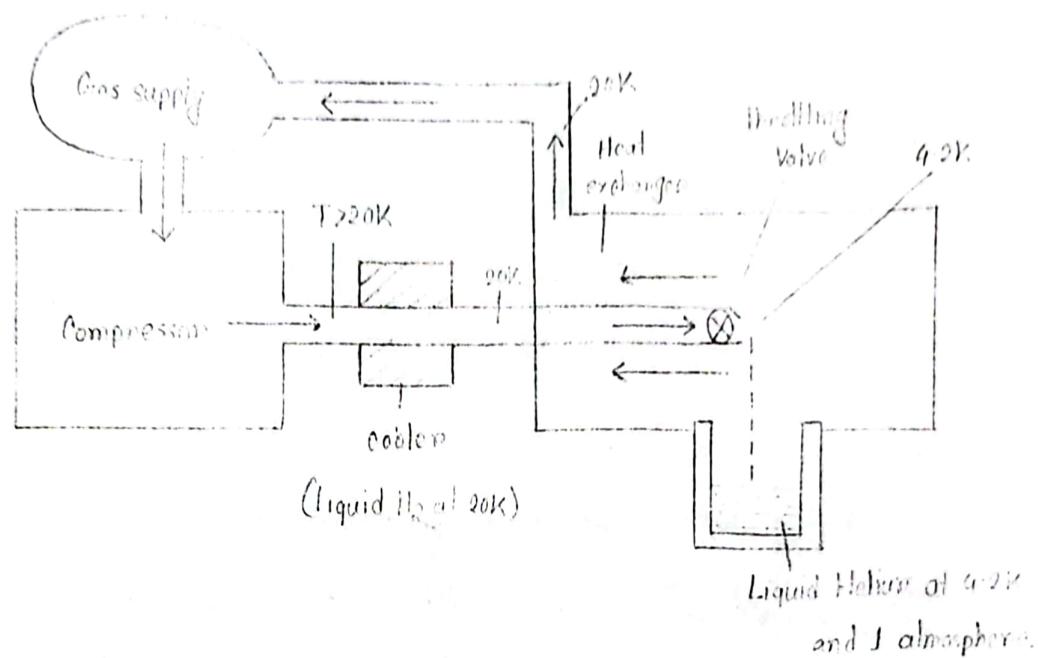


Fig. 1. Schematic representation of a Linde liquefier.

In order for there to be any cooling using the throttling process the helium gas has first to be cooled below the inversion temperature of  $51\text{K}$  by passing it through a cooler, which is typically a coiled pipe immersed in a bath of liquid hydrogen at  $20\text{K}$ . The gas then enters the countercurrent heat exchanger at  $20\text{K}$  at high pressure, where it is throttled through a valve. Then it undergoes cooling, but not enough to immediately cause liquification. The cool gas passes out through the heat

exchanger and, in doing so, cools the incoming gas below 20K. This gas in its turn expands and cools the next amount of incoming gas even more. Eventually, the temperature on the inlet side of the throttling valve is low enough for liquification to occurs and the liquid helium collects at the bottom of the heat exchanger container at 4.2K and at a pressure of 1 atm.

The compressor drives the helium gas around the circuit and provides the necessary high pressure at the inlet side of the throttling valve. After compression and consequent heating , the gas is cooled back to 20K again by the liquid hydrogen cooler so that the helium always enters the heat exchanger at this temperature. It must be understood that the liquifier does not work on the principle that a given mass of gas completes several circuits suffering successive and additive temperature drops until it eventually liquefies.

### ■ Phase:

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

The three fundamental phases are -

Solid, liquid, gas.

### ■ Phase transition:

It is the transformation of a thermodynamic system from one phase or state of matter to another state.

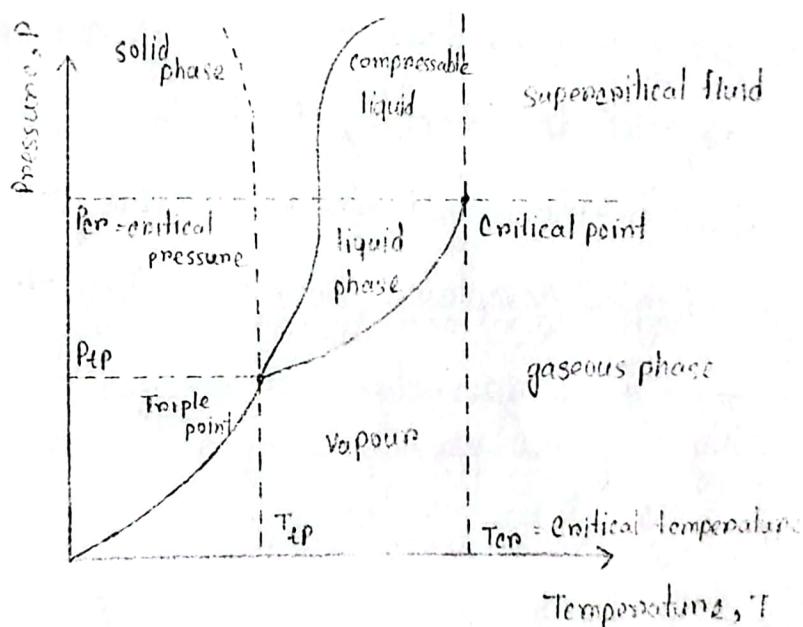


Fig.1 Phase diagram

Solid — liquid — Gas/Vapour  
[ Melting — Vapourising ]

## ■ Equilibrium between Liquid and its Vapour:

Applying Gibbs's potential ( $G_c$ ), it is possible to investigate the equilibrium between liquid and its vapour or between any two phases of a substance. Consider a closed system containing a liquid in equilibrium with its saturated vapour. The temperature and pressure are equal in both the phase. As each of the phases are in equilibrium, the temperature and pressure must remain constant throughout the phase and hence the thermodynamical coordinates  $V, S, U$  and  $G_c$  will be equal to the product of the specific value and the mass of the substance in that phase.

Let  $m_1$  and  $m_2$  are the masses in the liquid and vapour phases and  $g_1$  and  $g_2$  are the specific value of the Gibbs's potential in the two phases. Then for the whole system,

$$G_c = m_1 g_1 + m_2 g_2 \quad \text{--- (1)}$$

If a small quantity of liquid changes into vapour, differentiating equation (1)

$$\delta G_c = \delta m_1 g_1 + \delta m_2 g_2 \quad \text{--- (2)}$$

As the changes takes place at constant temperature and pressure, the process is isothermal and isobaric.

$$\therefore \delta G_c = 0$$

From equation (2),  $\delta m_1 g_1 + \delta m_2 g_2 = 0$

$$\Rightarrow \delta m_1 g_1 = - \delta m_2 g_2 \quad \text{--- (3)}$$

As it is a closed system mass is fixed,

$$dM = dm_1 + dm_2 = 0$$

$$\Rightarrow dm_1 = - dm_2 \quad \text{--- (4)}$$

From (3) and (4)

$$g_1 = g_2 \quad \text{--- (5)}$$

This shows that the thermodynamical potential per unit mass will be equal in two phases. Equation (5) is applicable to the process of evaporation, fusion and sublimation.

■ First order phase transitions :

■ Clausius-Clapeyron latent heat equation :

The changes of phase which take place at constant pressure and temperature 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 (or volume) change. The Gibbs function,  $G$ , remains constant

in both phases, while its derivative with respect to the temperature and pressure is discontinuous at transition point.

Consider an enclosure containing a liquid and its saturated vapour in equilibrium. If this system undergoes an isothermal isobaric changes, then

$$g_1 = g_2 \quad \dots \quad (1)$$

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

$$g_1 + dg_1 = g_2 + dg_2 \quad \dots \quad (2)$$

$$\Rightarrow dg_1 = dg_2 \quad \dots \quad (3)$$

If the condition of saturation is satisfied,

$$\left(\frac{dg_1}{dT}\right)_{sat} = \left(\frac{dg_2}{dT}\right)_{sat} \quad \dots \quad (4)$$

The pressure also changes from  $P$  to  $P + dP$ ,

$$dg_1 = \left(\frac{\partial g_1}{\partial T}\right)_P dT + \left(\frac{\partial g_1}{\partial P}\right)_T dP$$

$$\Rightarrow \left(\frac{\partial g_1}{\partial T}\right) = \left(\frac{\partial g_1}{\partial T}\right)_P + \left(\frac{\partial g_1}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right) \quad \dots \quad (5)$$

But for a unit mass,

$$dg = v dP + S dT \quad \dots \quad (6)$$

$$G = H - TS$$

$$\Delta G = \Delta U + PV - TS$$

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

$$= TdS - PdV + PdV -$$

$$vdP - SdT - TdS$$

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

Substituting these value in equation (5),

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

Similarly,

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

Substituting these value in equation (4),

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

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

$$\Rightarrow \left(\frac{\partial P}{\partial T}\right)_{sat} = \frac{s_2 - s_1}{v_2 - v_1} \quad \text{--- (6)}$$

$$\text{But } s_2 - s_1 = \frac{\delta Q}{T} = \frac{L}{T}$$

Here, L is latent heat of vapourization.

$$\frac{dP}{dT} = \frac{L}{T(v_2 - v_1)} \quad \text{--- (7)}$$

This is Clausius-Clapeyron latent heat equation, on this equation is first order phase transitions.

In this process, there is transference of heat and hence there is change in entropy and volume. Therefore a first order transitions 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 Gibbs function is the same in both phases at equilibrium.

### Graphical representation of changes -

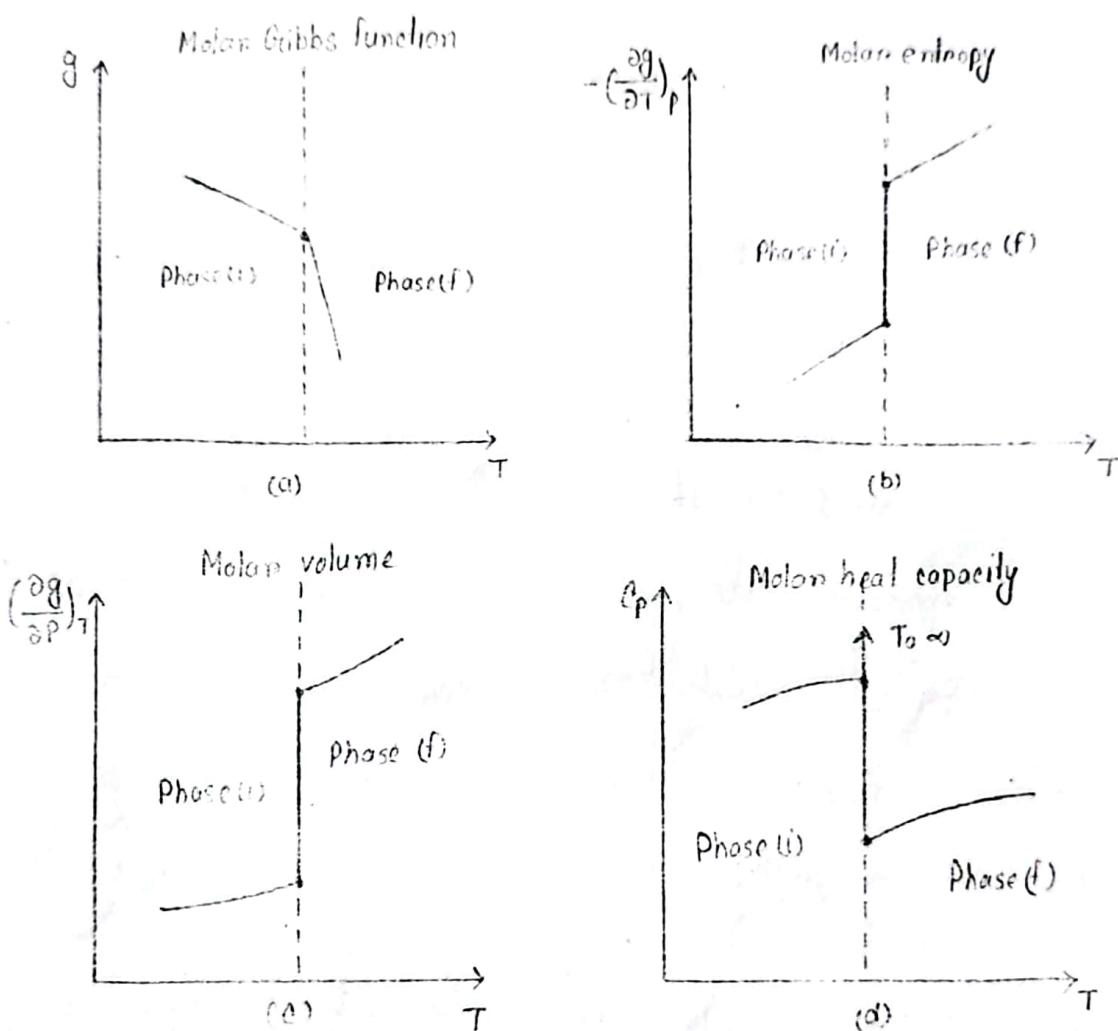


Fig.1. Characteristics of 1st order phase transition.

(a) Molar Gibbs function ; (b) Molar entropy ; (c) Molar volume ; (d) Molar heat capacity .

Examples:

When heat is given to water at  $100^{\circ}\text{C}$  and 1 atmospheric pressure, it changes from liquid to vapour state. The density of water is  $1000\text{ kg/m}^3$  while that of vapour is  $0.6\text{ kg/m}^3$ . Therefore, the transformation of water into vapor at constant temperature and volume is first order phase transitions. Similarly, the transformation of ice into water at  $0^{\circ}\text{C}$  and 1 atmospheric pressure is an example of first 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. Chemical potential can be expressed as following :

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

The thermodynamic identity is,

$$dU = TdS - PdV \quad \text{--- (1)}$$

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 same form. Suppose for a moment that the system consists of any one type of particles, and  $dn$  particles are added. Then equation (1) can be modified as,

$$dU = TdS - PdV + \mu dn \quad \text{---(2)}$$

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

$$\text{That is, } \mu = \left(\frac{\partial U}{\partial n}\right)_{S,V} \quad \text{---(3)}$$

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

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

$$F = U - TS$$

Differentiating,

$$\begin{aligned} dF &= dU - TdS - SdT \\ &= TdS - PdV - TdS - SdT \quad [\because dU = TdS - PdV] \\ \therefore dF &= -PdV - SdT \quad \text{---(1)} \end{aligned}$$

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

$$dF = -PdV - SdT + \mu dN$$

Therefore,

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

That is  $\mu$  is the increase of the Helmholtz free energy upon the addition of one particle under condition 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 from  $F$  in the expression for  $\mu$  in equation (Q)

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

(iii) Chemical potential and Gibbs function,  $G_f$ :

Chemical potential can be linked to the Gibbs function,  $G_f$

The equation is,

$$G_f = H - TS$$

$$\Rightarrow G_f = U + PV - TS \quad \text{--- (1)}$$

Differentiating,

$$dG_f = dU + PdV + VdP - Tds - SdT$$

$$\Rightarrow dG_c = TdS - PdV + PdV + VdP - TdS - SdT$$

$$\Rightarrow dG_c = VdP - SdT \quad \text{--- (2)}$$

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

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

Therefore,

$$\mu = \left( \frac{\partial G_c}{\partial N} \right)_{T, P} \quad \text{--- (3)}$$

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

(iv) Chemical potential and Enthalpy,  $H$ :

Chemical potential can be linked to the enthalpy,  $H$ .

The equation of enthalpy,

$$H = U + PV \quad \text{--- (4)}$$

Differentiating,

$$dH = dU + PdV + VdP \quad \text{--- (5)}$$

We know,

$$dQ = dU + PdV$$

$$\Rightarrow dU = dQ - dPV$$

$$\Rightarrow dU = TdS - PdV \quad \text{--- (6)}$$

From (2) and (3),

$$dH = TdS - PdV + PdV + VdP$$

$$\Rightarrow dH = TdS + VdP$$

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

$$dH = TdS + VdP + \mu dN$$

Therefore,

$$\mu = \left(\frac{\partial H}{\partial N}\right)_{S,P}$$

That is,  $\mu$  is the increase of enthalpy upon the addition of one particle under condition of constant  $S$  and  $P$ .

$[\mu = \left(\frac{\partial G_r}{\partial N}\right)_{P,T}$  are used in most case as it is easy to keep the pressure and temperature constant.]

## Chemical potential and phase equilibrium (Phase rule):

The internal energy of phase composed of  $k$  constituents rather than just one,

$$U = U(s, v, n_1, n_2, \dots, n_k) \quad \text{--- (1)}$$

where,  $n_i$  is the number of moles of the  $i$ th constituent present in the phase. From equation (1),

$$dU = \left(\frac{\partial U}{\partial s}\right)_{v,n} ds + \left(\frac{\partial U}{\partial v}\right)_{s,n} dv + \left(\frac{\partial U}{\partial n_1}\right)_{s,v,n'} dn_1 + \dots + \left(\frac{\partial U}{\partial n_k}\right)_{s,v,n'} dn_k \quad \text{--- (2)}$$

where, the subscript  $n'$  signifies that the number of moles of all constituents is constant except for the constituents appearing in the derivative. Then internal energy equation

$$dU = Tds - Pdv + \mu_1 dn_1 + \dots + \mu_k dn_k \quad \text{--- (3)}$$

where,  $\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{s,v,n'}$

The difference in the Gibbs function between two states at the same temperature and pressure for an open system of  $k$  constituents is,

$$\begin{aligned} \Delta G &= H - TS \\ &= U + PV - TS \Rightarrow dG = dU + Pdv + VdP - Tds - SdT \\ dG &= dU - Tds + Pdv \quad \text{--- (4)} \end{aligned}$$

same temperature  
and pressure  
 $\therefore dP = 0, dT = 0$

Comparing equation (3) and (4),

$$dG_c = \mu_1 dn_1 + \dots + \mu_k dn_k \quad (5)$$

and,  $\mu_i = \left(\frac{\partial G_c}{\partial n_i}\right)_{P, T, n'}$

Consider the phase to consist of two parts which are equal in every respect. If  $\Delta n_i$  moles of constituent  $i$  are added to each of the phases without changing the pressure or the temperature of either half, the pressure and the temperature of the whole phase do not change and we can write for each half,

$$\mu_i = \frac{\Delta G_c}{\Delta n_i}$$

For two halves,  $\mu_i = \frac{2\Delta G_c}{2n_i} = \frac{\Delta G_c}{n_i}$

Hence the chemical potential  $\mu$  is independent of the size of the phase. Now if we have a phase at temperature  $T$ , pressure  $P$ , and Gibbs function  $G_0$  and added mass which is at the same temperature and pressure,

$$G_c - G_0 = \mu_1 n_1 + \dots + \mu_k n_k \quad (6)$$

Therefore we can also write,

$$U = TS - PV + \mu_1 n_1 + \dots + \mu_k n_k + G_0,$$

$$H = TS + \mu_1 n_1 + \dots + \mu_k n_k + G_0,$$

$$F = -PV + \mu_1 n_1 + \dots + \mu_k n_k + G_0$$

————— (x)

We consider a closed system consisting of  $n$  phases and  $k$  constituents in equilibrium at constant temperature and pressure. A constituent will be designated by a subscript  $i = 1, 2, 3, \dots, k$  and a phase by a superscript  $(j) = 1, 2, 3, \dots, n$ ,

Thus the symbol  $\mu_i^{(2)}$  means the chemical potential of constituent  $i$  in phase  $2$ .

The Gibbs function of constituent  $i$  in phase  $j$  is the product of the chemical potential  $\mu_i^{(j)}$  of that constituent in phase  $j$  and the number of moles  $n_i^{(j)}$  of the constituent in phase  $j$ . The total gibbs function,

$$\sum_{i=1}^{i=k} \mu_i^{(j)} n_i^{(j)}$$

Finally the total Gibbs function of the entire system,

$$G_c = \sum_{j=1}^{j=n} \sum_{i=1}^{i=k} \mu_i^{(j)} n_i^{(j)}$$

$$dG_c = \sum_{j=1}^{j=n} \sum_{i=1}^{i=k} \mu_i^{(j)} dn_i^{(j)}$$

In equilibrium state,  $dG_{c,T,p} = 0$

$$\therefore dG_c = \sum_{j=1}^{j=n} \sum_{i=1}^{i=k} \mu_i^{(j)} dn_i^{(j)} = 0 \quad \text{--- (8)}$$

where any  $d\eta_i^{(j)}$  represents the small difference in the number of moles of constituent  $i$  in phase  $j$ . So, From (8),

$$\begin{aligned}
 & \mu_1^{(1)} d\eta_1^{(1)} + \mu_1^{(2)} d\eta_1^{(2)} + \dots + \mu_1^{(n)} d\eta_1^{(n)} \\
 & + \mu_2^{(1)} d\eta_2^{(1)} + \mu_2^{(2)} d\eta_2^{(2)} + \dots + \mu_2^{(n)} d\eta_2^{(n)} \\
 & \vdots \\
 & + \mu_k^{(1)} d\eta_k^{(1)} + \mu_k^{(2)} d\eta_k^{(2)} + \dots + \mu_k^{(n)} d\eta_k^{(n)} = 0
 \end{aligned} \tag{9}$$

The differentials  $d\eta_i^{(j)}$  are not independent ; but,

$$\begin{aligned}
 d\eta_1^{(1)} + d\eta_1^{(2)} + \dots + d\eta_1^{(n)} &= 0 \\
 d\eta_2^{(1)} + d\eta_2^{(2)} + \dots + d\eta_2^{(n)} &= 0 \\
 \vdots & \\
 d\eta_k^{(1)} + d\eta_k^{(2)} + \dots + d\eta_k^{(n)} &= 0
 \end{aligned} \tag{10}$$

To find the solution of equation (9) the value of  $d\eta_i^{(1)}$  obtained from equation (10) is substituted into the corresponding lines of equation (9). The first line of equation (9) becomes,

$$\begin{aligned}
 -\mu_1^{(1)} (d\eta_1^{(2)} + d\eta_1^{(3)} + \dots + d\eta_1^{(n)}) + \mu_1^{(2)} d\eta_1^{(2)} + \dots \\
 + \mu_1^{(n)} d\eta_1^{(n)}
 \end{aligned}$$

which can be written as,

$$\{\mu_1^{(2)} - \mu_1^{(1)}\} dn_1^{(2)} + \{\mu_1^{(3)} - \mu_1^{(1)}\} dn_1^{(3)} + \dots + \{\mu_1^{(n)} - \mu_1^{(1)}\} dn_1^{(n)}$$

Similar expression can be written for each line. each of these remaining  $dn_i^{(j)}$  is independent and can be varied arbitrarily.

From the upper equation we obtain,

$$\mu_1^{(2)} = \mu_1^{(1)}, \mu_1^{(3)} = \mu_1^{(1)}, \dots, \mu_1^{(n)} = \mu_1^{(1)};$$

that is the chemical potential of this constituent must have the same value in all phase. Continuing the procedure for each constituent gives the result that the chemical potential of each constituent must have the same value in all phases,

$$\mu_1^{(1)} = \mu_1^{(2)} = \dots = \mu_1^{(n)}$$

$$\mu_2^{(1)} = \mu_2^{(2)} = \dots = \mu_2^{(n)}$$

$$\vdots$$

$$\mu_k^{(1)} = \mu_k^{(2)} = \dots = \mu_k^{(n)}$$

If this is the case we can omit the subscripts in the preceding equations and simply write  $\mu_1, \mu_2, \dots$  etc. for the chemical potentials. The first line becomes,

$$\mu_1 \{ d\eta_1^{(1)} + d\eta_1^{(2)} + \dots + d\eta_1^{(n)} \}$$

which from the first of the condition equations equal to zero. This is true for every other constituent and equation (8) is satisfied.

Equation (11) which specify the conditions of phase equilibrium and which will be called the equations of phase equilibrium are  $n(n-1)$  in number. Now the composition of each phase containing  $k$  constituents is fixed if  $k-1$  constituents are known, since the sum of the mole fractions of each constituent in the phase must equal unity. Therefore, for  $n$  phases, there are total of  $n(k-1)$  variables, in addition to temperature and pressure, which must be specified. There are then  $n(k-1)+2$  variables altogether.

In general, the variance  $f$  is defined as the excess of the number of variables over the number of equations, and

$$f = [n(k-1) + 2] - [k(n-1)]$$

$$\Rightarrow f = k-n+2 \quad [\text{no chemical reaction}] \quad (12)$$

This equation is called the Gibbs phase rule.

Examples -

Consider liquid water in equilibrium with its vapor. There is only one constituent ( $\text{H}_2\text{O}$ ) and  $k=1$ . There are two phases  $n=2$ , and the number of equations of phase equilibrium is,

$$k(n-1)=1$$

The number of variables,  $n(k-1)+2=2$

These variables are the pressure and temperature, the chemical potential  $\mu$  has the same value for both phases.

The variance  $f$  is therefore,

$$f = k-n+2 = 1$$

which means that an arbitrary value can be assigned to either the temperature  $T$  or the pressure  $P$ , but not the both. The system is called monovariant.

At the triple point of water, all three phases are in equilibrium and  $n=3$ . Then,  $k(n-1)=2$  and there are two equations of phase equilibrium stating that the chemical potential in any one phase is equal to its value in each of the other phases. The number of variables is  $n(k-1)+2=2$  which is equal to the number of equations. The variance is,

$$f = k-n+2 = 0,$$

and therefore the system is invariant.

### Q) Third law of thermodynamics :

The principle known as the third law of thermodynamics governs the behaviour of systems, which are in internal equilibrium, as their temperature approaches absolute zero.

Gibbs function equation in term of enthalpy,

$$G_c = H - TS$$

Using .  $S = -\left(\frac{\partial G_c}{\partial T}\right)_P$

$$\therefore G_c = H + T\left(\frac{\partial G_c}{\partial T}\right)_P$$

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

This is called the Gibbs-Helmholtz equation.

Thus the change in enthalpy and the change in Gibbs function are equal only when  $T\left(\frac{\partial \Delta G_c}{\partial T}\right)_P$  approaches zero.

From (1)

$$\Delta G_c = \Delta H + T \left\{ \frac{\partial(G_{c2} - G_{c1})}{\partial T} \right\}_P \quad \text{--- (2)}$$

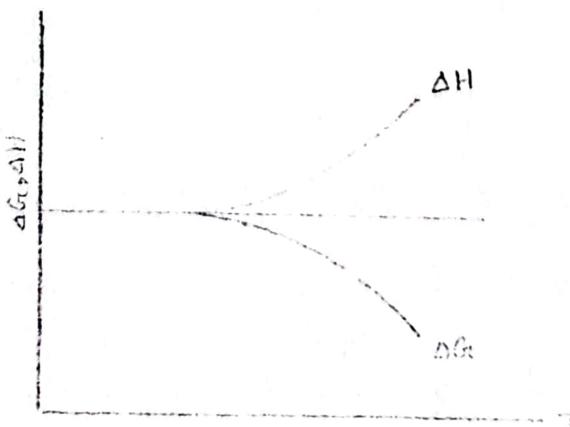


Fig.1 The temperature dependence of the change in the gibbs function and in the enthalpy for an isobaric process.

Nernst noted from the results of the experiments that in a reaction  $\Delta G_c$  generally approached  $\Delta H$  more closely as the temperature was reduced, even at quite high temperatures. In 1906, he therefore proposed as a general principle that as the temperature approached zero, not only did  $\Delta G_c$  and  $\Delta H$  approach equality, but their rates of change with temperature both approached zero. That is,

$$\lim_{T \rightarrow 0} \left( \frac{\partial \Delta G_c}{\partial T} \right)_P = 0, \quad \lim_{T \rightarrow 0} \left( \frac{\partial \Delta H}{\partial T} \right)_P = 0$$

This means that the graphs of  $\Delta G_c$  and  $\Delta H$  as a function of  $T$  both have the same horizontal tangent at  $T=0$ .

From (2),

$$\lim_{T \rightarrow 0} \left\{ \frac{\partial (G_{T_2} - G_{T_1})}{\partial T} \right\}_P = \lim_{T \rightarrow 0} \left[ \left( \frac{\partial G_T}{\partial T} \right)_P - \left( \frac{\partial G_{T_1}}{\partial T} \right)_P \right] = 0$$

But  $\left( \frac{\partial G_T}{\partial T} \right)_P = -S$  then,

$$\lim_{T \rightarrow 0} (S_2 - S_1) = 0 \quad \text{--- (3)} \quad (\cancel{S_1} - \cancel{S_2})$$

This is the Nernst heat theorem.

Statement:

"In the neighbourhood of absolute zero, all reactions in a liquid or solid in internal equilibrium take place with no change in entropy."

Planck, in 1911, made the further hypothesis that not only does the entropy difference vanish as  $T \rightarrow 0$ ,

"The entropy of every solid or liquid substance in internal equilibrium at absolute zero is itself zero."

that is,

$$\lim_{T \rightarrow 0} S = 0$$

This is known as the third law of thermodynamics.

#### ⇒ Thermal death of universe :

In the universe the natural processes that are taking place such as flow of heat, conduction, radiation, mixing, diffusion and so on are all irreversible and in these processes, the system tends to have maximum value of entropy by attaining a uniform state of temperature, pressure, composition etc. Therefore we conclude that the entire universe would attain a state of absolute uniformity at some distant future. In such a state all physical, chemical and biological processes would stop, although

there would be no change in the total energy of the universe. As there will be no temperature differences, it will not be possible to convert any amount of heat into even a small amount of useful work. This means that we are heading towards the Heat death of the universe from thermal death. This state being inevitably approached, although it may take millions of billions of years.

