imp Q

Chapter-10: Thermodynamics Relation

Maxwell thermodynamic Relation.

There are four thermodynamics variables P, V, T and entropy (S) to study the thermodynamics state of a system. Out of this four variables, two are independent and other two can be expressed as some function of the two independent variables.

For the complete knowledge of thermodynamic state of any system we can devise some relations connecting these four variables. The relations so obtain are called thermodynamic relation and functions define are called thermodynamic functions or thermodynamic potential. Principle of thermodynamic potential are as follows:

1. Internal energy :- We have first law of thermodynamics the internal energy associated to any system is given by $du = dq - dw$

or, $du = dq - Pdv \longrightarrow (1)$

Similarly, from II-law of thermodynamics

$$ds = \frac{dQ}{T} \qquad \therefore dq = Tds.$$

$$\therefore du = Tds - Pdv \longrightarrow (2)$$

From equation (2), it is seen that the variables S & V are independent and the function U is expressed in terms of P, S, T and V. Since S and V are independent variables of U, taking partial derivation, we have

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

$$\left(\frac{\partial U}{\partial V}\right)_S = -p \longrightarrow (3)$$

Since the internal energy is the path independent function, it is perfect differential. For U (S, V) to be perfect differential,

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

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V \longrightarrow (4)$$

Which is the first thermodynamic relation of Maxwell.

2 Helmholtz's free energy :- To define this function we start from the combined form of I and II law of thermodynamics

i.e. $dU = TdS - pdV \longrightarrow (1)$

If the thermodynamic system exchanges heat such that the temperature becomes steady. we must have, $TdS = d(TS) \longrightarrow (2)$

Then eq^n (2) reducas to....

$Du = d(TS) - pdV$

or, $d(U-TS) = -pdV$.

or, $dF = -pdV = -dW \longrightarrow (3)$

Where, $F = U - TS$ is called the Helmholtz's function from eq^n (3) it is seen that the decrease in Helmholtz's function is equal to the amount of work done by the system. So the function 'F' is also called work function.

Now, $F = U - Ts$

$\therefore dF = dU - d(TS)$

Using I we get

$dF = Tds - Pdv - sdT - Tds$

$\therefore dF = -pdV - sdT \longrightarrow (4)$

From eq^n (4) the Helmholtz's free energy has two independent variables V and T. It is also expressed in terms of four fundamental variables (P, V, T & S).

Taking partial derivatives, we have

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

$\left(\frac{\partial F}{\partial T}\right)_V = -S \longrightarrow (5)$

The function $F = U - TS$ is also a state function then we must have the condition of perfect

perfect differential is

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

Using eqn. (5), we get

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

$$\therefore \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \longrightarrow (6)$$

Which is the second thermodynamic relation of maxwell.

3. **Enthalpy** :- The enthalpy of any thermodynamic system is denoted by 'H' and is given by

$$H = U + PV \longrightarrow (1)$$

Where U be the internal energy.

On differentiation, we get

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

$$dH = dU + pdV + Vdp \longrightarrow (2)$$

Now, the combined from I and II laws of thermodynamics gives

$$dU = Tds - PdV \longrightarrow (3)$$

From equation (2) and (3),

$$dH = Tds - pdV + pdV + Vdp$$

$$dH = Tds + Vdp \longrightarrow (4)$$

From eqⁿ. (4) S and p are independent variables for dH.

Now taking partial derivation, we have,

$$\left(\frac{\partial H}{\partial S}\right)_p = T \text{ and}$$

$$\left(\frac{\partial H}{\partial p}\right)_s = V \longrightarrow (5).$$

For dH to be perfect differential the conditions is

$$\left[\frac{\partial}{\partial S}\left(\frac{\partial H}{\partial p}\right)_s\right]_p = \left[\frac{\partial}{\partial p}\left(\frac{\partial H}{\partial S}\right)_p\right]_s$$

Using eqⁿ. (5), we get

$$\left(\frac{\partial V}{\partial S}\right)_p = \left(\frac{\partial T}{\partial p}\right)_S \longrightarrow (6)$$

This is the 3rd thermodynamic relation of maxwell.

4. Gibb's Function :-

From defination of enthalpy,

$$H = U + PV$$

On differentiating, we get

$$dH = dU + pdV + Vdp$$

But $dU = Tds - pdV$

Then,

$dH = Tds - pdv + pdv + vdp$

$\therefore dH = Tds + vdp$

If the system exchanges heat in such a way that it attains the steady value of temperature, we must have

$Tds = d(TS)$

Then, $d(H - TS) = Vdp$

or, $dG = Vdp \longrightarrow (2)$

Where $G = H - TS$ in the Gibb's function from eq^n. (2), at isobaric condition,

$dG = 0 \quad \therefore G = \text{constant}$

Now, $G = H - TS$

$= U + PV - TS$

$= Tds - pdv + pdv + vdp - Tds - sdT$

$\therefore dG = Vdp - SdT \longrightarrow (3)$

From eq^n. (3), P and T are independent variables for dG. Therefore the partial derivative are

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

$\left(\frac{\partial G}{\partial P}\right)_T = V \longrightarrow (4)$

Since dG is perfect differential, we must have

$$\left[\frac{\partial}{\partial p}\left(\frac{\partial G}{\partial P}\right)_p\right]_T = \left[\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial p}\right)_T\right]_p$$

Using eqn. (4), we get

$$-\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p \longrightarrow (5)$$

This is forth thermodynamic relation of maxwell.

Clausius clapeyron's latent heat equation

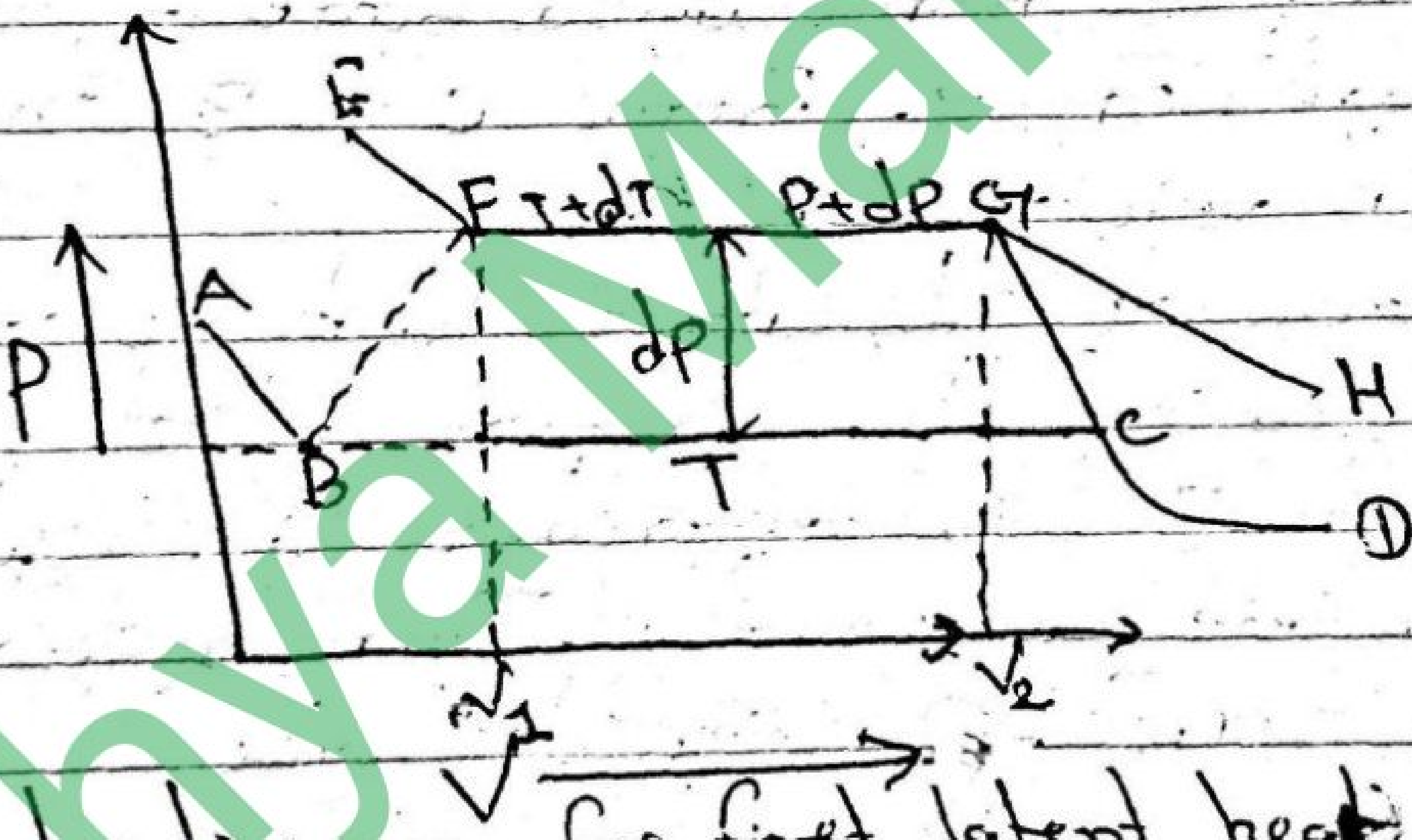

Fig :- Indicator diagram for first latent heat eqn.

The melting point and boiling point have got a specific value at specific pressure and vice-versa. There is a relation showing how melting point and boiling point vary with pressure by applying the second law of thermodynamics. This relation is known as clausius clapeyron's eqn. or first latent heat eqn.

Let ABCD and EFGH represents the two isothermals at close temp^{re}. T and T+dT resp. Let P and P+dP be the saturated vapour pressure of liquid at liquid at temperature T and T+dT respectively. Let V_1 and V_2 be the volume of substances at F and G resp.

The amount of heat Q_1 absorbed along FG is equal to the latent heat of vaporisation (L+dL) at temperature (T+dT) as the liquid changing from liquid state F to the vapour state of G. From C to B, the amount of heat rejected is Q_2.
Here, $Q_2 = L$, latent heat at temp^r T. By increasing the pressure a little, the original point F is restored. So the cycle FGCBF is completely reversible. Then, applying the principle of carnot's reversible cycle,

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

$$\frac{Q_1}{Q_2} - 1 = \frac{T_1}{T_2} - 1$$

$$\frac{Q_1 - Q_2}{Q_2} = \frac{T_1 - T_2}{T_2} \longrightarrow (1)$$

We have

$Q_1 = L + dL$

$Q_2 = L$

$T_1 = T + dT$

$T_2 = T$

Then eq^n.(1) becomes

or, $\frac{Q_1 - Q_2}{Q_2} = \frac{T + dT - T}{T}$

or, $\frac{L + dL - L}{L} = \frac{T + dT - T}{T}$

or, $\frac{dL}{L} = \frac{dT}{T} \longrightarrow (2)$

The amount of heat converted into work during cycle FGCBF

$Q_1 - Q_2 = dL$

But the work done during carnot cycle is given by the area FGCBF i.e.

$dL = FG \times$ perp. distance between FG and CB

$= (V_2 - V_1)\, dP$

Then eq^n.(2) becomes,

$\frac{(V_2 - V_1)\, dP}{L} = \frac{dT}{T}$

$\therefore \frac{dP}{dT} = \frac{L}{T(V_2 - V_1)} \longrightarrow (5)$

This is I-latent heat eq^n.

Applications

1. **Effect of pressure on boiling point of liquid:**
When a liquid boils $V_2 > V_1$ or $V_2 - V_1$ is the positive. The $\frac{dP}{dT}$ is positive, means the boiling point of liquid rises with increase in pressure and vice-versa.

2. **Effect of pressure on melting point of solid**
When a solid melts, there may be an increase in volume as in the case of certain substances like wax sulphur etc. or there may be decrease in volume as in the case of ice, bismuth etc.

a. When $V_2 > V_1$ (wax), $\frac{dP}{dT}$ is +ve quantity. This means the melting point of such substance rises with increase in pressure.

b. When $V_2 < V_1$ (ice), $V_2 - V_1$ is -ve quantity. Hence $\frac{dP}{dT}$ is also -ve which means melting point of such substance decreases with increase in pressure.

First and second latent heat equation

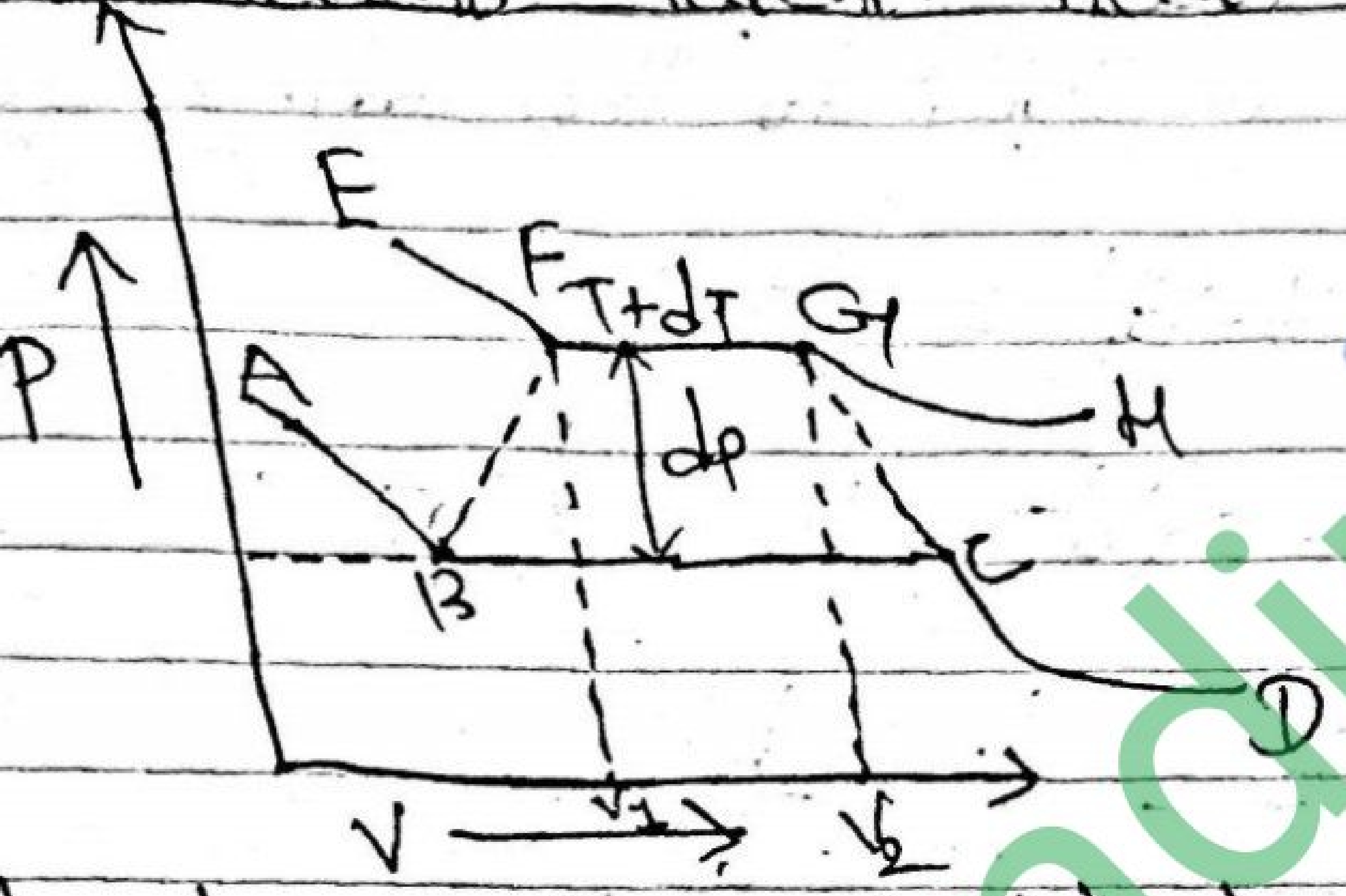

fig: Indicator diagram for second latent eqn.

Suppose 1gm of substance is taken round the cycle BFGCB. The quantity of heat absorbed by the substance in passing from B to F, when its temp. rises by dT is C_1dT. So passing along FG when substance changes from liquid to vapour at constant temp. T+dT. It absorbs a quantity of heat L+dL in passing from G to e.

The temp. of substance falls by dT and hence it gives out a quantity of heat C_2dT, while in passing along CB when it condenses from vapour to liquid at constant temperature T gives out a quantity of heat L.

∴ The total amount of heat absorbed during cycle is

$C_1dT + L + dL - C_2dT - L = (C_1 - C_2)dT + dL$

This must be equal to workdone which is which is equal to the area of cycle,

$$dp(V_2-V_1) = \frac{L}{T}dT$$

$$\therefore (C_1-C_2)dT + dL = \frac{L}{T}dT$$

$$C_1-C_2 = \frac{L}{T} - \frac{dL}{dT}$$

or, $$\boxed{C_2-C_1 = \frac{dL}{dT} - \frac{L}{T}}$$

This is 2nd latent heat equation of clausius.

Clausis clapeyron's eqn from maxwell's Thermodynamic Relation

Consider maxwell's second thermodynamic relation,

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

Multiply both side by T, we get

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

But Tds = dQ (from 2nd law of thermodynamics)

$$\therefore \left(\frac{\partial Q}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V \longrightarrow (I)$$

Consider unit mass of substance, Let 'L' be the latent heat when the substance changes in volume from V_1 to V_2 at constant temp, then

$\partial Q = L$, $\partial V = V_2 - V_1$ then

$$\left(\frac{L}{V_2-V_1}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V$$

or $$\frac{L}{V_2-V_1} = T\frac{\partial P}{\partial T}$$

$$\therefore \frac{dP}{dT} = \frac{L}{T(V_2-V_1)}$$

This is clausis's claypeyron's equation.