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B-1 (H), Paper II.

Maxwell's Thermodynamical Relations.

Q:- Derive Maxwell's thermodynamical relations and prove that

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

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

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

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

Ans:- Maxwell's thermodynamical relations can be deduced by making use of the first and second law of thermodynamics.

First law:- If a substance absorbs a very small amount of heat dQ at a constant pressure, then part of this heat is used up to raise the temperature which results in the increase of internal energy du. The rest of the heat is used in doing work allowing the substance to increase in volume by an amount dv against the external pressure P. Thus according to the first law, we have

$$dQ = du + Pdv$$

or $$du = dQ - Pdv \quad \text{——} \quad (1)$$

<u>Second law</u> :- If a substance absorbs a very small amount of heat dQ at a temperature T and if all the changes that it undergoes are perfectly reversible, then the changes in intropy ds is equal to $\frac{dQ}{T}$

or $$dQ = Tds$$

Substituting the value of dQ in eqn. (i) we have

$$du = Tds - Pdv \quad \text{——} \quad (11)$$

The thermodynamical state of any system is defined by the varibles T, S, P and v. All these variables are not independent. If any two of them are known the others can be found out. Example :- the internal energy u is completely known if the volume v and the temperature T are given.

Perfect differential :- The change in internal energy du brought about by changeng v and T is the same whether we first make the change dv in v and then the change dT in T or in the reverse order. Mathematically this is expressed by sayeng that du is a perfect differential.

If u is a function of two independent variables x and y (x and y may be any two of the quantities T, S, P and v.), then du is a perfect differential, if

$$\left[\frac{\partial}{\partial x}\left(\frac{\partial u}{\partial y}\right)_x\right]_y = \left[\frac{\partial}{\partial y}\left(\frac{\partial u}{\partial x}\right)_y\right]_x$$