Maxwell's Thermodynamic Equations

For deriving the Maxwell's thermodynamic equations we need to know the meaning of "hydrostatic system .

Hydrostatic system

A gas taken in a cylinder is an example of hydrostatic system. Not only pure gas, but a pure substance in the form of solid, a liquid, homogeneous mixture of inert gases, are also examples of hydrostatic system. So a hydrostatic system means any system of constant mass which exerts on the surrounding a uniform hydrostatic pressure in the absence of surface, gravitational, electric and magnetic forces. The equilibrium states of hydrostatic system can be specified using three thermodynamic coordinates the pressure exerted by the system on the surroundings P, the volume V, and T the absolute temperature.

Derivation of Maxwell's Equations

The four thermodynamic functions or potentials are

I) the internal energy function U

II) the enthalpy $H = U+PV$

III) the Helmholtz function $F = U - TS$

IV) the Gibbs function $G = H - TS$

Any one of these can be expressed as a function of any two of P, V and T.

Let U be a function of V & T and S be a function of V and T

i . e ,

$$U = U(V,T) \quad (1)$$

$$S = S(V,T) \quad (2)$$

We can solve (2) and express the value of temperature T in terms of S and V. substituting the value of T in equation (1), we get an equation for U in terms of V and S.

$$U = U(V, S) \qquad (3)$$

Similarly we can express any of the eight quantities P, V, T ,S ,U , H, and F and G as a function of any two other quantities.

Consider a hydrostatic system undergoing an infinitesimal reversible process from one equilibrium state to another.

I) The change in internal energy of the system is dU

$$dU = dQ - PdV$$

$$= TdS - PdV \qquad (4)$$

Here U, T and P are the functions of S and V.

II) The change in enthalpy of the system is dH

$$dH = dU + PdV + VdP$$

$$= TdS + VdP \qquad (5)$$

H, T and V are functions of S and P.

III) The change in Helmholtz function is dF.

$$dF = dU - TdS - SdT$$

$$= - SdT - PdV \qquad (6)$$

IV) The change in Gibbs function is dG.

$$dG = dH - TdS - SdT$$

$$= -SdT + VdP \qquad (7)$$

Here G, S and V are functions of T and P.

The differentials of U, H, F and G should be exact differentials because these quantities are actual functions. In general these differentials should be of the form,

$$dz = Mdx + Ndy$$

Where z, M, N are all functions of x and y.

Hence $\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$

Let us apply this result to the four exact differentials dU , dH, dF , and dG. Then we get the following relations.

1. dU = TdS - PdV . Hence $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_v$ (8)

2. dH = TdS + VdP. Hence $\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$ (9)

3. dF = - SdT - PdV. Hence $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v$ (10)

4. dG = -SdT + VdP. Hence $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$ (11)

These equations (8) , (9), (10), (11) are called Maxwell's relations.