Maxwell thermodynamic Relations

The various expressions connecting internal energy (U) enthalpy (H), Helmholtz free energy (A) and Gibbs free energy (G) with relevant parameters such as P, T, and V may put as.

$$dU = TdS - PdV \quad \text{——(i)}$$
$$dH = TdS + VdP \quad \text{——(ii)}$$
$$dA = -SdT - PdV \quad \text{——(iii)}$$
$$dG = -SdT + VdP \quad \text{——(iv)}$$

Maxwell thermodynamic Relations

Taking eqn $dU = T.dS - PdV$

If V is constant so, $dV = 0$

then $dU = TdS$.

$$\text{or} \left(\frac{\partial U}{\partial S}\right)_V = T \quad \text{——— (1)}$$

Again eqn $dU = TdS - PdV$

If S is constant, $dS = 0$

$dU = -PdV$

$$\text{or} \left(\frac{\partial U}{\partial V}\right)_S = -P \quad \text{——— (2)}$$

Differentiating eqn ① with respect to V, where S is constant.

$$\frac{\partial^2 U}{(\partial S)_V (\partial V)_S} = \left(\frac{\partial T}{\partial V}\right)_S \quad \text{——— (3)}$$

Again Differentiating eqn ② w.r.to S, where V is constant.

$$\frac{\partial^2 U}{(\partial V)_S (\partial S)_V} = -\left(\frac{\partial P}{\partial S}\right)_V \quad \text{—— (4)}$$

from equation ③ and equation ④

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \quad \text{—— (5)}$$

This eqn ⑤ is Maxwell Relation.

— x —

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

2nd Relation

We know, $dH = TdS + VdP$

If P is constant, $dP = 0$

$$dH = TdS$$

$$\text{or } \left(\frac{\partial H}{\partial S}\right)_P = T \quad \text{———} \quad (1)$$

If S is constant, $dS = 0$

from eqn $dH = TdS + VdP$

$$\left(\frac{\partial H}{\partial P}\right)_S = V \quad \text{———} \quad (2)$$

On differentiating eqn (1) w.r.t. P where S is constant

$$\frac{\partial^2 H}{(\partial S)_P (\partial P)_S} = \left(\frac{\partial T}{\partial P}\right)_S \quad \text{———} \quad (3)$$

And eqn (2) is differentiating w.r.t. S where P is constant

$$\frac{\partial^2 H}{(\partial P)_S (\partial S)_P} = \left(\frac{\partial V}{\partial S}\right)_P \quad \text{———} \quad (4)$$

From equation (3) and equation (4), we have.

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \quad \text{———} \quad (5)$$

The above equation (5) is also Maxwell relation.