S. S. College. Jehanabad (Magadh University)

Department : Physics

Subject : Thermodynamics

Class : B.Sc(H) Physics Part I

Topic: Application of Maxwell's Thermodynamical Relation

Teacher : M. K. Singh

- Using Maxwell's thermodynamical relations, To show that

$$\left(\frac{\partial C_V}{\partial V}\right) = T\left(\frac{\partial^2 S}{\partial V.\partial T}\right) = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V$$

From Maxwell's relation we have

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad \text{…….. (i)}$$

Differentiating equation *(i)* with respect to temperature we have

$$\left(\frac{\partial^2 S}{\partial T.\partial V}\right) = \left(\frac{\partial^2 P}{\partial T^2}\right)_V \quad \text{…… (ii)}$$

We know that

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V \quad \text{…….. (iii)}$$

Differentiating equation *(iii)* with respect to volume we have

$$\left(\frac{\partial C_V}{\partial V}\right) = T\left(\frac{\partial^2 S}{\partial T.\partial V}\right) \quad \text{…… (iv)}$$

From equation *(ii)* and *(iv) we have*

$$\left(\frac{\partial C_V}{\partial V}\right) = T\left(\frac{\partial^2 S}{\partial T.\partial V}\right)$$

$$= T\left(\frac{\partial^2 P}{\partial T^2}\right)_V \quad \text{…….. (v)}$$

- Using Maxwell's thermodynamical relations, To show that

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

Sol. From Maxwell's relations we have

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

Differentiating equation *(i)* with respect to temperature we get

$$\left(\frac{\partial^2 S}{\partial T.\partial P}\right) = -\left(\frac{\partial^2 V}{\partial T}\right)_P \quad \text{..... (ii)}$$

We know that

$$C_P = T\left(\frac{\partial S}{\partial T}\right)_P \quad \text{..... (iii)}$$

Differentiating equation *(iii)* with respect to pressure we get

$$\left(\frac{\partial C_P}{\partial P}\right) = T\left(\frac{\partial^2 S}{\partial T \partial P}\right) \quad \text{..... (iv)}$$

From equations *(ii)* and *(iv) we get*

$$\left(\frac{\partial C_P}{\partial P}\right) = T\left(\frac{\partial^2 S}{\partial T \partial P}\right) \quad \text{..... (v)}$$

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