S. S. College. Jehanabad (Magadh University)

Department : Physics

Subject : Quantum Mechanics

Class : B.Sc(H) Physics Part III

Topic: Maxwell's Thermodynamical Relations.

Teacher : M. K. Singh

Maxwell's Thermodynamical Relations

First Relation

Putting $x = S$ and $y = V$ in equation (5), we get

$$\frac{\partial S}{\partial x} = 1,$$

$$\frac{\partial V}{\partial y} = 1$$

and

$$\frac{\partial S}{\partial y} = 0,$$

$$\frac{\partial V}{\partial x} = 0$$

Substituting in equation (5), we have

$$\left(\frac{\partial T}{\partial y}\right)_x = -\left(\frac{\partial P}{\partial x}\right)_y$$

$\partial y = \partial V$ (as $y = V$) and $\partial s = \partial S$ (as $x = S$). Hence

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \quad \text{…….. (6)}$$

This is the Maxwell's first thermodynamical relation.

The first relation tells us that for a thermodynamic system, increase in temperature per unit increase in volume at constant entropy is equal to the decrease in pressure per unit increase in entropy at constant volume.

Second Relation

We get the second relation by putting $x = T$ and $y = V$ in equation (5),

then

$$\frac{\partial T}{\partial x} = 1,$$

$$\frac{\partial V}{\partial y} = 1$$

and

$$\frac{\partial T}{\partial y} = 0,$$

$$\frac{\partial V}{\partial x} = 0$$

Substituting in equation (5), we have

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad \text{..... (7)}$$

This is the Maxwell's second thermodynamical relation.

This relation tells us that increase in entropy per unit increase in volume at constant temperature is equal to increase in pressure per unit increase in temperature at constant volume.

Third Relation

By putting $x = S$ and $y = P$, in equation (5) we get

$$\frac{\partial S}{\partial x} = 1,$$

$$\frac{\partial P}{\partial y} = 1,$$

$$\frac{\partial S}{\partial y} = 0$$

$$\frac{\partial P}{\partial x} = 0$$

Substituting these in equation (5), we have

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \quad \text{…….. (8)}$$

This is the Maxwell's third thermodynamical relation.

The third relation tells us that increase in temperature per unit increase in pressure at constant entropy is equal to the increase in volume per unit increase in entropy at constant pressure.