S. S. College. Jehanabad (Magadh University)

Department : Physics

Subject : Thermodynamics

Class : B.Sc(H) Physics Part I

Topic: Application of Maxwell's Thermodynamical Relation

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- To show that for a perfect gas

$$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

Sol. From the Maxwell's first equation we have

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

$$\frac{1}{T}\left(\frac{\partial Q}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

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

From first law of thermodynamics

$$dQ = dU + PdV$$

Substituting in the above equation we have

$$\left(\frac{dU + PdV}{dV}\right) = T\left(\frac{\partial P}{\partial T}\right)_V$$

$$\frac{dU}{dV} + P = T\left(\frac{\partial P}{\partial T}\right)_V$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

from perfect gas equation we have

$$PV = RT$$

Using the perfect gas equation, we get

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V}$$

We get

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{R}{V}\right) - P$$

$$\left(\frac{\partial U}{\partial V}\right)_T = P - P$$

$$= 0$$

$$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

- To Prove the thermodynamical relation

$$\left(\frac{\partial Q}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P = -TV\alpha$$

show that heat is generated when a substance which expands on heating is compressed and for substance which contracts cooling takes place

Sol. From Maxwell's fourth thermodynamical relation we have

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

Multiplying both sides by T, we have

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

We know

$T.\partial S = \partial Q$, substituting we get

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

this is the required relation.

$\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$ represents the increase in volume per unit rise of temperature at constant pressure. This is called the coefficient of volume expansion and is represented by α.

$$\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \alpha$$

$$\left(\frac{\partial V}{\partial T}\right)_P = V\alpha \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(ii)}$$

Substituting this in eqn. *(i)*, we get

$$\left(\frac{\partial Q}{\partial P}\right)_T = -TV\alpha \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(iii)}$$

This is another form of the required relation.

From this equation it is clear that if α is positive *.ie.* if the substance expands on heating then $\left(\frac{\partial Q}{\partial P}\right)_T$ will be negative. It means heat must be withdrawn from the substance in order to keep the temperature constant when the pressure is increased. We can say that increase in pressure heats a body that expands on rise of temperature.

if α is negative which means that the substance contracts on heating, then $\left(\frac{\partial Q}{\partial P}\right)_T$ will be positive i.e. heat must be added to keep its temperature constant, when the pressure increases i.e., cooling is produced when a substance, which contracts on heating, suddenly compresses.