B-1 (H), Paper II

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Maxwell's Thermodynamical Relations

[Continued ---]

(1) Maxwell's first thermodynamical relⁿs.

Let us take the volume v and entropy S as independent variables, then

$$S = x \text{ and } v = y$$

$$\therefore \frac{\partial S}{\partial x} = 1 \text{ and } \frac{\partial V}{\partial y} = 1 \text{ also}$$

$$\frac{\partial S}{\partial y} = 0 \text{ and } \frac{\partial V}{\partial x} = 0$$

Substituting these values in (vii), we get

$$\left(\frac{\partial T}{\partial x}\right)_y \left(\frac{\partial S}{\partial y}\right)_x = 0 \text{ and } \left(\frac{\partial P}{\partial y}\right)_x \left(\frac{\partial V}{\partial x}\right)_y = 0$$

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

Replacing y by v and x by s, we have

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

This is known as Maxwell's first thermodynamical relation.

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(ii) Maxwell's second thermodynamical relation.

Let us take the temperature T and volume v as independent variables, then -

$$T = x \quad \text{and} \quad v = y$$

$$\left(\frac{\partial T}{\partial y}\right)_x = 1 \quad \text{and} \quad \frac{\partial v}{\partial y} = 1$$

$$\text{also} \quad \frac{\partial T}{\partial y} = 0 \quad \text{and} \quad \frac{\partial v}{\partial x} = 0$$

Substituting these values in (vii), we have

$$\left(\frac{\partial T}{\partial y}\right)_x \left(\frac{\partial S}{\partial x}\right)_y = 0, \left(\frac{\partial P}{\partial y}\right)_x \left(\frac{\partial v}{\partial x}\right)_y = 0$$

$$\therefore \left(\frac{\partial S}{\partial y}\right)_x - \left(\frac{\partial P}{\partial x}\right)_y = 0 \text{ or } \left(\frac{\partial S}{\partial y}\right)_x = \left(\frac{\partial P}{\partial x}\right)_y$$

Replacing x by T and y by V, we have

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

This is known as Maxwell's second thermodynamical relation.

Multiply both sides of (ix) by T, we have

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

$$\text{but} \quad T\partial S = \partial \theta$$

$$\therefore \left(\frac{\partial \theta}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_v$$