(1)

Maxwell's Thermodynamical Relations

- From the two laws of thermodynamics Maxwell was able to derive six fundamental thermodynamic relations.
- The state of the System can be Specified by any pair of quantities viz.,
  - Pressure (p)
  - Volume (V)
  - Temperature (T) and
  - Entrophy (S)
- In Solving, any thermodynamical problem, the most Suitable pair is choosen and the quantities Constituting the pair are taken as independent variables.

(2) From the first law of thermodynamic

$$\delta H = dU + \delta w$$

$$\delta H = dU + PdV \quad (or)$$

$$\boxed{dU = \delta H - pdV}$$

From the Second law of thermodynamic

$$dS = \frac{\delta H}{T} \quad (or)$$

$$\boxed{\delta H = TdS}$$

Substituting this value of δH in the first equation

$$dU = TdS - pdV \quad \text{—— (1)}$$

Considering S, U and V to be function of two independent variables x and y (here x and y can be any two variable out of P, V, T and S),

$$dS = \left(\frac{\partial S}{\partial x}\right)_y dx + \left(\frac{\partial S}{\partial y}\right)_x dy$$

$$dU = \left(\frac{\partial U}{\partial x}\right)_y dx + \left(\frac{\partial U}{\partial y}\right)_x dy$$

$$dV = \left(\frac{\partial V}{\partial x}\right)_y dx + \left(\frac{\partial V}{\partial y}\right)_x dy$$

Substituting these values in eq (i)

$$\left(\frac{\partial U}{\partial x}\right)_y dx + \left(\frac{\partial U}{\partial y}\right)_x dy = T\left[\left(\frac{\partial S}{\partial x}\right)_y dx + \left(\frac{\partial S}{\partial y}\right)_x dy\right] - P\left[\left(\frac{\partial V}{\partial x}\right)_y dx + \left(\frac{\partial V}{\partial y}\right)_x dy\right]$$

$$\left(\frac{\partial U}{\partial x}\right)_y dx + \left(\frac{\partial U}{\partial y}\right)_x dy = \left[T\left(\frac{\partial S}{\partial x}\right)_y dx + T\left(\frac{\partial S}{\partial y}\right)_x dy\right] - \left[P\left(\frac{\partial V}{\partial x}\right)_y dx - P\left(\frac{\partial V}{\partial y}\right)_x dy\right]$$

$$= \left[T\left(\frac{\partial S}{\partial x}\right)_y dx - P\left(\frac{\partial V}{\partial x}\right)_y dx\right] + \left[T\left(\frac{\partial S}{\partial y}\right)_x dy - P\left(\frac{\partial V}{\partial y}\right)_x dy\right]$$

(4) · Comparing the co-efficient of dx and dy, we get:

$$\left(\frac{\partial U}{\partial x}\right)_y \cancel{dx} = T\left(\frac{\partial S}{\partial x}\right)_y - P\left(\frac{\partial V}{\partial x}\right)_y \cancel{dx} \quad \text{—— (2)}$$

$$\left(\frac{\partial U}{\partial y}\right)_x \cancel{dy} = T\left(\frac{\partial S}{\partial y}\right)_x - P\left(\frac{\partial V}{\partial y}\right)_x \cancel{dy} \quad \text{—— (3)}$$

$$\left(\frac{\partial U}{\partial x}\right)_y = T\left(\frac{\partial S}{\partial x}\right)_y - P\left(\frac{\partial V}{\partial x}\right) \quad \text{—— (4)}$$

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

Differentiating eq (4) with respect to y and equation (5) with respect to x

5)

$$\frac{\partial^2 U}{\partial y \cdot \partial x} = \left(\frac{\partial T}{\partial y}\right)_x \left(\frac{\partial S}{\partial x}\right)_y + T \cdot \frac{\partial^2 S}{\partial y \partial x} - \left(\frac{\partial P}{\partial y}\right)_x \left(\frac{\partial V}{\partial x}\right)_y - P\left(\frac{\partial^2 V}{\partial y \partial x}\right)$$

$$\frac{\partial^2 U}{\partial x \partial y} = \left(\frac{\partial T}{\partial x}\right)_y \left(\frac{\partial S}{\partial y}\right)_x + T\left(\frac{\partial^2 S}{\partial x \partial y}\right) - \left(\frac{\partial P}{\partial x}\right)_y \left(\frac{\partial V}{\partial y}\right)_x - P\left(\frac{\partial^2 V}{\partial x \partial y}\right)$$

The change in internal energy brought about by changing V and T whether V is changed by dV first and T by dT later (or) vice-versa is the same.

6 It means dU is a perfect differential

$$\therefore \quad \frac{\partial^2 U}{\partial y\,\partial x} = \frac{\partial^2 U}{\partial x\,\partial y}$$

$$\left(\frac{\partial T}{\partial y}\right)_x \left(\frac{\partial S}{\partial x}\right)_y + \cancel{T\,\frac{\partial^2 S}{\partial y\,\partial x}} - \left(\frac{\partial P}{\partial y}\right)_x \left(\frac{\partial V}{\partial x}\right)_y - \cancel{P\left(\frac{\partial^2 V}{\partial y\,\partial x}\right)}$$

$$= \left(\frac{\partial T}{\partial x}\right)_y \left(\frac{\partial S}{\partial y}\right)_x + \cancel{T\left(\frac{\partial^2 S}{\partial x\,\partial y}\right)} - \left(\frac{\partial P}{\partial x}\right)_y \left(\frac{\partial V}{\partial y}\right)_x - \cancel{P\left(\frac{\partial^2 V}{\partial x\,\partial y}\right)}$$

Simplifying

$$\left(\frac{\partial T}{\partial y}\right)_x \left(\frac{\partial S}{\partial x}\right)_y - \left(\frac{\partial P}{\partial y}\right)_x \left(\frac{\partial V}{\partial x}\right)_y = \left(\frac{\partial T}{\partial x}\right)_y \left(\frac{\partial S}{\partial y}\right)_x - \left(\frac{\partial P}{\partial x}\right)_y \left(\frac{\partial V}{\partial y}\right)_x \quad \text{--- } 6$$

Here x and y can be any two variables out of P, V, T and S.

(4)- Derivation of Relations.

(1). Taking T and V are independent variables

$$x = T, \quad y = V$$

$$\frac{\partial T}{\partial x} = 1, \quad \frac{\partial V}{\partial y} = 1$$

$$\frac{\partial T}{\partial y} = 0, \quad \frac{\partial V}{\partial x} = 0$$

Substituting these value in eq (6)

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

this is maxwell first thermodynamic relationship

(2). Taking T and P are independent variable

(3) Taking S and V

(4) " S and P

(5) " P and V

(6) " T and S