Maxwell's Thermodynamical Relations

Maxwell derived four fundamental thermodynamical relations by using first law and second law of thermodynamics which are known as Maxwell's thermodynamical relations. The state of a system can be specified by any pair of quantities namely pressure (P), volume (V), temperature (T) and entropy (S). In solving any thermodynamical problem, the most suitable pair is choosen and the quantities constituting the pair are taken as independent variables.

From first law of thermodynamics,

$$dQ = dU + dW \Rightarrow dQ = dU + PdV$$

Where dQ = Heat change, dU = Change in internal energy of the system

dW = PdV = Work done , P = Pressure and dV = Change in volume

$$\Rightarrow dU = dQ - PdV \;\ldots\ldots\ldots\ldots\ldots\; (1)$$

From second law of thermodynamics, $dS = \frac{dQ}{T} \Rightarrow dQ = TdS \;\ldots\ldots\ldots\; (2)$

Where dS = Change in entropy and T = Absolute temperature

From equations (1) and (2), We get

$$dU = TdS - PdV \;\ldots\ldots\ldots\ldots\ldots\; (3)$$

Suppose U, S and V may be functions of two independent variables x and y where x and y can be any two variables out of P, V, T and S.

Here $U = U(x,y) \Rightarrow dU = \left(\frac{\partial U}{\partial x}\right)_y \cdot dx + \left(\frac{\partial U}{\partial y}\right)_x \cdot dy \;\ldots\ldots\ldots\ldots\; (4)$

Again $S = S(x,y) \Rightarrow dS = \left(\frac{\partial S}{\partial x}\right)_y \cdot dx + \left(\frac{\partial S}{\partial y}\right)_x \cdot dy \;\ldots\ldots\ldots\ldots\; (5)$

Again $V = V(x,y) \Rightarrow dV = \left(\frac{\partial V}{\partial x}\right)_y \cdot dx + \left(\frac{\partial V}{\partial y}\right)_x \cdot dy \;\ldots\ldots\ldots\ldots\; (6)$

Using equations (4), (5) and (6) in equation (3), we get

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

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

Equating the coefficients of dx and dy, we get

$$\left(\frac{\partial U}{\partial x}\right)_y = T\left(\frac{\partial S}{\partial x}\right)_y - P\left(\frac{\partial V}{\partial x}\right)_y \;\ldots\ldots\ldots\ldots\ldots\; (7)$$

and $\left(\frac{\partial U}{\partial y}\right)_x = T\left(\frac{\partial S}{\partial y}\right)_x - P\left(\frac{\partial V}{\partial y}\right)_x \;\ldots\ldots\ldots\ldots\ldots\; (8)$

Differentiating equation (7) w. r. t. y, we get

$$\frac{\partial^2 U}{\partial y \partial x} = T\frac{\partial^2 S}{\partial y \partial x} + \left(\frac{\partial T}{\partial y}\right)_x \cdot \left(\frac{\partial S}{\partial x}\right)_y - P\frac{\partial^2 V}{\partial y \partial x} - \left(\frac{\partial P}{\partial y}\right)_x \cdot \left(\frac{\partial V}{\partial x}\right)_y \quad \ldots\ldots\ldots\ldots\ldots \quad (9)$$

Again differentiating equation (8) w. r. t. x, we get

$$\frac{\partial^2 U}{\partial x \partial y} = T\frac{\partial^2 S}{\partial x \partial y} + \left(\frac{\partial T}{\partial x}\right)_y \cdot \left(\frac{\partial S}{\partial y}\right)_x - P\frac{\partial^2 V}{\partial x \partial y} - \left(\frac{\partial P}{\partial x}\right)_y \cdot \left(\frac{\partial V}{\partial y}\right)_x \quad \ldots\ldots\ldots\ldots\ldots \quad (10)$$

Change in internal energy by changing V and T, whether V is changed by dV first and T by dT later or vice versa, is the same. It means dU is perfect differential.

$$\text{So, } \frac{\partial^2 U}{\partial y \partial x} = \frac{\partial^2 U}{\partial x \partial y} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (11)$$

From equations (9), (10) and (11), We get

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

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

Since dV and dS are also perfect differential so $\frac{\partial^2 V}{\partial y \partial x} = \frac{\partial^2 V}{\partial x \partial y}$ and $\frac{\partial^2 S}{\partial y \partial x} = \frac{\partial^2 S}{\partial x \partial y}$

Using these in above equation, we get

$$\left(\frac{\partial T}{\partial y}\right)_x \cdot \left(\frac{\partial S}{\partial x}\right)_y - \left(\frac{\partial P}{\partial y}\right)_x \cdot \left(\frac{\partial V}{\partial x}\right)_y = \left(\frac{\partial T}{\partial x}\right)_y \cdot \left(\frac{\partial S}{\partial y}\right)_x - \left(\frac{\partial P}{\partial x}\right)_y \cdot \left(\frac{\partial V}{\partial y}\right)_x \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (12)$$

It is general expression for Maxwell's thermodynamical relations. In place of two independent variables x and y any two of the four variables S, T, P, and V can be substituted so that thare may be one mechanical varible (P or V) and one thermal variable (S or T). Thus there may be four sets of possible substitutions (S, V), (T, V), (S, P), (T, P) providing the four Maxwell's thermodynamical relations.

First Thermodynamical relation : For This we take S and V as independent variables.

Put x = S and y = V in general equation (12), We get

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

$$\Rightarrow \left(\frac{\partial T}{\partial V}\right)_S \cdot 1 - \left(\frac{\partial P}{\partial V}\right)_S \cdot 0 = \left(\frac{\partial T}{\partial S}\right)_V \cdot 0 - \left(\frac{\partial P}{\partial S}\right)_V \cdot 1$$

$$\Rightarrow \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \text{(A)}$$ It is Maxwell's first thermodynamical relation.

Second Thermodynamical relation : For This we take T and V as independent variables.

Put x = T and y = V in general equation (12), We get

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

$$\Rightarrow 0 \cdot \left(\frac{\partial S}{\partial T}\right)_V - \left(\frac{\partial P}{\partial V}\right)_T \cdot 0 = 1 \cdot \left(\frac{\partial S}{\partial V}\right)_T - \left(\frac{\partial P}{\partial T}\right)_V \cdot 1$$

$$\Rightarrow \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$ .... (B) It is Maxwell's second thermodynamical relation.

Third Thermodynamical relation : For This we take S and P as independent variables.
Put x = S and y = P in general equation (12), We get

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

$$\Rightarrow \left(\frac{\partial T}{\partial P}\right)_S \cdot 1 - 1 \cdot \left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial S}\right)_P \cdot 0 - 0 \cdot \left(\frac{\partial V}{\partial P}\right)_S$$

$$\Rightarrow \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$ .... (C) It is Maxwell's third thermodynamical relation.

Foutrh Thermodynamical relation : For This we take T and P as independent variables.
Put x = T and y = P in general equation (12), We get

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

$$\Rightarrow 0 \cdot \left(\frac{\partial S}{\partial T}\right)_P - 1 \cdot \left(\frac{\partial V}{\partial T}\right)_P = 1 \cdot \left(\frac{\partial S}{\partial P}\right)_T - 0 \cdot \left(\frac{\partial V}{\partial P}\right)_T$$

$$\Rightarrow \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$ .... (D) It is Maxwell's fourth thermodynamical relation.

Relations (A), (B), (C) and (D) are the Maxwell's fundamental thermodynamical relations.

Maxwell's thermodynamical relations can be easily written with the help of diagram as follows:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$ .... (A)

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

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

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