Ques : Establish Maxwell's thermodynamical relation and use them to obtain the two TdS equation. (2012, 2014,2016) Dr. Md. NAIYAR PERWEZ

Ans : Maxwell derived six fundamental thermodynamical relations by using first law and second law of thermodynamics. 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, $dQ = dU + dW \Rightarrow dQ = dU + PdV$

$$\Rightarrow dU = dQ - PdV \quad ....(1)$$

From second law of thermodynamics, $dS = \frac{dQ}{T} \Rightarrow dQ = TdS$ Put in equation (1)

$$dU = TdS - PdV \quad ....(2)$$

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

$$dU = \left(\frac{\delta U}{\delta x}\right)_y \cdot dx + \left(\frac{\delta U}{\delta y}\right)_x \cdot dy, \; dS = \left(\frac{\delta S}{\delta x}\right)_y \cdot dx + \left(\frac{\delta S}{\delta y}\right)_x \cdot dy, \; dV = \left(\frac{\delta V}{\delta x}\right)_y \cdot dx + \left(\frac{\delta V}{\delta y}\right)_x \cdot dy$$

Putting these values in equation (2), we get

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

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

Equating the coefficients of dx and dy, we get

$$\left(\frac{\delta U}{\delta x}\right)_y = T\left(\frac{\delta S}{\delta x}\right)_y - P\left(\frac{\delta V}{\delta x}\right)_y \; .... \; (3) \text{ and } \left(\frac{\delta U}{\delta y}\right)_x = T\left(\frac{\delta S}{\delta y}\right)_x - P\left(\frac{\delta V}{\delta y}\right)_x \; .... \; (4)$$

Dr. Md. NAIYAR PERWEZ

Differentiating equation (3) w. r. t. y and equation (4) w. r. t. x, we get

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

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

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.

So,
$$\frac{\delta^2 U}{\delta y \delta x} = \frac{\delta^2 U}{\delta x \delta y}$$

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

$$= \left(\frac{\delta T}{\delta x}\right)_y \left(\frac{\delta S}{\delta y}\right)_x + T\frac{\delta^2 S}{\delta x \delta y} - \left(\frac{\delta P}{\delta x}\right)_y \left(\frac{\delta V}{\delta y}\right)_x - P\frac{\delta^2 V}{\delta x \delta y} \quad \text{....... (5)}$$

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

Using these in equation (5), we get

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

It is general expression for Maxwell's thermodynamical relations. In place of two independent variables 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 stes of possible substitutions (S, V), (T, V), (S, P), (T, P) providing the four Maxwell's thermodynamical relations.

First Thermodynamical relation :- Put x = S and y = V in equation (6), we get

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

$$\Rightarrow \left(\frac{\delta T}{\delta V}\right)_S \cdot 1 - \left(\frac{\delta P}{\delta V}\right)_S \cdot 0 = \left(\frac{\delta T}{\delta S}\right)_V \cdot 0 - \left(\frac{\delta P}{\delta S}\right)_V \cdot 1 \Rightarrow \boxed{\left(\frac{\delta T}{\delta V}\right)_S = -\left(\frac{\delta P}{\delta S}\right)_V} \quad \text{................ (A)}$$

It is Maxwell's first thermodynamical relation.

Second Thermodynamical relation :- Put x = T and y = V in equation (6), we get

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

$$\Rightarrow 0 \cdot \left(\frac{\delta S}{\delta T}\right)_V - \left(\frac{\delta P}{\delta V}\right)_T \cdot 0 = 1 \cdot \left(\frac{\delta S}{\delta V}\right)_T - \left(\frac{\delta P}{\delta T}\right)_V \cdot 1 \Rightarrow \boxed{\left(\frac{\delta S}{\delta V}\right)_T = \left(\frac{\delta P}{\delta T}\right)_V} \quad \text{............... (B)}$$

It is Maxwell's second thermodynamical relation.

Dr. Md. NAIYAR PERWEZ

Third Thermodynamical relation :- Put x = S and y = P in equation (6), we get

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

$$\Rightarrow\left(\frac{\delta T}{\delta P}\right)_S\cdot 1-1\cdot\left(\frac{\delta V}{\delta S}\right)_P=\left(\frac{\delta T}{\delta S}\right)_P\cdot 0-0\cdot\left(\frac{\delta V}{\delta P}\right)_S\Rightarrow\boxed{\left(\frac{\delta T}{\delta P}\right)_S=\left(\frac{\delta V}{\delta S}\right)_P}\quad \text{.............. (C)}$$

It is Maxwell's third thermodynamical relation.

Fourth Thermodynamical relation :- Put x = T and y = P in equation (6), we get

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

$$\Rightarrow 0\cdot\left(\frac{\delta S}{\delta T}\right)_P-1\cdot\left(\frac{\delta V}{\delta T}\right)_P=1\cdot\left(\frac{\delta S}{\delta P}\right)_T-0\cdot\left(\frac{\delta V}{\delta P}\right)_T\Rightarrow\boxed{\left(\frac{\delta S}{\delta P}\right)_T=-\left(\frac{\delta V}{\delta T}\right)_P}\quad \text{................ (D)}$$

It is Maxwell's fourth thermodynamical relation.

Relations (A), (B), (C) and (D) are the four Maxwell's fundamental thermodynamical relations. Further there are two more relations within mechanical variables (P, V) and thermal variables (T, S).

Fifth Thermodynamical relation :- Put x = P and y = V in equation (6), we get

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

$$\Rightarrow\left(\frac{\delta T}{\delta V}\right)_P\left(\frac{\delta S}{\delta P}\right)_V-0\cdot 0=\left(\frac{\delta T}{\delta P}\right)_V\left(\frac{\delta S}{\delta V}\right)_P-1\cdot 1\Rightarrow\boxed{\left(\frac{\delta T}{\delta P}\right)_V\left(\frac{\delta S}{\delta V}\right)_P-\left(\frac{\delta T}{\delta V}\right)_P\left(\frac{\delta S}{\delta P}\right)_V=1}\quad \text{..... (E)}$$

It is Maxwell's fifth thermodynamical relation.

Sixth Thermodynamical relation :- Put x = T and y = S in equation (6), we get

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

$$\Rightarrow 0\cdot 0-\left(\frac{\delta P}{\delta S}\right)_T\left(\frac{\delta V}{\delta T}\right)_S=1\cdot 1-\left(\frac{\delta P}{\delta T}\right)_S\left(\frac{\delta V}{\delta S}\right)_T\Rightarrow\left(\frac{\delta P}{\delta T}\right)_S\left(\frac{\delta V}{\delta S}\right)_T-\left(\frac{\delta P}{\delta S}\right)_T\left(\frac{\delta V}{\delta T}\right)_S=1\quad \text{..... (F)}$$

It is Maxwell's sixth thermodynamical relation.

Out of these six thermodynamical relations, the one suited for a particular problem is used and poblem is solved.

<u>The T.dS Equations :</u>

First T.dS equation : The entropy S of a pure substance can be taken as a function of temperature T and volume V.

$$dS=\left(\frac{\delta S}{\delta T}\right)_V\cdot dT+\left(\frac{\delta S}{\delta V}\right)_T\cdot dV$$

Multiplying both sides by T, we get

$$TdS=T\left(\frac{\delta S}{\delta T}\right)_V\cdot dT+T\left(\frac{\delta S}{\delta V}\right)_T\cdot dV\quad \text{.............. (i)}$$

Dr. Md NAIYAR PERWEZ

But $C_V = T\left(\frac{\delta S}{\delta T}\right)_V$ and from Maxwell's second thermodynamical relation $\left(\frac{\delta S}{\delta V}\right)_T = \left(\frac{\delta P}{\delta T}\right)_V$

Put these values in equation (i), we get

$$TdS = C_V \cdot dT + T\left(\frac{\delta P}{\delta T}\right)_V \cdot dV \quad \text{.................. (G)}$$

It is first TdS equation.

Second T.dS equation : The entropy S of a pure substance can be taken as a function of temperature T and pressure P.

$$dS = \left(\frac{\delta S}{\delta T}\right)_P \cdot dT + \left(\frac{\delta S}{\delta P}\right)_T \cdot dP$$

Multiplying both sides by T, we get

$$TdS = T\left(\frac{\delta S}{\delta T}\right)_P \cdot dT + T\left(\frac{\delta S}{\delta P}\right)_T \cdot dP \quad \text{.................. (ii)}$$

But $C_P = T\left(\frac{\delta S}{\delta T}\right)_P$ and from Maxwell's fourth thermodynamical relation, $\left(\frac{\delta S}{\delta P}\right)_T = -\left(\frac{\delta V}{\delta T}\right)_P$

Put these values in equation (ii), We get

$$TdS = C_P \cdot dT - T\left(\frac{\delta V}{\delta T}\right)_P \cdot dP \quad \text{............... (H)}$$

It is second TdS equation.

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