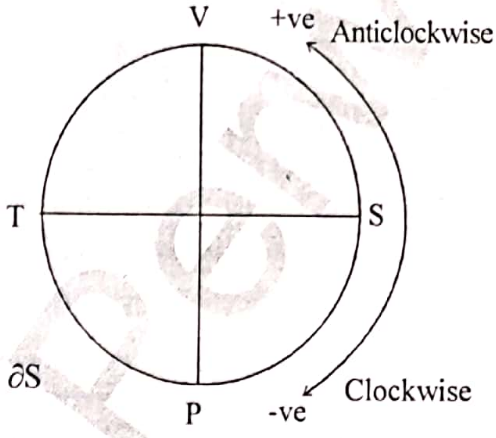
Applications of Maxwell's thermodynamical relatios:

(A) The T.dS Equations : Using These Maxwell's thermodynamical relations, the Two TdS equations can be derived.

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



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

Multiplying both sides by T, We get

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

$$\Rightarrow \boxed{TdS = \left(\frac{\partial Q}{\partial T}\right)_V \cdot dT + T\left(\frac{\partial S}{\partial V}\right)_T \cdot dV} \quad \text{since } \partial Q = T\,\partial S$$

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

$\left(\text{since } C_V = \left(\frac{\partial Q}{\partial T}\right)_V = \text{sp. heat at constant volume}\right)$

From Maxwell's Thermodynamical relation, $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ put in equation (i), we get

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

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.

So, $S = S(T, V) \Rightarrow dS = \left(\frac{\partial S}{\partial T}\right)_P \cdot dT + \left(\frac{\partial S}{\partial P}\right)_T \cdot dP$

Multiplying both sides by T, We get

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

$$\Rightarrow TdS = \left(\frac{\partial Q}{\partial T}\right)_P \cdot dT + T\left(\frac{\partial S}{\partial P}\right)_T \cdot dP \quad \text{since } \partial Q = T\,\partial S$$

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

$\left(\text{since } C_P = \left(\frac{\partial Q}{\partial T}\right)_P = \text{sp. heat at constant pressure}\right)$

From Maxwell's Thermodynamical relation, $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$ put in equation (i), we get

$$TdS = C_P \cdot dT - T\left(\frac{\partial V}{\partial T}\right)_P \cdot dP \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(F)}$$

It is second TdS equation.

(B) Derivation of Clausius Clapeyron equation or Latent heat equation:

From Maxwell's thermodynamical relation

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(1)}$$

Multiplying both sides by T, We get

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

But $T\partial S = \partial Q$

So, $$\left(\frac{\partial Q}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(2)}$$

The quantity $\left(\frac{\partial Q}{\partial V}\right)_T$ represents the amount of heat absorbed or released per unit change in volume at constant temperature. If there is change in volume of substance due to heat absorbed or released by the substance at constant temperature then the heat represents latent heat used when the substance changes from solid to liquid (melting) state or from liquid to vapour (boiling) state and vice versa when temperature remains constant during the change of state.

$(\partial Q)_T$ = Heat absorbed or released per unit mass at constant temperature = Sp. latent heat

Suppose $(\partial Q)_T = L$ = Specific latent heat

V_1 = Volume per unit mass (Sp. volume) of the substance in first phase

V_2 = Volume per unit mass (Sp. volume) of the substance in first phase

Then change in volume per unit volume during change in phase will be $\partial V = V_2 - V_1$

Hence $\left(\frac{\partial Q}{\partial V}\right)_T = \frac{L}{V_2 - V_1}$ Put in equation (2), We get

$$\frac{L}{V_2 - V_1} = T\left(\frac{\partial P}{\partial T}\right)_V$$

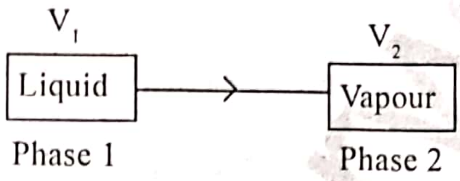
$$\Rightarrow \frac{dP}{dT} = \frac{L}{T(V_2 - V_1)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(3)}$$

Where dT represents change in melting point or boiling point of the substance due to change in pressure dP. This equation is known as Clausius-Clapeyron's equation or Clausius-Clapeyron latent heat equation.

Application of Clausius-Clapeyron equation or Latent heat equation:

(1) Effect of pressure on boiling point of a liquid : When a liquid substance is converted into its vapour form at constant temperature (boiling point) and if V_1 be its volume in liquid phase (Phase 1) and if V_2 be its volume in vapour phase (Phase 2) then for all liquids

$V_2 > V_1$ or $V_2 - V_1 = +ve$



From Clausius-Clapeyron equation,

$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)} = +ve$$

It means that boiling point T of liquid increases with the increase of pressure. It is also known as elevation of boiling point. Therefore boiling point of a liquid is pressure dependent.

On increasing pressure, boiling point of a liquid increases and vice versa.

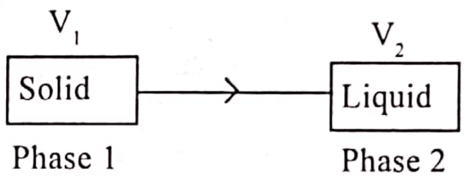
* Foods are quickly cooked in pressure cooker because pressure inside the cooker gets increased and therefore boiling point of liquid gets also increased.

* It is very difficult to cook food on mountain because pressure on the mountain gets decreased due to increase in height and therefore boiling point of liquid gets decreased.

(2) Effect of pressure on melting point of a solid :

(i) When a solid substance like ice is converted into its liquid state at constant temperature (melting point) and if V_1 be its volume in solid phase (Phase 1) and if V_2 be its volume in liquid phase (Phase 2) then for the solid like ice,

$V_2 < V_1$ or $V_2 - V_1 = -ve$



From Clausius-Clapeyron equation,

$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)} = -ve$$

It means that melting point T of the solid substance like ice decreases with the increase of pressure. It is also known as Depression of melting point of solid.

(ii) When a solid substance like wax is converted into its liquid state at constant temperature (melting point) and if V_1 be its volume in solid phase (Phase 1) and if V_2 be its volume in liquid phase (Phase 2) then for the solid like wax,

$V_2 > V_1$ or $V_2 - V_1 = +ve$

From Clausius-Clapeyron equation,

$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)} = +ve$$

It means that melting point T of the solid substance like wax increases with the increase of pressure. It is also known as Elevation of melting point of solid.

Ques : Establish Maxwell's thermodynamical relations and use them to obtain the two TdS equations.

Ques : Obtain Clausius-Clapeyron equation and hence discuss the effect of change of pressure on (1) the boiling point of liquid and (2) the melting point of solid.