6.8 Relation between C_P, C_V and μ

The specific heat at constant pressure C_P, the specific heat at constant volume C_V and the Kelvin coefficient μ are defined as follows:

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

$$\mu = \left(\frac{\partial T}{\partial P}\right)_h$$

These three quantities are defined in terms of the thermodynamic properties *viz.* pressure, volume temperature, internal energy and enthalpy. Hence C_P, C_V and μ are also thermodynamic properties of a substance.

6.9 The *T. dS* Equations

1. *First T.dS Equation.* The entropy S of a pure substance can be taken as a function of temperature and volume.

$$\therefore \quad dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

Multiplying both sides by T

$$T.dS = T\left(\frac{\partial S}{\partial T}\right)_V dV + T\left(\frac{\partial S}{\partial V}\right)_T dV$$

$$\therefore \quad \text{But} \qquad C_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

and from Maxwell's relations

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

Substituting these values in equation (*ii*)

$$T\,dS = C_V\,dT + T\left(\frac{\partial P}{\partial T}\right)_V dV \qquad \ldots(6.42)$$

Equation (6.42) is called the first *T. dS* equation.

2. ***Second T.dS Equation.*** The entropy S of a pure substance can also be regarded as a function of temperature and pressure

$$\therefore \quad dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

Multiplying both sides by T

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

But $$C_P = T\left(\frac{\partial S}{\partial T}\right)_P$$

and from Maxwell's relations

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

Substituting these values in equation (v)

$$T.dS = C_P\, dT - T\left(\frac{\partial V}{\partial T}\right)_P dP \qquad \ldots(6.43)$$

Equation (6.43) is called the second $T\,dS$ equation.

6.10 Clapeyron's Latent Heat Equation using Maxwell's Thermodynamical Relations

From Maxwell's second thermodynamical relation

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \qquad (\because \text{eqn. 6.36})$$

Multiplying by T, we get

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

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

Here $\left(\frac{\partial Q}{\partial V}\right)_T$ represents the quantity of heat absorbed per unit increase in volume at constant temperature. This quantity of heat asborbed at constant temperature is the latent heat (L).

Thus, $\partial Q = L$ and $\partial V = V_2 - V_1$, for unit mass of a substance.

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

or $$\frac{L}{V_2 - V_1} = T\frac{dP}{dT}$$

or $$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)} \qquad \ldots(6.44)$$

This is **Clapeyron's latent heat equation.**

6.11 Clapeyron Latent Heat Equation using Carnot's Cycle

Consider the isothermals FBAE at temperature $T + dT$ and $GCDH$ at temperature T. Here EA and HD show the liquid state of the substance. At A and D, the substance is purely in the liquid state (Fig. 6.1). From A to B or D to C, the substance is in transition from the liquid to the gaseous state and *vice*

versa. At B and C, the substance is purely in the gaseous state. From B to F or C to G, the substance is in the gaseous state. Join A to D and B to C by dotted lines.

Fig. 6.1

The cycle $ABCD$ represents a complete cycle and Carnot's theorem can be applied. Suppose the volume at the point A is V_1 and temperature is $T + dT$. The pressure is just below its saturation pressure and the liquid begins to evaporate and at the point B the volume is V_2. The substance is in the vapour state. Suppose the mass of the liquid at B is one gram the amount of heat absorbed is Q_1, here $Q_1 = L + dL$, where $L + dL$ is the latent heat of the liquid at temperature $(T + dT)$.

At the point B, the pressure is decreased by dP. The vapour will expand and its temperature falls. The temperature at C is T. At this pressure and temperature T, the gas begins to condense and is converted into the liquid state. At the point D, the substance is in the liquid state. From C to D, the amount of heat rejected (given out) is Q_2. Here $Q_2 = L$ where L is latent heat at temperature T. By increasing the pressure a little, the original point A is restored. The cycle $ABCDA$ is completely reversible. Applying the principle of Carnot's reversible cycle

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$

or
$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

$$\frac{Q_1 - Q_2}{Q_2} = \frac{T_1 - T_2}{T_1}$$

Here,
$$Q_1 = L + dL,\ Q_2 = L,$$
$$T_1 = T + dT,\ T_2 = T$$
$$Q_1 - Q_2 = L + dL - L = dL$$
$$T_1 - T_2 = T + dT - T = dT$$

$\therefore$
$$\frac{dL}{L} = \frac{dT}{T}$$

The area of the figure
$$ABCD = Q_1 - Q_2 = dL$$
$$= dP\,(V_2 - V_1)$$

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

$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)} \quad \ldots(6.45)$$

This is called the **Clapeyron's latent heat equation.**

Applications

1. *Effect of change of pressure on the melting point.*

When a solid is converted into a liquid, there is change in volume.

(*i*) If V_2 is greater than V_1.

$\frac{dP}{dT}$ is a positive quantity. It means that the rate of change of pressure with respect to