

31.8.2020

Page 1

Applications of Clapeyron and Clausius Clapeyron Equation to phase equilibria

① Solid-Liquid Equilibrium

Applying Clapeyron equation

$$\frac{dp}{dT} = \frac{\Delta H_f}{T(V_L - V_S)} \quad \text{--- (1)}$$

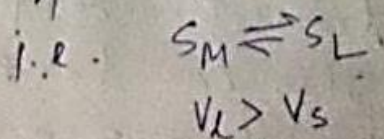
Where ΔH_f is the molar heat of fusion, V_L and V_S are the volumes of liquid and solid

Writing the equation (1) as

$$\frac{dT}{dp} = T \frac{(V_L - V_S)}{\Delta H_f} \quad \text{--- (2)}$$

ΔH_f is always positive but $\Delta V = V_L - V_S$ can be both positive and negative. Thus for liquid expanding on fusion, m.p. increases with increase of pressure, whereas if there is decrease in volume, m.p. decrease with increase of pressure.

Let us apply the equation to the fusion of sulphur.



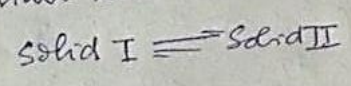
$$V_L > V_S$$

The L.H.S. of the equation is, therefore, positive. Hence, $\frac{dT}{dp}$ should have positive sign.

Thus increase of pressure raises the m.p.

② Solid-Solid Equilibria

Certain substances occur in several crystalline forms (i.e. Sulphur, carbon etc) and under certain conditions of temperature and pressure, the two forms may be in equilibrium with each other.



$\Delta H_{trans} = \Delta H_{transition}$

$\Delta V = V_{II} - V_I$

From Clapeyron equation

$\frac{dP}{dT} = \frac{\Delta H_{trans}}{T(V_{II} - V_I)}$ - (3)

The change in volume in solids are very small, so only a large change in pressure can bring about any change in the transition temperature of solids. This can be explained by writing the equation 3 as

$\frac{dT}{dP} = \frac{T(V_{II} - V_I)}{\Delta H_{trans}}$ - (4)

The variation in transition temperature of S_R and S_M can be explained with the help of equation 4

Since density of S_M (1.95) is less than that of S_R (2.25), V_M is larger than V_R . The right-hand side of the equation is positive. Thus increase of pressure will raise the transition temperature of S_R .

③ Solid-Vapour Equilibria.

For such equilibria

$$\frac{dP}{dT} = \frac{1}{T} \left(\frac{\Delta H_{sub}}{V_{vap} - V_{solid}} \right) \quad \text{--- (5)}$$

where ΔH_{sub} is the molar heat of sublimation. Since $V_{vap} \gg V_{solid}$, the vapour behaves like an ideal gas, we obtain

$$\frac{dP}{dT} = \frac{1}{T} \frac{\Delta H_{sub}}{V_{vap}} \quad \text{--- (6)}$$

$$= \frac{\Delta H_{sub}}{RT^2} \cdot P \quad (\because PV_{vap} = RT) \quad \text{--- (7)}$$

$$\text{or } \frac{d \ln P}{dT} = \frac{\Delta H_{\text{sub}}}{RT^2} \quad (8)$$

On integration, the equation

$$\ln P = - \frac{\Delta H_{\text{sub}}}{RT} + \text{Constant}$$

$$\text{or } \log P = - \frac{\Delta H_{\text{sub}}}{2.303 RT} + \text{Const} \quad (9)$$

This equation can be used to determine the enthalpy of sublimation from the vapour pressure of solid at two or more than two temperatures using more simplified equation - 9

$$2.303 \log \frac{P_2}{P_1} = \frac{\Delta H_{\text{sub}}}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right] \quad (10)$$

From the knowledge of ΔH_{sub} and ΔH_{vap} it is possible to determine the enthalpy of fusion

$$\Delta H_f = \Delta H_{\text{sub}} - \Delta H_{\text{vap}} \quad (11)$$

④ Liquid-Vapour equilibrium

liquid \rightleftharpoons Vapour
 Applying Clapeyron equation

$$\frac{dp}{dT} = \frac{1}{T} \frac{\Delta H_v}{(V_v - V_l)}$$

$$V_v \gg V_l$$

$$\frac{dp}{dT} = \frac{1}{T} \frac{\Delta H_v}{V_v}$$

On integration, the equation is

$$\log P = - \frac{\Delta H_v}{2.303 RT} + \text{const.} \quad (12)$$

Equation 12 indicates that the plots of $\log P$ vs $\frac{1}{T}$ should be straight lines with the slope equal to $-\frac{\Delta H_v}{2.303R}$.

The values of ΔH_v can also be calculated if the values of vapour pressure are known at two temperatures.

