

Phase Transitions

“Several substances undergo phase transitions under change of temp and pressure.”

There are two types of phase transitions”

1) First kind Transition :

- In the first order transition the density changes suddenly at the instant of change of phase. [For example, water boils and is converted into water vapour at 100°C and 1 atm pressure]
- Density of water 1000 kg/m^3 and that of vapour is 0.6 kg/m^3 , a sudden change in density occurs at 100°C and 1 atmosphere.
- Therefore conversion of water into water vapour at its transition temperature and pressure is first order phase transition.

→ To obtain the equilibrium condition b/w the phases, let us consider a vapour-liquid mixture in equilibrium at vapour pressure and temperature T . Both P and T remain constant. Let m_1 and m_2 the masses of liquid and vapour phases and g_1 and g_2 their specific Gibbs functions.

(or)

“We consider a system whose phase are in equilibrium. In slight variation of external condition (T, P) results a certain amount of the substance passing from one phase to another and this phenomena is called phase transitions.”

→ "The change in phase which take place at constant temperature and pressure.

In which heat is either absorbed (or) evolved during change of phase are called "first order phase transitions"

→ In first order phase transition the entropy (S) and density (or) volume change. Gibb's Function G remain constant.

$$\left[\frac{dP}{dT} \right] = \frac{S_2 - S_1}{V_2 - V_1}$$

From second law of thermodynamics

$$dq = T ds$$

$$dq = T(S_2 - S_1) \text{ (ie) } (S_2 - S_1) = \frac{L}{T}$$

$$[T ds = T(S_2 - S_1)]$$

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

This equation is known as

Clausius - Clapeyron latent heat equation

→ The first order transition can be characterised by either of the following statements.

- ① The changes in entropy, volume and latent heat exist.
- ② The density changes are discontinuous at transition temperature and pressure
- ③ The first order derivatives of Gibbs' function changes discontinuously

2) Second order Transition

In second order transition the density of substance changes slowly and smoothly at the instant of change of phase.

→ In fact in second order transition the first order differentials are continuous at transition point and the discontinuity appears in the second order differentials of Gibbs' function. (ie) second order transition.

$$\left(\frac{\partial g_1}{\partial T}\right)_P = \left(\frac{\partial g_2}{\partial T}\right)_P \quad \text{and} \quad \left(\frac{\partial g_1}{\partial P}\right)_T = \left(\frac{\partial g_2}{\partial P}\right)_T$$

→ A well known example of second order phase transition is provided by the transition of liquid Helium I into liquid Helium II for the common isotope of He^4 .

→ In going from liquid phase II no latent heat is involved and density of Helium II is same as of Helium I at transition point called λ point

→ Other example of second order transition is the transition from non-ferromagnetic state to ferromagnetic state.

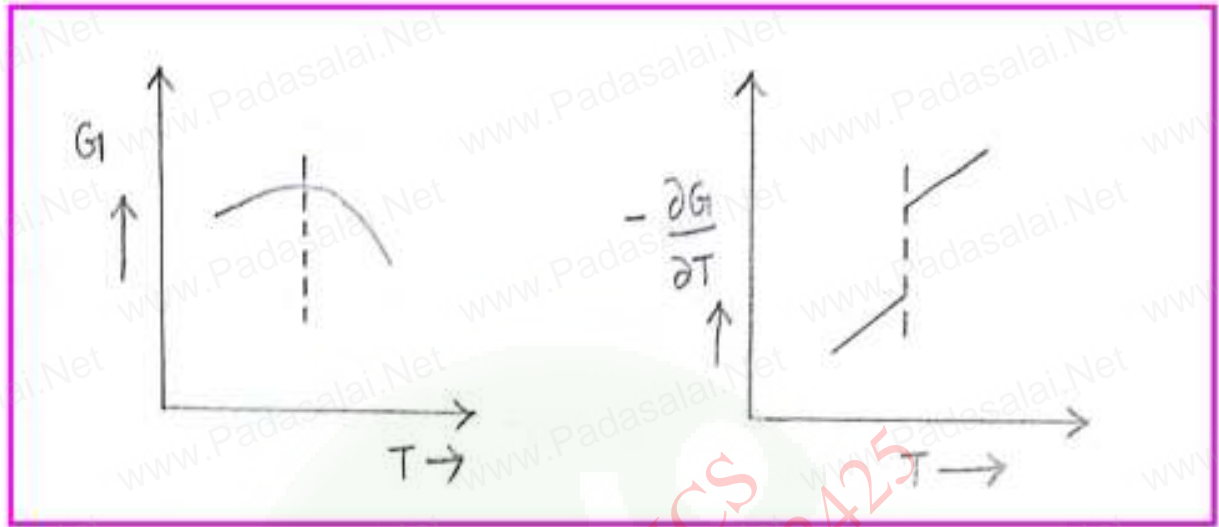
→ There is transference of heat and hence there is change in entropy and volume

→ The values of Gibbs's Function is the same in both the phases at equilibrium.

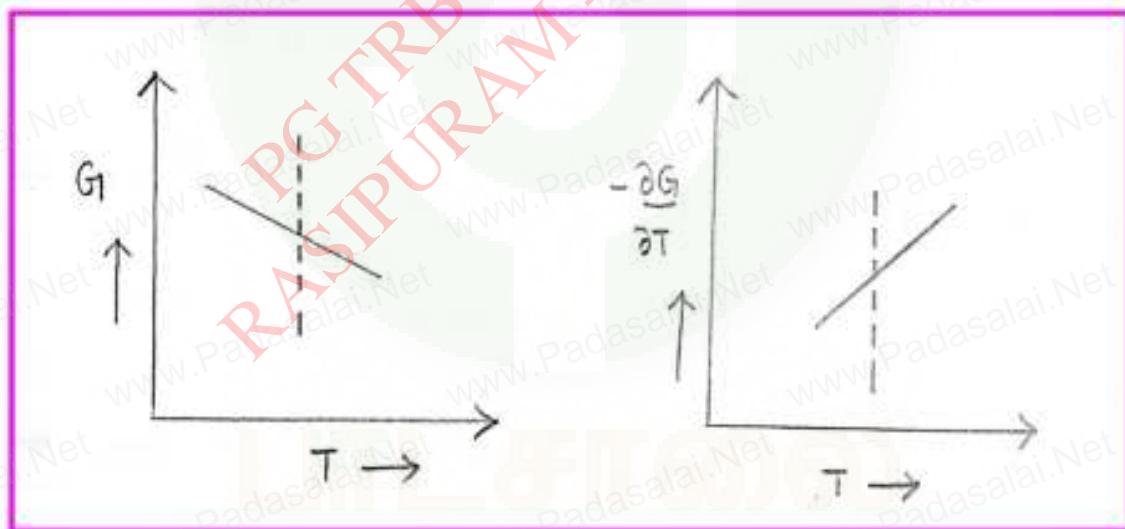
→ The transformation of water to vapour at constant temp & volume

→ The transformation of ice to water

→ First order phase transition - discontinuity



→ Second order phase transition - No discontinuity



→ In second order phase transition No change in entropy and volume at constant temperature & pressure.

Example :

→ Transition of liquid He-I to liquid He-II at λ point (2.19 K)

→ Transition of ferromagnetic material to a paramagnetic material at Curie point.

→ Transition of superconducting metal into an ordinary conductor in the absence of the magnetic field.

→ All the disorder transitions in chemical compound and alloys.

→ For the phase transitions,

$$g_1 = g_2$$

$$g_1 - g_2 = 0$$

$$C_p = T \left(\frac{\partial S}{\partial T} \right)_p$$

→ Isothermal Compressibility (κ) is given by,

$$\kappa = -\frac{1}{V} \left[\frac{\partial V}{\partial P} \right]_T$$

→ Volume Co-efficient of expansion (α) is given by,

$$\alpha = \frac{1}{V} \left[\frac{\partial V}{\partial T} \right]_P$$

$$\rightarrow \frac{dP}{dT} = \frac{C_{P2} - C_{P1}}{TV(\alpha_2 - \alpha_1)}$$

$$\rightarrow \frac{dP}{dT} = \frac{\alpha_2 - \alpha_1}{\kappa_2 - \kappa_1}$$

→ These equations are Ehrenfest Equation

→ These equation represent the condition of equilibrium b/w the two phases.