

# Chapter 11

# Phase Transition and

# Low Temperature Physics

## 2. Phase Transition

A phase of a thermodynamic system and the state of matter has uniform physical properties.

A phase transition is the transformation of thermodynamic system from one phase or state of matter to another.

During a phase transition of a given medium certain properties of the medium change, often discontinuously, as a result of some external condition, such as temperature, pressure and others.

Gibbs phase rule: It is proposed by Josiah Willard Gibbs, which is given by

$$F = C - P + 2$$

Where  $C$  is number of components,  $P$  is the number of phase in thermodynamic equilibrium with each other and  $F$  is number of degree of freedom.

**Phase:** A phase is form of matter that is homogeneous in chemical composition and physical state.

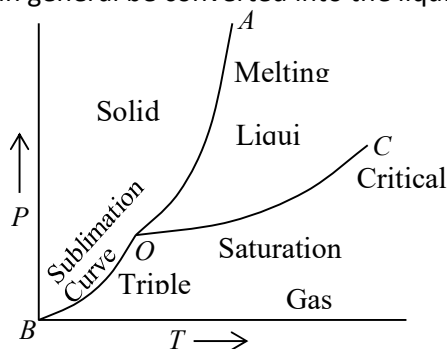
Typical phases are solid, liquid and gas. Two immiscible (or liquid mixture with different compositions) separated by distinct boundary are counted as two different phase.

**Components:** The number of components is the number of chemically independent constituents of the system, i.e. minimum number of independent species necessary to define the composition of all phase of the system.

The number of degree of freedom ( $F$ ) in the context is the number of intensive variable which are independent to each other.

### First Order Phase Transition

Let us consider one component system in which system having only one kind of constituent particles. For first order phase transition  $P-T$  diagram are shown in fig 1. Depending on the system, at some values for temperature and pressure, the three phases of the system may be found in equilibrium. In the P-T diagram, the line OA represents equilibrium between solid and liquid phases, the line OB represents equilibrium between solid and gas phases, and the line OC represents equilibrium between liquid and gas phases. The point O where all the three phases are in equilibrium, is known as a **triple point**. The line OC terminates at the point C, called the **critical point**. Beyond this point, the gas phase cannot be converted into the liquid phase. In figure 1, the point C is at the apex of the P-V curve at the critical temperature  $T_c$ . For the temperature  $T > T_c$ , the gas phase of the matter cannot be converted into the liquid phase, but for  $T < T_c$ , the gas phase can in general be converted into the liquid phase.



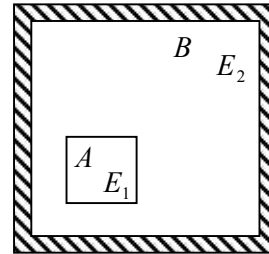
**Figure:** P-T phase of one component

## Equilibrium Between Two Phases

Let us consider an isolated system having a matter which is existing in two phases, denoted by 1 and 2, simultaneously in equilibrium with each other (Figure 2). Suppose  $V_1$  and  $V_2$  are volumes,  $N_1$  and  $N_2$  the number of particles,  $E_1$  and  $E_2$  the internal energies, and  $S_1$  and  $S_2$  the entropies of the two phases, respectively. For each phase, entropy is a function of its volume, number of particles (mass) and internal energy.

From these relations, it follows that

$$\begin{aligned} T_1 &= T_2 && \text{thermal equilibrium} \\ P_1 &= P_2 && \text{mechanical equilibrium} \\ \mu_1 &= \mu_2 && \text{chemical equilibrium} \end{aligned}$$



**Figure 2:** Equilibrium of two phases of an isolated one component system

Hence, when two different phases of the matter are in equilibrium, their temperatures, pressures and chemical potentials must be equal. If the chemical potentials are expressed as functions of pressure and temperature, we have

$$\mu_1(P, T) = \mu_2(P, T)$$

where  $P$  ( $= P_1 = P_2$ ) and  $T$  ( $= T_1 = T_2$ ) are the common pressure and temperature, respectively, of the two phases in equilibrium. Thus, from above equation, we have

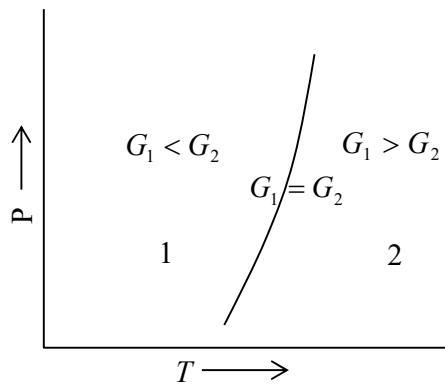
$$G_1(P, T)N_1 = G_2(P, T)N_2$$

$$\frac{G_1}{N_1} = \frac{G_2}{N_2}$$

where  $G_1(P, T)$  and  $G_2(P, T)$  are the Gibbs free energies, and  $N_1$  and  $N_2$  the number of particles in the two phases, respectively. Since during the phase transition, the number of particles is not changing (i.e.,  $N_1 = N_2$ ), we have

$$G_1(P, T) = G_2(P, T)$$

Hence, during the phase transition, the Gibbs free energy does not change. Gibbs energies  $G_1$  and  $G_2$  of the two phases 1 and 2, respectively, can be exhibited as shown in figure 4.



**Figure 3:** Phase equilibrium curve ( $G_1 - G_2$ ) separating two phases 1 and 2.

### Clapeyron-Clausius Equation

When the two phases, denoted by 1 and 2, of the given matter are in equilibrium, we have

$$G_1(P, T) = G_2(P, T)$$

where  $G_1$  and  $G_2$  are Gibbs free energies of the two phases, respectively, and  $P$  ( $= P_1 = P_2$ ) and  $T$  ( $= T_1 = T_2$ ) are the common pressure and temperature, respectively, of the two phases. In the  $P$ - $T$  diagram, along the phase-transition line, let us consider a point, where the pressure is  $P + dP$  and the temperature is  $T + dT$  so that we have

$$G_1(P + dP, T + dT) = G_2(P + dP, T + dT)$$

Using Taylor series expansion and neglecting the higher order terms, we have

$$G_1(P, T) + \left(\frac{\partial G_1}{\partial P}\right)_T dP + \left(\frac{\partial G_1}{\partial T}\right)_P dT = G_2(P, T) + \left(\frac{\partial G_2}{\partial P}\right)_T dP + \left(\frac{\partial G_2}{\partial T}\right)_P dT$$

Using above two equation we get

$$V_1 dP - V_2 dP - S_1 dT + S_2 dT = 0$$

$$\frac{dP}{dT} = \frac{S_2 - S_1}{V_2 - V_1} = \frac{\Delta S}{\Delta V}$$

$$\Delta S = \frac{\Delta H}{T} = \frac{L}{T}$$

where  $\Delta H (= H_2 - H_1)$  is the change in heat (enthalpy) which is the molar latent heat  $L$ . thus, from equation an we have

$$\frac{dP}{dT} = \frac{L}{T \Delta V}$$

for  $V_2 > V_1$ , we have

$$\left(\frac{\partial G_2}{\partial P}\right)_T \left/ \left(\frac{\partial G_1}{\partial P}\right)_T \right. \quad (A)$$

further, for  $S_2 > S_1$ , we have

$$\left(\frac{\partial G_2}{\partial T}\right)_P \left\langle \left(\frac{\partial G_1}{\partial T}\right)_P \right\rangle \quad (B)$$

### Liquid-Vapour Phase Transition

Let us consider a phase transition from a liquid state to a vapor one. If  $V_l$  and  $V_g$ , respectively, denote the volume in the liquid and gas phases, and  $L_v$  is the heat of vaporization (latent heat for the transition from liquid to vapour), the Clapeyron-Clausius equation is

$$\frac{dP}{dT} = \frac{L_v}{T(V_g - V_l)}$$

Since in the phase transition,  $V_g$  is always greater than  $V_l$  and the heat of vaporization  $L_v$  is positive and we have

$$\frac{dP}{dT} > 0$$

It shows that the boiling point of a liquid increases with the increase in pressure.

Now, if the vapour pressure is low, i.e.,  $V_g \gg V_l$ , in comparison to  $V_g$ , and we have

$$\frac{dP}{dT} = \frac{L_v}{TV_g}$$

Using the ideal gas equation,  $PV_g = RT$ , we have

$$\frac{dP}{dT} = \frac{L_v P}{RT^2} \qquad \frac{dP}{P} = \frac{L_v}{R} \frac{dT}{T^2}$$

$$\ln[P(T)] = -\frac{L_v}{R} \frac{1}{T} + C$$

where  $C$  is a constant of integration. At the critical point, we have  $P = P_c$ ,  $T = T_c$  and equation is

$$\ln[P_c(T_c)] = -\frac{L_v}{R} \frac{1}{T_c} + C$$

$$P(T) = P_c(T_c) \exp\left[\frac{L_v}{R} \left(\frac{1}{T_c} - \frac{1}{T}\right)\right]$$

Here, we have assumed that the heat of vapourisation  $L_v$  is independent of the temperature.

However, it depends on the temperature. Suppose it varies as  $L_v = a - bT$ , then for an ideal gas at low pressure, we have

$$\frac{dP}{P} = \frac{(a - bT)}{R} \frac{dT}{T^2}$$

$$\ln[P(T)] = -\frac{a}{R} \frac{1}{T} - \frac{b}{R} \ln(T) + C$$

where  $C$  is a constant of integration. At the critical point, we have  $P = P_c, T = T_c$  and equation is

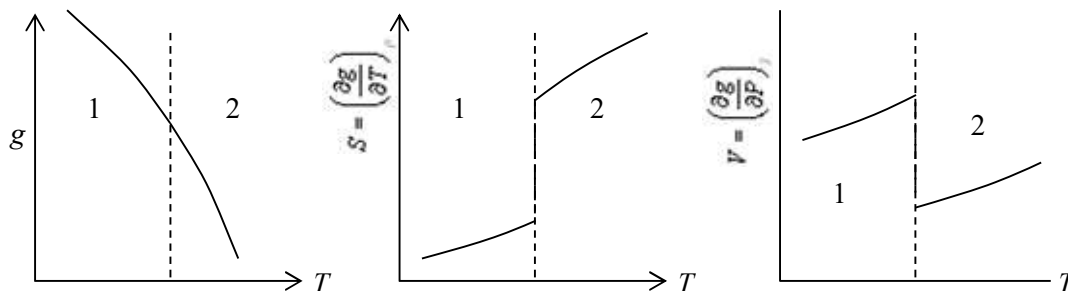
$$\ln[P_c(T_c)] = -\frac{a}{R} \frac{1}{T_c} - \frac{b}{R} \ln(T_c) + C$$

On subtracting equation from and rearranging, we have

$$\ln\left[\frac{P(T)}{P_c(T_c)}\right] = \frac{a}{R} \left(\frac{1}{T_c} - \frac{1}{T}\right) + \frac{b}{R} \ln\left(\frac{T_c}{T}\right)$$

### Properties of First Order Phase Transition

- (1) Gibbs free energy is continuous
- (2) First order derivative with respect to temperature and pressure have finite discontinuity i.e. entropy ( $S$ ) and pressures ( $P$ ) have finite discontinuity.
- (3) Second and more higher order differential is infinite



**Fig. 4:** A schematic representation of first order phase transitions

**Example:** For a two phase system in equilibrium,  $p$  is a function of  $T$  only, so that

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial P}{\partial T}\right)_S$$

Show that

$$\frac{C_V}{\beta_S} = TV \left(\frac{dP}{dT}\right)^2$$

**Solution:** Let us take  $T$  and  $V$  as independent variables and write

$$S = S(T, V)$$

so that,

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

For an adiabatic process, it yields

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

Using first Maxwell relation, we obtain

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

Since  $C_V = T \left(\frac{\partial P}{\partial T}\right)_V$  we can write

$$\begin{aligned} C_V &= -T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_S = -T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial P}\right)_S \left(\frac{\partial P}{\partial T}\right)_S \\ &= TV \beta_S \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial P}{\partial T}\right)_S = TV \beta_S \left(\frac{dP}{dT}\right)^2 \end{aligned}$$

where  $\beta_S$  is adiabatic compressibility.

**Example:** Calculate under what Pressure water would boil at  $120^\circ \text{C}$ . One gram of steam occupies a volume of  $1677 \text{ cm}^3$ . Latent heat of steam =  $540 \text{ cal/g}$ ,  $J = 4.2 \times 10^7 \text{ erg/cal}$ . atmospheric pressure =  $1.0 \times 10^6 \text{ dyne/cm}^2$

**Solution:**  $\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$        $dP = \frac{L \times dT}{(V_2 - V_1)}$

$V_2 = 1677 \text{ cm}^3/\text{g}$        $V_1 = 1 \text{ cm}^3/\text{g}$

$L = 4.2 \times 10^7 \times 540 \text{ erg/g}$        $dT = 20^\circ \text{ K}$

$dP = 0.725$        $P_2 - P_1 = .725$

$P_2 = 0.725 + P_1 = 1 + 0.725 = 1.725$

**Example:** Liquid helium – 4 has normal boiling point of 4.2 k. However, at pressure at 1 mm of mercury it boils at 1.2 k. Estimate the average latent heat of vaporization of helium in this temperature range.

**Solution:** 
$$\frac{dP}{dT} = \frac{L}{T(V_g - V_e)} = \frac{L}{TV_g}$$

$$PV_g = RT \quad V_g = \frac{RT}{P}$$

$$\frac{dP}{dT} = \frac{L}{T \frac{RT}{P}} \Rightarrow \frac{dP}{dT} = \frac{LP}{RT^2}$$

$$\int_{P_0}^P \frac{dP}{P} = \frac{L}{R} \int_{T_0}^T \frac{dT}{T^2} \quad \ln \frac{P}{P_0} = \frac{L}{R} \left( \frac{1}{T_0} - \frac{1}{T} \right) \quad L = \frac{R \ln \frac{P}{P_0}}{\frac{1}{T_0} - \frac{1}{T}}$$

$$P_0 = 746 \text{ mm} \quad T_0 = 4.2 \text{ k}$$

$$P_1 = 1 \text{ mm} \quad T = 1.2$$

$$L = 93 \text{ J/mol.}$$

**Example:** Liquid helium boils at temperature  $T_0$  when its vapour pressure is equal to  $P_0$  we now pump on the vapour and reduce the pressure to much smaller value  $P$ . Assume that the Latent heat  $L$  is approximately independent of temperature and helium vapour density is much smaller than that of liquid, calculate the approximate temperature  $T_m$  of the liquid in equilibrium with its vapour at pressure  $P$ .

Express your answer in terms of  $L$ ,  $T_0$ ,  $P_0$ ,  $P_m$  and any other required constants.

**Solution:** 
$$\frac{dP}{dT} = \frac{L}{T\Delta V} \quad \Delta V = V_{gas} - V_{liq} \approx V_{gas}$$

$$\frac{dP}{dT} = \frac{LP}{RT^2} \quad \int_{P_0}^{P_m} \frac{dP}{P} = \frac{L}{R} \int_{T_0}^{T_m} \frac{dT}{T^2}$$

$$T_m = \frac{T_0}{1 + \frac{RT_0}{L} \ln \frac{P_0}{P_m}}$$



**Example:** In the phase transition from a liquid state to a vapour state. The heat of vapourisation  $L_v$  varies with temperature  $T$  as  $L_v = a - bT^{1/2}$ . Considering the gas as an ideal one at low pressure, show that the pressure  $P(T)$  at temperature  $T$  in terms of the critical pressure  $P_c(T_c)$  at critical temperature  $T_c$  is given by

$$\ln \left[ \frac{P(T)}{P_c(T_c)} \right] = \frac{a}{R} \left( \frac{1}{T_c} - \frac{1}{T} \right) + 2 \frac{b}{R} \left( \frac{1}{T^{1/2}} - \frac{1}{T_c^{1/2}} \right)$$

**Solution:** Clapeyron-Clausius equation for the phase transition from liquid to vapour is

$$\frac{dP}{dT} = \frac{L_v}{T(V_g - V_l)}$$

where  $L_v$  is the heat of vapourisation and  $V_l$  and  $V_g$ , respectively, denote the volume is the liquid and gas phase. For low pressure,  $V_g \gg V_l$

$$\frac{dP}{dT} = \frac{L_v}{TV_g}$$

Using  $L_v = a - bT^{1/2}$ , we have

$$\frac{dP}{dT} = \frac{a - bT^{1/2}}{TV_g}$$

For an ideal gas equation,  $PV_g = RT$ , and thus,

$$\begin{aligned} \frac{dP}{dT} &= \frac{(a - bT^{1/2})P}{RT^2} = \frac{(a - bT^{1/2})P}{RT^2} dT = \frac{a}{R} \frac{dT}{T^2} - \frac{b}{R} \frac{dT}{T^{3/2}} \\ \ln[P(T)] &= -\frac{a}{R} \frac{1}{T} + \frac{b}{R} \frac{1}{T^{1/2}} + C \end{aligned}$$

On subtracting equation above and rearranging, we have

$$\ln \left[ \frac{P(T)}{P_c(T_c)} \right] = \frac{a}{R} \left( \frac{1}{T_c} - \frac{1}{T} \right) + \frac{2b}{R} \left( \frac{1}{T^{1/2}} - \frac{1}{T_c^{1/2}} \right)$$

Derive Clausius-Clapeyron equation from Maxwell relation  $\left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V$ .

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

$$\delta Q = L dm$$

$$T \left( \frac{\partial P}{\partial T} \right)_V = \frac{L}{V_{vap} - V_{liq}} \quad \left( \frac{\partial P}{\partial T} \right)_V = \frac{L}{T(V_{vap} - V_{liq})}$$

(b) Draw Phase diagram for water and explain why water expand after freezing.

Phase diagram for water

The slope of solid liquid phase is negative.

So from Clausius:-

Clapeyron equation

$$\left(\frac{\partial P}{\partial T}\right)_{sat} = \frac{L}{T(V_{liq} - V_{solid})}$$

$$\left(\frac{\partial P}{\partial T}\right) = -ve \quad V_{liq} - V_{solid} < 0 \quad V_{liq} < V_{solid}$$

so water expand on freezing

