



**Discipline Course-I**

**Semester-II**

**Paper No: Thermal Physics : Physics-IIA**

**Lesson: Phase transition**

**Lesson Developer: Dr. Ajay Kumar**

**College/ Department: Deshbandhu College, Physics**

**Department, University of Delhi**

## Table of Contents

Chapter 13:	Phase transitions
	13.1 Introduction
	13.2 Phase change and latent heat
	13.3 Chemical potential
	13.4 Clausius-Clapeyron equation
	13.5 Classification of phase transitions
	13.5.1 First order phase transitions
	13.5.2 Second order phase transitions
	13.6 Gibb's phase rule
	13.7 Summary
	13.8 Exercises
	13.9 Glossary
	13.10 References

# Phase transitions

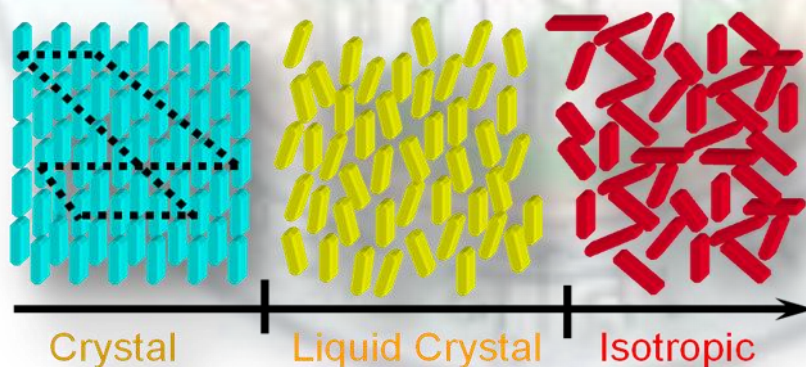
## Objectives

By reading this lesson, you will be able to understand;

- ✓ What is phase transition?
- ✓ How phase of a substance changes?
- ✓ How phase transitions are categorized?
- ✓ What is the Clausius-Clapeyron equation?
- ✓ What is Gibbs phase rule?
- ✓ The significance of studying phase transition in thermodynamics

## 13.1 Introduction

A phase of the matter may be defined as a thermodynamic system of which all the physical properties (such as density, refractive index, magnetization and chemical composition *etc.*) are essentially uniform. In simple words, a region of matter that is chemically uniform, physically distinct, and mechanically separable may be thought of a phase. We are familiar with different forms of water *i.e.* ice (solid), water (liquid), and vapor/steam (gas). These three forms are three different phases of the water. In general the distinct phases may be described as different states of matter such as gas, liquid, solid, plasma or Bose-Einstein condensate. Liquid crystals, the useful components of the display devices, form different meso-phases between solid and liquid phases. Below is given the cartoon showing the molecular arrangements in solid (crystal), liquid (isotropic) and liquid crystal phases (arrow represents the temperature).



**Figure 1:** Molecular arrangements in solid, liquid, and liquid crystals

The uniformity in the physical properties of certain phase is due to the uniform interactions such as attractive forces between the constituents forming the phase under some fixed external thermodynamic conditions *i.e.* temperature, pressure *etc.* However, the change in the external conditions may result into the change in the kind

## Phase transitions

and/or strength of the interactions, which in turn, gives some different phase. The ice (solid phase) when heated up to its melting point, changes into water (liquid phase) and water when further heated up to its boiling point changes into the gaseous phase. This phenomenon of transition of the matter from one to another phase is termed as phase transition. During a phase transition of a given medium, certain properties of the medium change and these are common occurrences observed in nature. The studies about the phase transitions of the materials are very important as they provide proper understanding of the phenomena and their applications in thermodynamics. In this lesson, we will discuss different aspects of phase transitions and their significance.

### 13.2 Phase change and latent heat

Often, the change in the state or phase of matter takes place when sufficient amount of heat (for a given amount of the matter) is transferred *i.e.* absorbed or released. The requirement of this heat energy is used to compensate the intermolecular attractive forces present in the matter itself. For example, in the atmosphere, during the evaporation of water molecule from the surface of any water body, heat energy is needed to overcome the molecular forces of attraction between water molecules. On the other hand, if the water vapor condenses back to a liquid or solid phase onto a surface, the heat energy absorbed (during evaporation) is released back onto the surface. During such phase transitions, the thermometer reading remains unchanged and the heat transferred for this process is known as Latent heat for that phase transition. Most of the natural phase transitions require latent heat and are listed under the category of first order phase transitions which will be discussed later. To have an idea about the required heat (as latent heat) for some substances in different phase changes is shown below:

Substance	Latent Heat Fusion kJ/kg	Melting Point °C	Latent Heat Vaporization kJ/kg	Boiling Point °C
Water	334	0	2260	100
Toluene	72.1	-93	351	110.6
Oxygen	13.9	-219	213	-183
Nitrogen	25.7	-210	200	-196
Hydrogen	58	-259	455	-253
Helium			21	-268.93
Carbon dioxide	184	-78	574	-57
Ammonia	339	-75	1369	-33.34

Now, the heat energy needed to increase the temperature of a substance can be calculated from the heat capacity which increases on addition of heat. The heat capacity can be expressed as;

$$C_{p/V} = T \left( \frac{\partial S}{\partial T} \right)_{p \text{ or } V} \quad (13.1)$$

## Phase transitions

For the phase transition to take place from a phase 1 to phase 2, the required heat energy is supplied at constant temperature (say  $T_C$ ) i.e. latent heat ( $L$ ) is expressed by:

$$L = \Delta Q_{rev} = T_C dS = T_C(S_2 - S_1) \quad (13.2)$$

Where  $S_1$  and  $S_2$  are the entropies of phase 1 and phase 2.

### 13.3 Chemical potential

During the phase transition the motion of material molecules takes place from one phase to another. In thermodynamics, the direction of motion of molecules is determined by the chemical potential ( $\mu$ ). The particles tend to move from a region of higher chemical potential towards having lower chemical potential. It may be understood as the generalization of "potential energy" such as gravitational potential. A ball can move from a higher gravitational potential to a lower gravitational potential (free fall) but opposite is not possible. In the same way, as molecules move, react, dissolve, melt, etc., they always tend to go from a higher chemical potential to a lower one. It may also be defined as Gibbs free energy per particle and in phase equilibrium; each co-existing phase has the same chemical potential. The co-existence of two phases of a matter has been shown below (Figure 2) where the solid line represents the phase co-existence and along this line  $\mu_1 = \mu_2$ .

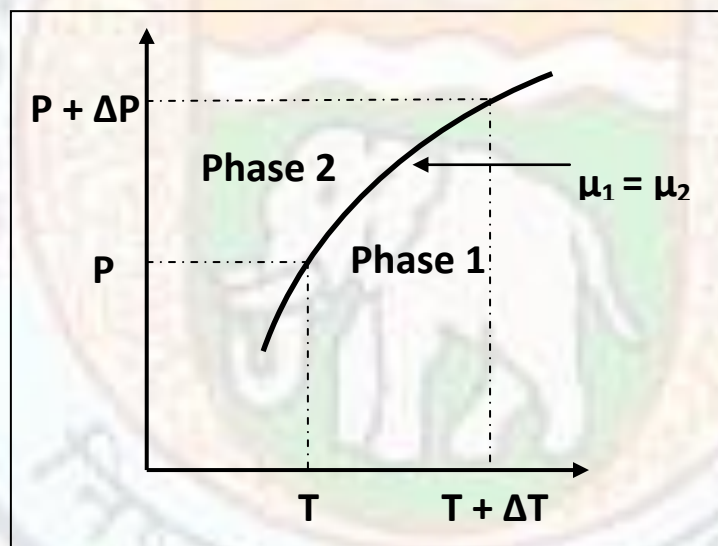


Figure 2: Phase diagram (in p-T plane) of a substance.

### 13.4 Clausius-Clapeyron equation

Now, let us find out the equation which describes the phase boundary in the pressure – temperature ( $p - T$ ) plane. Along the line of phase co-existence, the chemical potentials of both the phases will be the same and we can write:

$$\mu_1(p, T) = \mu_2(p, T) \quad (13.3)$$

And if we move along this phase boundary, we must have

## Phase transitions

$$\mu_1(p + dp, T + dT) = \mu_2(p + dp, T + dT) \quad (13.4)$$

So, for the changes of the pressure from  $p$  to  $p + dp$  and temperature from  $T$  to  $T + dT$ , we must have;

$$d\mu_1 = d\mu_2 \quad (13.5)$$

Now from the definition of chemical potential (in terms of Gibbs function) and the expression for the change in the Gibbs function:  $dG = -SdT + Vdp$ , we can have;

$$d\mu_1 = dG_1 = -S_1dT + V_1dp \quad (13.6)$$

And

$$d\mu_2 = dG_2 = -S_2dT + V_2dp \quad (13.7)$$

Along the line of co-existence of phases;

$$-S_1dT + V_1dp = -S_2dT + V_2dp$$

Where  $S_1$  and  $S_2$  are the entropies and  $V_1$  and  $V_2$  are the volumes per particle in phase 1 and phase 2 respectively.

Re-arrangement of the above equation;

$$-S_1dT + V_1dp = -S_2dT + V_2dp$$

Or

$$(S_2 - S_1)dT = (V_2 - V_1)dp$$

Or

$$\frac{dp}{dT} = \frac{(S_2 - S_1)}{(V_2 - V_1)} \quad (13.8)$$

Now from the definition of latent heat (equation 13.2), equation (13.8) may be written as;

$$\frac{dp}{dT} = \frac{L}{T(V_2 - V_1)} \quad (13.9)$$

Equation (13.9) is known as Clausius-Clapeyron equation. This equation represents the gradient of the phase boundary of the  $p - T$  plane which can be determined by the latent heat, the temperature at the phase boundary and the difference in volume between the two phases.

### **Did you know?**

- ✓ **Why food is cooked and we save fuel by using pressure cooker?**
- ✓ **Why is it difficult to make boiled potatoes and cook food at high altitudes?**

**Hint:** The volume of vapor is always greater than that of liquid *i.e.*  $V_2 > V_1$  and hence the value of  $\frac{dp}{dT}$  will always be positive which implies that the boiling point raises when pressure increases and vice-versa.

## Phase transitions

---

### Problems based on Clausius-Clapeyron equation:

**Example 1:** Calculate the change in the melting point of ice at 0°C when pressure is increased by 2 atm. How much pressure is required to lower the melting point by 1°C? [Latent heat for fusion=80 cal/g, specific volumes of water and ice are 1.0001 cm<sup>3</sup>/g and 1.0908 cm<sup>3</sup>/g].

**Solution:** Putting the values of L= 80 cal/g or 80x4.2x10<sup>7</sup> erg/g, V<sub>water</sub>=1.0001 cm<sup>3</sup>/g, V<sub>ice</sub>=1.0908 cm<sup>3</sup>/g, and T=0°C=273 K, we get

$$\frac{dp}{dT} = \frac{80 \times 4.2 \times 10^7}{273 \times (1.0001 - 1.0908)}$$

$$\frac{dp}{dT} = -13.57 \times 10^7 \text{ dyne/cmK}$$

But  $dp = 2 \text{ atm} = 2 \times 2.026 \times 10^6 \text{ dyne/cm}^2$ , so we get,

$$\begin{aligned} dT &= -\frac{2.026 \times 10^6}{13.57 \times 10^7} \\ &= -0.0149 \\ &\cong -0.015 \text{ K} \end{aligned}$$

Clearly, the melting point of the ice falls with pressure and as per above example this drop is about 0.0075K per atmosphere. The pressure required to lower the melting point by 1 K will be 1/0.0075=133 atm.

## Phase transitions

**Example 2: Find the equation in the  $p - T$  plane for the phase boundary between the liquid and solid phases of a substance.**

**Solution:** The gradient of the phase boundary in  $p - T$  plane can be written as Clausius-Clapeyron equation *i.e.*

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

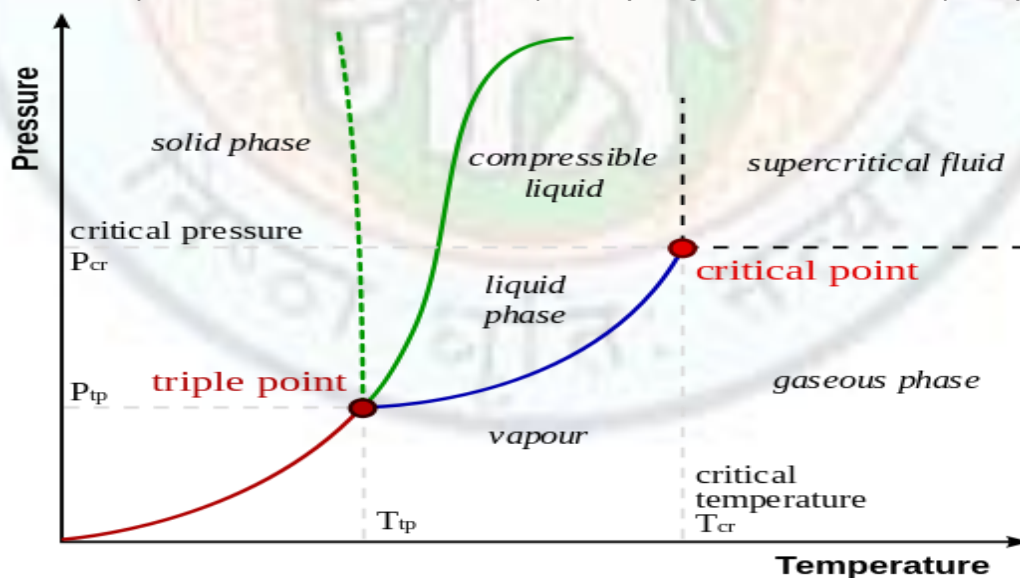
$$\text{Or, } dp = \frac{LdT}{T\Delta V}$$

Now neglecting the change in the values of latent heat and volume and integrating above equation, we get the required equation *i.e.*

$$\int dp = \frac{L}{\Delta V} \int \frac{dT}{T} + \text{Constant}$$

$$\text{or, } p = \frac{L}{\Delta V} \log\left(\frac{T}{T_0}\right) + p_0$$

Where  $T_0$  and  $p_0$  are constants such that;  $(T, p) = (T_0, p_0)$  is a point on phase boundary. Here, it can easily be shown that the gradient (inclination) of the **phase boundary** ( $= \frac{L}{\Delta V}$ ) **in the  $p - T$  plane is very steep** as the volume change  $\Delta V$  on melting is relatively small. Below is shown a typical phase diagram of water from which the steepness of the phase boundaries can be compared (Image taken from Wikipedia).





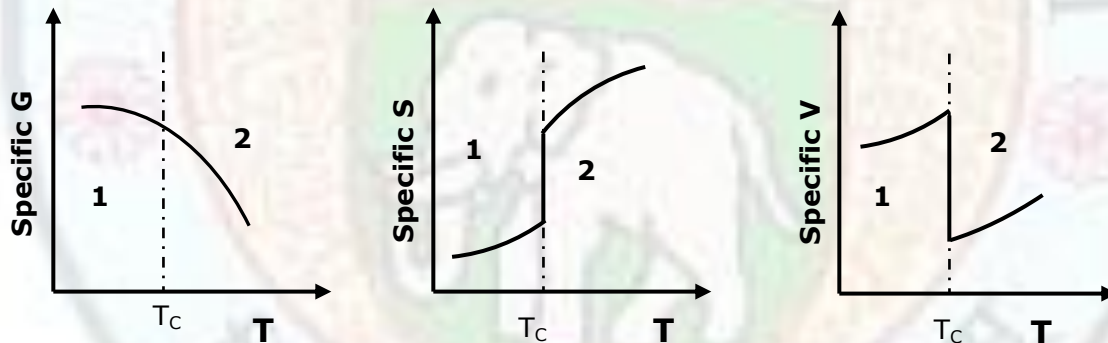
# Phase transitions

## 13.5 Classification of phase transitions

As discussed in section 13.2, most of the natural phase transitions occur at constant temperature and latent heat is required for such transitions to take place. On the other hand, some phase changes such as transition of material from ferromagnetic to paramagnetic phase at its Curie temperature, do not require latent heat. Depending upon whether latent heat is involved or not during a phase transition, P. Ehrenfest proposed a classification of phase transitions and categorized them as first and second order phase transitions.

### 13.5.1 First order phase transitions

Ehrenfest defined **order** of a phase transition as the order of the lowest differential of Gibbs function  $G$  (or  $\mu$ ) which shows a discontinuity at transition temperature. For the phase transitions which involve latent heat, the entropy shows a discontinuity. The entropy may be expressed as the first differential of Gibbs energy;  $S = \left(\frac{\partial G}{\partial T}\right)_p$  and hence, the phase transitions which involve the latent heat are first order phase transition *e.g.* transitions from solid to liquid, liquid to vapor *etc* at constant temperature. The volume may also be expressed as the first differential of Gibbs energy;  $V = \left(\frac{\partial G}{\partial p}\right)_T$  and it, too, shows discontinuity at phase transition. However, the Gibbs energy function itself is continuous. The variations of specific Gibbs function, entropy and volume with temperature have been shown below:



**Figure 3:** Temperature variation of specific Gibbs function, entropy, and volume in first order phase transition.  $T_c$  is the phase transition temperature.

**Example 3: Obtain the equation showing the temperature dependence of vapor pressure for the first order phase transition if the variation of latent heat with temperature is neglected and vapor may be assumed to behave like an ideal gas.**

## Phase transitions

**Solution:** For the first order phase transition, we may use Clausius-Clapeyron heat equation;

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

Suppose  $V_1$  and  $V_2$  are the molar volumes of the liquid and vapor respectively. Clearly,  $V_1 \ll V_2$  and hence may be ignored. With the ideal gas equation, we can express  $V_2$  as;

$$V_2 = \frac{RT}{p}$$

With this value of  $V_2$ , we have;

$$\left(\frac{dp}{dT}\right)_{\text{vapor}} = \frac{L_{\text{vapor}} p}{RT^2}$$

or

$$\left(\frac{dp}{p}\right)_{\text{vapor}} = \frac{L_{\text{vapor}} dT}{RT^2}$$

Integration of above equation gives;

$$\ln p = -\frac{L_{\text{vapor}}}{RT} + \text{Constant } (K)$$

On taking antilogarithms on both sides, we get the required equation i.e.

$$p = K_0 \exp\left[-\frac{L_{\text{vapor}}}{RT}\right]$$

Clearly, the vapor pressure decreases exponentially with temperature.

### Second latent heat equation: Clausius equation

Consider a first order phase transition take place at constant temperature  $T$  and pressure  $p$ . The latent heat involved in this transition can be obtained as;

$$L = T\Delta S$$

where  $\Delta S = S_2 - S_1$  is the difference in the entropies of phase 2 and phase 1 respectively. We may write above equation as'

$$\Delta S = S_2 - S_1 = \frac{L}{T}$$

$$\text{or, } \frac{d}{dT}\left(\frac{L}{T}\right) = \frac{d}{dT}(S_2 - S_1)$$

## Phase transitions

$$\text{or, } \frac{d}{dT} \left( \frac{L}{T} \right) = \frac{d}{dT} (S_2 - S_1)$$

$$\text{or, } \frac{1}{T} \frac{dL}{dT} - \frac{L}{T^2} = \frac{dS_2}{dT} - \frac{dS_1}{dT}$$

$$\text{or, } \frac{dL}{dT} - \frac{L}{T} = T \frac{dS_2}{dT} - T \frac{dS_1}{dT}$$

But from the definition of heat capacity:  $C = T \left( \frac{dS}{dT} \right)_p$ , we can have;

$$\frac{dL}{dT} - \frac{L}{T} = (c_2)_{sat} - (c_1)_{sat} \quad (13.10)$$

Equation (13.10) is known as *second latent heat equation* and is helpful in determining the specific heat capacity of saturated vapor. It may be noted that the molar heat capacities of two phases are defined for **constant saturation** rather than constant temperature or pressure. On raising the temperature of a saturated vapor, it becomes unsaturated and to keep it saturated, we have to decrease its volume by applying pressure from outside. The pressure and volume, in this way, undergo a change and may have to be adjusted to maintain the vapor pressure to a constant. Moreover, due to the application of pressure and hence the external work done appears as heat to raise its temperature. That is why the specific heat capacity is defined for constant saturation and not with reference to constant pressure or volume. Depending upon the heat of compression, there may be three possibilities regarding the specific heat capacity:

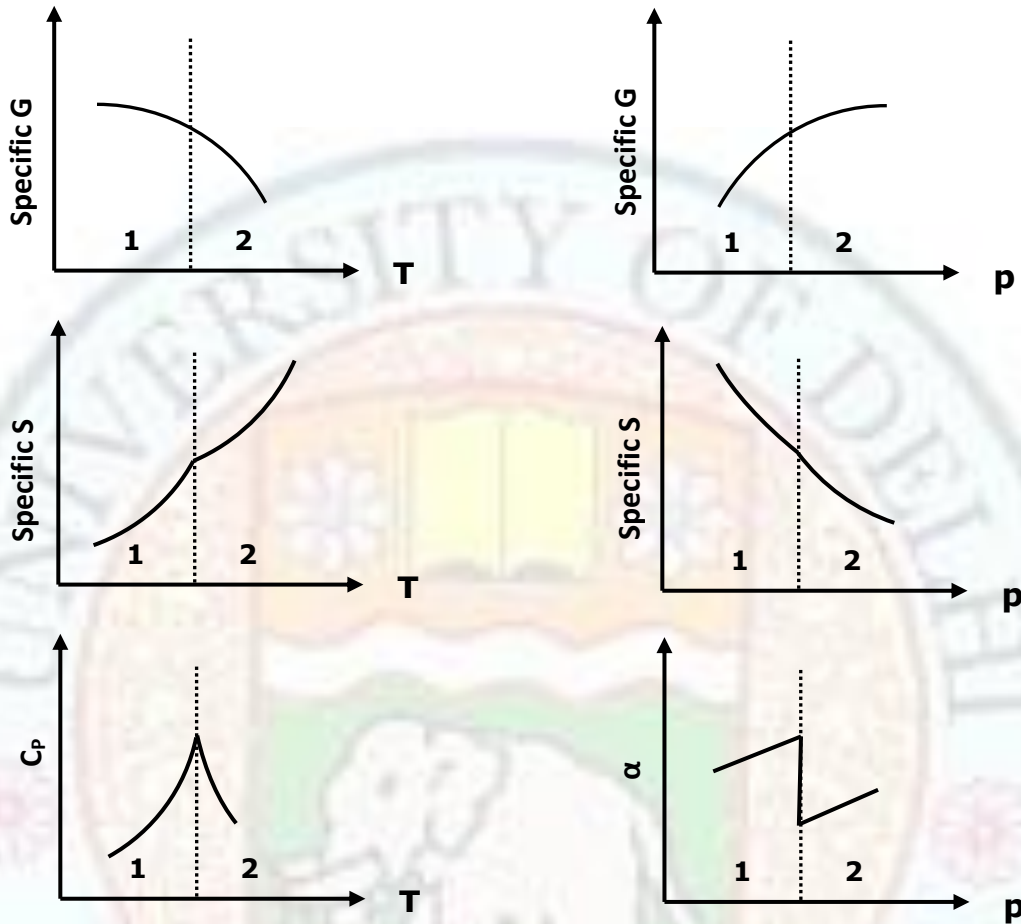
- 1 If heat of compression is just equal to the total heat needed to raise the temperature of the vapor through 1°C and no heat is transferred to the system, then specific heat capacity of vapor will be zero.
- 2 If heat of compression is less than the total heat needed to raise the temperature of the vapor through 1°C and a net amount of heat is supplied to the system then specific heat capacity of vapor will be positive.
- 3 If heat of compression is greater than the total heat needed to raise the temperature of the vapor through 1°C and a net amount of heat is removed from the system then specific heat capacity of vapor will be negative.

### 13.5.2 Second order phase transition

According to the definition proposed by Ehrenfest, the phase transitions in which the second derivatives of Gibbs function are discontinuous whereas the Gibbs function and its first derivatives are continuous at phase transition are termed as second order phase transitions. The phase transition possessed by helium ( $^4\text{He}$ ) is a good example of phase second order phase transition. It has been observed that, during a phase transition of helium (also known as **lambda transition**), specific Gibbs energy, entropy and volume remain the same (continuous) but constant pressure heat capacity and isobaric volume expansivity ( $\alpha$ ) show discontinuity at transition point. The transition of conductors in their superconducting states and order-disorder transition in  $\beta$ -brass are some other examples of second order. The

## Phase transitions

continuity/discontinuity of thermodynamic entities during second order phase transition is shown below:



**Figure 4:** Pictorial representation of second order phase transition

### Ehrenfest's equation for second order phase transition

Let us assume that a second order phase transition occur at temperature  $T$  and pressure  $p$ . Being a continuous function, the value of entropy remains the same in such a transition and we may write;

$$S_1 = S_2 \tag{13.11}$$

where subscripts 1 and 2 represents phase 1 and 2 respectively.

Now, suppose the pressure of the system changes from  $p$  to  $p + \Delta p$ , when its temperature is raised from  $T$  to  $T + \Delta T$  and if the resulting changes in entropy values in phase 1 and 2 be  $dS_1$  and  $dS_2$  then;

$$S_1 + dS_1 = S_2 + dS_2$$

## Phase transitions

---

or

$$dS_1 = dS_2 \quad (13.12)$$

Here, we may take entropy as a function of p and T i.e.

$$S = S(T, p)$$

$$\text{or } dS = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp$$

$$\text{or } dS = \left(\frac{\partial S}{\partial T}\right)_p dT - \left(\frac{\partial V}{\partial T}\right)_p dp \quad (\text{Using II Maxwell equation})$$

$$\text{or } dS = \frac{C_p}{T} dT - V \alpha dp$$

where  $C_p = T \left(\frac{\partial S}{\partial T}\right)_p$  is specific heat capacity at constant pressure and  $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p$  is isobaric volume expansivity.

Since specific volume, too, is continuous in second order phase transition, we can write;

$$dS_1 = \frac{C_{p1}}{T} dT - V \alpha_1 dp \quad \text{and}$$

$$dS_2 = \frac{C_{p2}}{T} dT - V \alpha_2 dp$$

With the values of  $dS_1$  and  $dS_2$ , equation (13.12) yields;

$$\frac{dp}{dT} = \frac{C_{p2} - C_{p1}}{TV(\alpha_2 - \alpha_1)} \quad (13.13)$$

Similarly, we may start by taking into account the continuity of volume during the second order phase transition to obtain the following result;

$$\frac{dp}{dT} = \frac{(\alpha_2 - \alpha_1)}{\beta_{T2} - \beta_{T1}} \quad (13.14)$$

where  $\beta_{T1}$  and  $\beta_{T2}$  are coefficients of isothermal compressibility's in phase 1 and phase 2 respectively. Equations (13.13) and (13.14) are known as Ehrenfest equations for second order phase transition.

## Phase transitions

### ***Did you know?***

- ✓ **Why Clausius-Clapeyron equation can not be used for second order phase transition?**

**Hint:** In a second order phase transition, latent heat is not required ( $L=0$ ) and volume remains the same *i.e.* ( $V_2-V_1$ ) will be zero. With these values, the right hand side of the Clausius-Clapeyron equation becomes indeterminate.

- ✚ **Infinite-order phase transitions:**

There are some continuous phase transitions which break no symmetries. Such transitions are called as infinite-order phase transitions. The most famous example is the **Kosterlitz–Thouless transition** in the two-dimensional XY model. Many quantum phase transitions such as observed in two-dimensional electron gases come into this category.

### **13.6 Gibbs phase rule**

Gibbs rigorously studied and analyzed the thermodynamic properties of heterogeneous systems (mixtures) having one and more than one different substances or **components** in their various combination of phases in equilibrium with each other. Based on his results, he introduced a method to find out the number of degrees of freedom ( $F$ ) the system may have while keeping the different phases in equilibrium with each other. The expression showing the possible degrees of freedom of a system in terms of number of components ( $C$ ) and number of different phases ( $\phi$ ) is known as Gibbs phase rule. Let us discuss the formulation of this rule in brief.

Consider a heterogeneous system having  $C$  components each of which can be in any one of  $P$  different phases. We may characterize the system by taking into account the intensive variables: the pressure  $p$ , temperature  $T$ , and the mole fractions of the components for each of  $\phi$  phases. We may take the value for mole fractions  $C\phi$ .

The mole fraction ( $x_i$ ) for a multi-component system may be defined as the ratio of the number of moles  $N_i$ , of the  $i^{\text{th}}$  substance and the total number of moles  $N$  present in the system *i.e.*

$$X_i = \frac{N_i}{N}$$

And by the definition, we may write;

$$\sum_i^C X_i = 1 \quad (13.15)$$

So, the total number of variables for characterization of a heterogeneous system may be taken as;

## Phase transitions

---

$$\text{Total number of variables} = 2 + C\phi \quad (13.16)$$

Here the number 2 corresponds to two variables  $p$  and  $T$ . The term  $C\phi$  represents the system's variables due to the combination of components and their different phases.

Now, at the phase equilibrium condition, the specific Gibbs function or chemical potential of one component in each of the different phases will be the same *i.e.*

$$\mu_1^{(1)} = \mu_1^{(2)} = \mu_1^{(3)} \dots \dots = \mu_1^{(\phi)} \quad (13.17)$$

Similarly, for the heterogeneous system having  $C$  components, we may write the following equations:

$$\mu_1^{(1)} = \mu_1^{(2)} = \mu_1^{(3)} \dots \dots = \mu_1^{(\phi)}$$

$$\mu_2^{(1)} = \mu_2^{(2)} = \mu_2^{(3)} \dots \dots = \mu_2^{(\phi)}$$

.....

$$\mu_C^{(1)} = \mu_C^{(2)} = \mu_C^{(3)} \dots \dots = \mu_C^{(\phi)}$$

Above equations,  $C(\phi - 1)$  in number, are known as equations of phase equilibrium. These equations express the fact that the chemical potential of a constituent in one phase must be equal to the chemical potential of the same constituent in every other phase.

Among the total variables given by equation (13.16), we have two types of equations: equation (13.15), which are  $\phi$  in numbers, and equations of phase equilibrium. Hence the total number of equations will be;

$$\text{Total number of equation} = C(\phi - 1) + \phi \quad (13.16)$$

So, the variance or degrees of freedom  $F$  for the system is given by;

$$F = \text{number of variables} - \text{number of equations}$$

$$\text{Or,} \quad F = C\phi + 2 - [C(\phi - 1) + \phi]$$

$$\text{Or,} \quad F = C - \phi + 2 \quad (13.17)$$

This is known as **Gibbs phase rule**.

## Phase transitions

### Example

#### **For a single component system:**

In this case, we have  $C=1$  and hence the degrees of freedom  $F$  will be given by  $F = 3 - \Phi$ , so,

- If there is one phase *i.e.*  $\Phi = 1$ , then  $F = 2$ ; which means the system possesses two degrees of freedom (*vis.* pressure  $p$  and temperature  $T$ ) and the whole  $p - T$  plane is accessible.
- If there are two phases *i.e.*  $\Phi = 2$ , then  $F = 1$ ; which means the system possesses only one degree of freedom. One can vary either  $p$  or  $T$  and yet keep equilibrium *i.e.* these two phases can only coexist at a common line of coexistence in the  $p - T$  plane.
- For three phases *i.e.*  $\Phi = 3$ , we have  $F = 0$ ; and these three phases can only coexist at a common point (**triple point**) of coexistence in the  $p - T$  plane.

#### **For a two component system:**

In such a case we have  $C = 2$ , and hence the degrees of freedom will be  $F = 4 - \Phi$ . Now if pressure is fixed, the system will remain  $3 - \Phi$  degrees of freedom and the remaining two variables will be the temperature  $T$  and the mole fraction (say  $X_1$ ) of first component. The mole fraction of the second component will be  $(1-X_1)$ , so,

- For the system having only one phase,  $F = 2$ , and the whole  $X_1 - T$  plane is accessible.
- If there are two phases,  $F = 1$  and these two phases can only coexist at a common line of coexistence in the  $X_1 - T$  plane.
- For three phases, we have  $F = 0$ ; and these three phases can only coexist at a common point of coexistence in the  $X_1 - T$  plane.

### 13.7 Summary



## Phase transitions

- ✓ **Phase transition** is a process in which a thermodynamic system changes from one state to another with different physical properties.
- ✓ **Latent heat** is related to the change in entropy at a first order phase transition.
- ✓ **The condition** for equilibrium of two phases to coexist at constant temperature and pressure is  $G_1 = G_2$  or  $\mu_1 = \mu_2$

- ✓ The **Clausius-Clapeyron equation** states that;

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

This equation is used to determine the shape of the phase boundary.

- ✓ According to **Ehrenfest**, the first differentials of the Gibbs free energy are discontinuous in first order phase transitions and the latent heat is required for such transitions.
- ✓ The phase transitions, in which the **second derivatives of Gibbs free energy** are discontinuous at phase transition, are second order phase transitions.

- ✓ The coexistence of phases in a second order phases transition is governed by **Ehrenfest equations** given by;

$$\frac{dp}{dT} = \frac{C_{p2} - C_{p1}}{TV(\alpha_2 - \alpha_1)}$$

And

$$\frac{dp}{dT} = \frac{(\alpha_2 - \alpha_1)}{\beta_{T_2} - \beta_{T_1}}$$

- ✓ According to the **Gibbs phase rule**, the number of degrees of freedoms  $F$  of a heterogeneous system is related to the components  $C$  and phases  $\Phi$  as;

$$F = C - \Phi + 2$$

### 13.8 Exercises

#### Long answer type questions:

## Phase transitions

---

1. What is phase transition? Discuss the classification of phase transition with examples.
2. Deduce Clausius-Clapeyron heat equation. Discuss the effect of pressure on the freezing point of ice with the help of this equation.
3. Derive Ehrenfest equation for second order phase transition.
4. State Gibbs phase rule and discuss about the degrees of freedom of a heterogeneous system in concern with it.
5. Represent the behavior of specific Gibbs function, entropy, volume and heat capacity with temperature by drawing plots for first and second order phase transitions.

### **Short answer type questions:**

1. What is latent heat? How is it related with the phase change of the matter?
2. Write down the significance of Clausius-Clapeyron heat equation.
3. What is continuous phase transition? Why is it named so?
4. What is order-disorder phase transition? Give examples.
5. Give two examples of first and second order phase transition.
6. What is lambda transition? Discuss with an example.

### **Fill in the blanks:**

1. The condition for equilibrium of two phases to coexist at constant temperature and pressure is.....
2. Melting of ice in the air is an example of .....order phase transition.
3. First order phase transitions are those in which .....heat involved.
4. Liquid crystals forms different ..... in between solid and liquid.
5. Entropy is continuous in a .....order phase transition.
6. Symmetry does not break in ..... order phase transition.
7. Volume remains unchanged during .....order phase transition.
8. The number of variance of a heterogeneous system are determined by ..... rule.
9. Second order phase transition are governed by ..... equation.
10. During first order phase transition, the heat is added to the system at constant .....
11. The transition from conductor to superconductor and sublimation are examples of .....order and .....order phase transitions.
12. The helium in its superfluid state possess ..... viscosity.

## 13.9 Glossary

**Bose–Einstein condensate:** It is a state of matter where a dilute gas of bosons is cooled at temperatures very close to absolute zero (0 K). In such conditions, a large fraction of bosons occupy the lowest quantum state.

**Mesophase:** A mesophase is a state of matter which possesses the properties of both i.e. solid and liquid. Gelatin is a common example of a partially ordered structure in a mesophase.

## Phase transitions

---

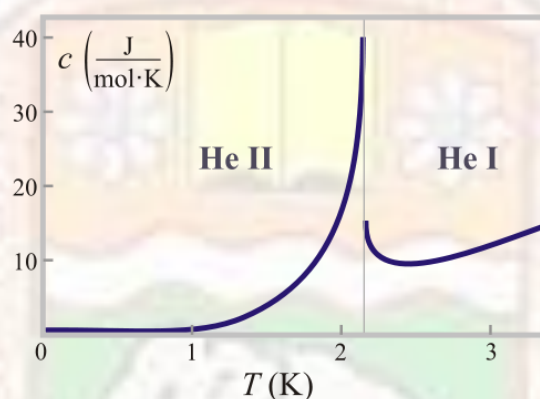
**Phase boundary:** It is a spatial interface between two or more phases of the matter due to the immiscibility of one phase with that in other side of the boundary.

**Critical point:** The critical point can be understood as a set of co-ordinates (thermodynamic conditions) on a phase diagram where no phase boundaries exist.

**Triple point:** The triple point of a substance is the temperature and pressure at which the three phases *i.e.* solid, liquid and gas of that substance coexist in equilibrium.

**Supercritical fluid:** A supercritical fluidity is a condition (temperature and pressure) of a substance above its critical point, where distinct liquid and gas phases do not exist.

**Lambda transition:** It is the phase transition observed in helium at 2.2 K where it undergoes a phase change to superfluidity. The name  $\lambda$  is due to the shape of the specific heat vs. temperature curve which is shown below (Image taken from [en.Wikipedia.org](http://en.Wikipedia.org)).



### 13.10 References

**Book cited:**

Concepts in Thermal Physics: by S. J. Blundell and K. M. Blundell, (Oxford University Press, 2006).

**Further readings**

1. Thermodynamics by Enrico Fermi (Courier Dover Publications, 1956)
2. Thermal Physics by Garg, Bansal and Ghosh (Tata McGra-Hill, 1993)
3. A Treatise on Heat: Including Kinetic Theory of Gases, Thermodynamics and Recent advances in Statistical Thermodynamics by Meghnad Saha, B.N. Srivastava (Indian Press, 1958).