UNIT 1

SOLUTIONS-I

Structure

1.1 INTRODUCTION

A solution may be defined as a homogeneous mixture of two or more substances, the composition of which may vary. It consists of two components, solute and solvent. Generally, the substance which is present in larger proportion is called the *solvent* and the substance which is present in smaller proportion is called the *solute*. Depending upon the number of constituents, a solution may be referred to as *binary* (two components), *ternary* (three components) or *quaternary* (four components). Depending upon the state of the solute and the solvent, there are nine types of solutions. The concentration of a solution can be expressed in different ways, e.g., molarity, molality, mole fraction, etc. The solubility of solids in liquids generally increases with rise in temperature. The solubility of gases in liquids is

A solution is always in the same physical state as the solvent irrespective of the relative proportions of the two components.

governed by Henry's law. Liquid solutions obeying Raoult's law are called *ideal solutions* and those solutions whichdo not obey Raoult's law are called *non-ideal solutions*. In this unit, we shall discuss the above aspects .In addition,you will also study about distillation of ideal and non-ideal solutions. Here, we will also discuss lever rule and the principle of fractional distillation.

In the next unit, we shall study partially miscible and completely immiscible liquid pairs.

Expected Learning Outcomes

After studying this unit, you should be able to:

- define a solution;
- list various types of solutions;
- express concentration of solutions in different ways;
- define solubility;
- explain the solubility curves;
- state Henry's law;
- state Raoult's law;
- distinguish between ideal and non-ideal solutions;
- draw and describe Raoult's law curves for ideal and non-ideal solutions;
- explain distillation of ideal and non-ideal solutions using boiling point-composition diagrams;
- describe the principle of fractional distillation; and
- define the term 'azeotrope' and give some examples of azeotropes.

Solutions of substances in water are called aqueous solutions while solutions in other solvents are called non-aqueous solutions. Solutions of mercury in metals are called amalgams e.g., sodium amalgam, zinc amalgam, etc. Amalgamation modifies the properties of metals. For example, sodium metal is a powerful reducing agent whereas sodium amalgam is a moderate reducing agent.

1.2 TYPES OF SOLUTIONS

A solution may exist in solid, liquid or gaseous state. Depending upon the physical state, a solution may be classified into various types as shown below in Table 1.1.

Table 1.1: Types of Solutions

Solute	Solvent	Example
Gas	gas	mixture of gases (e.g., air)
Gas	liquid	aerated water (which is a solution of CO_2 in water under pressure
Gas	solid	Gas absorbed by metals orminerals (e.g. H_2 in palladium)
liquid	gas	moist air
liquid	liquid	alcohol in water
liquid	solid	mercury in zinc (zinc amalgam)
solid	gas	camphor in air
solid	liquid	salt in water
solid	solid	alloys (e.g., brass)

In this unit, we shall study solid-liquid, gas-liquid and liquid-liquid solutions.

SAQ 1

Classify the following into the types of solutions to which they belong:

i) A five rupee coin

ii) Sodium amalgam

iii) Soda water

1.3 DIFFERENT MODES OF EXPRESSING CONCENTRATION OF SOLUTIONS

The relative amounts of a solute and a solvent in a solution are expressed through concentration terms. Some of the ways of expressing the concentration of a solution are described below:

i) Molarity (*M*)

Molarity is defined as the *number of moles of the solute present in 1 dm^3 (1 L or 10^{-3} m^3) of the solution*. When 0.1 mole of a solute is present in one cubic decimeter of the solution, we say that the solution is 0.1 molar (0.1 M).

A solution containing *x* mol of a substance in 1 dm^3 of a solution is called *x* molar or *x* M solution.

$$\text{Molarity } (M) = \frac{\text{Number of moles of the solute}}{\text{Volume of the solution in dm}^3} \quad \ldots (1.1)$$

Note that the volume of the solution should be expressed in dm^3 (or litre) for expressing the concentration in terms of molarity.

ii) Molality (*m*)

Molality is defined as the *number of moles of a solute present in one kilogram of the solvent.* When on mole of a solute is dissolved in one kilogram of water, the concentration of the solution is one molal (1 m).

Strength is defined as the mass of the solute (in gram) present in 1 dm^3 (or I L) of the solution.

$$\text{Molality } (m) = \frac{\text{Number of moles of the solute}}{\text{Mass of the solvent in kg}} \quad \ldots (1.2)$$

iii) Normality (*N*)

The *number of gram-equivalents of a solute present in 1 dm^3* (or IL) *of the solution* is called its normality. A one normal solution contains one gram-equivalent of a solute 1 dm^3 of solution and is denoted by 1 N.

The sum of the mole fractions of all the components in a solution is always equal to one.

$$\text{Normality } (N) = \frac{\text{Strength in g dm}^{-3}}{\text{Equivalent weight}} \quad \ldots (1.3)$$

iv) Mole fraction (*x*)

The mole fraction of a solute in a solution is the *ratio of the number of moles of the solute to the total number of moles of the solute and the solvent in a*

solution. If n_2 moles of a solute are dissolved in n_1 moles of solvent, the mole fractions of the solvent and the solute are given by the following expressions:

$$\text{Mole fraction of the solvent } (x_1) = \frac{n_1}{n_1 + n_2} \quad \ldots (1.4)$$

$$\text{Mole fraction of the solute } (x_2) = \frac{n_2}{n_1 + n_2} \quad \ldots (1.5)$$

v) Percentage

Unless specified, a 10% solution may always be taken as weight by weight (*W/W*).

In terms of percentage, the concentration of a solution may be expressed in the following four different ways:

10 mL alcohol present in 100 mL of solution = 10%(*V/V*)

10 g NaCl present in 100 mL of solution = 10%(*W/V*)

10 mL alcohol present in 100 g of solution = 10%(*V/W*)

10 g NaCl present in 100 g of solution = 10%(*W/W*)

All concentration units except mole fraction, molality, ppm, ppb and percentage (*W/W*), vary with temperature.

vi) Parts per million (ppm)

When a solute present in the solution is in very minute amounts, the concentration is usually expressed in parts per million (ppm). For example, the amount of oxygen dissolved in sea water is 5.8 g in 10^6 (1 million) gram of sea water. It means 5.8 parts of oxygen are present in one million parts of sea water. Hence, the concentration of oxygen in sea water is 5.8 ppm. The concentration of gases which pollute the atmosphere is also expressed in ppm.

$$\text{ppm of solute} = \frac{\text{Mass of solute (g))}}{\text{Tota mass of solution (g)}} \times 10^6 \quad \ldots (1.6)$$

Similar to Eq. 1.6., parts per billion (ppb) may be defined as follows.

$$\text{ppb of solute} = \frac{\text{Mass of solute (g))}}{\text{Tota mass of solution (g)}}$$

Let us work out an example using the molarity expression explained above.

Example 1

Concentrated sulphuric acid contains 98% acid by mass. Its density is 1.85 x 10^3 kg m^{-3}. Calculate its molarity.

1 m = 10 dm

1 m^3 = $(10\ dm)^3$

= 10^3 dm^3

Solution

$$\text{Molarity of sulphuric acid} = \frac{\text{Number of moles of sulphuric acid}}{\text{Volume in dm}^3}$$

Consider 1m^3 volume of the concentrated sulphuric acid.

$$= \frac{\text{Mass of sulphuric acid in 1 m}^3}{\text{Molar mass} \times 10^3\ \text{dm}^3}$$

$$= \frac{98 \times \text{mass of 1 m}^3 \text{ conc. sulphuric acid}}{100 \times \text{molar mass} \times 10^3\ \text{dm}^3}$$

$$= \frac{98 \times 1.85 \times 10^3 \text{ kg}}{100 \times 0.098 \text{ kg mol}^{-1}} \times \frac{1}{10^3 \text{ dm}^3}$$

= 18.5 M

SAQ 2

A solution contains 0.100 kg each of water and ethanol. Find the mole fraction of each component.

1.4 SOLUTIONS OF SOLIDS IN LIQUIDS

In solutions of solids in liquids, the liquid is referred to as the solvent and, the solid which is dissolved in it, as the solute. When a solid is added gradually to a given amount of a liquid (solvent) at constant temperature, a state is reached when some of the solid remains undissolved. The solution is then said to be *saturated.* The mass of the solute that the can be dissolved in 0.100 kg (or 100 g) of a solvent to form a saturated solution at a given temperature is called its **solubility.**

Solubility of a solid in a liquid varies with temperature. The plot of solubility against temperature is called the *solubility curve*. Some typical solubility curves are shown in Fig. 1.1.

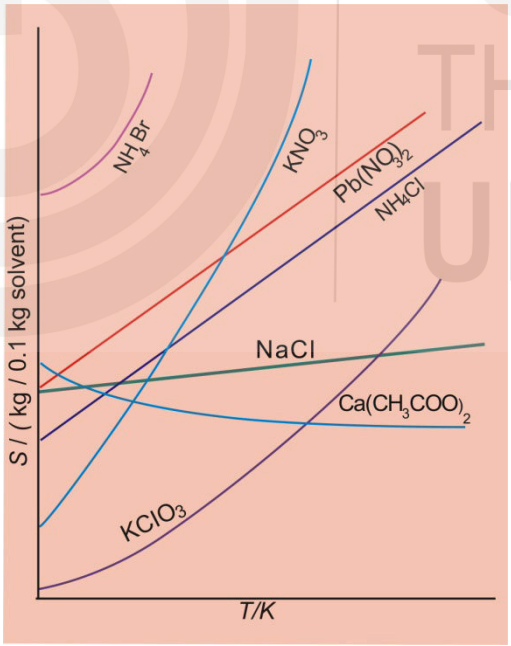


Fig. 1.1: Solubility curves of different solutes: *S* stands for solubility and *T* for temperature.

The solubilities of many of the ionic substances in water increase with temperature. The solubility of sodium chloride increases to a very small extent with rise in temperature. However, the solubility of calcium acetate decreases with rise in temperature.

In many cases, when a solute is dissolved in a solvent, heat is absorbed, i.e., cooling results. Then, according to Le Chatelier's principle, when the

According to Le Chatelier's principle, if a system under equilibrium is subjected to a change of concentration, pressure or temperature, the equilibrium shifts in such a way that tends to undo the effect of that change.

temperature of a saturated solution in contact with the solute is raised, a change will take place such that there is absorption of heat, i.e., along the direction in which cooling takes place. The solubility of the substance will, therefore, increase with rise in temperature.

The dissolution of some salts in water (e.g., calcium salts of organic acids) is accompanied by evolution of heat. Evidently, the solubility of such salts decreases with rise in temperature.

1.5 SOLUTIONS OF GASES IN LIQUIDS

Most of the gases dissolve in water or some other liquids to a greater or a lesser extent. In a gas, the molecules are quite far apart. After dissolution in a liquid solvent, the molecules of the gas come much closer. It is just like saying that before a gas dissolves in a liquid, it must be condensed to give a liquid. The condensation of gas is an exothermic process. The enthalpy of condensation is larger than the enthalpy of solution. Thus, the dissolution of a gas is an exothermic process (i.e., heat is evolved).

The solubility of a gas in a liquid is measured in terms of absorption coefficient or Bunsen coefficient. This coefficient has been named after the scientist, Bunsen, who introduced it. It is denoted by α. It is defined as the volume of a gas at normal (earlier called standard) temperature and pressure (273.15 K and 1.013 x 10^5 Pa) dissolved by unit volume of the solvent at the temperature of the experiment and under a pressure of 1.013 x 10^5 Pa. The absorption coefficients of some gases are given in Table 1.2.

Table 1.2: Absorption Coefficients at 293 K

Solvent	Carbon dioxide	Hydrogen	Oxygen	Nitrogen
Water	0.88	0.018	0.028	0.015
Ethanol	3.00	0.081	0.142	0.130
Benzene	–	0.060	0.165	0.105

Factors affecting the solubility of gases

The solubility of a gas in a liquid depends upon

- temperature,
- pressure,
- nature of the gas and the solvent.

We will now consider each of these factors separately.

1. Effect of temperature

The dissolution of a gas in a liquid is an exothermic process. Hence, according to Le Chatelier's principle, the solubility of a gas in a liquid decreases with rise in temperature. This behaviour can be seen when bubbles of dissolved air escape on heating water below 373 K.

2. Effect of pressure – Henry's law

The solubility of solids in liquids is not so much affected by pressure as the volume changes are not so high. But the solubility of a gas in a liquid varies considerably with pressure. In 1803, the English Chemist, Henry found that the solubility of a gas increases as the gas pressure is increased at a given temperature. He proposed the generalisation which is known as Henry's law. It may be stated as follows:

"At constant temperature, the partial pressure of a gas over a solution is directly proportional to the concentration of the gas in the solution."

For example, doubling the pressure of oxygen, doubles the amount of oxygen that will dissolve in a given amount of the solvent.

Mathematically, Henry's law is expressed as follows:

$$p = Kx \qquad \ldots (1.7)$$

where p is the partial pressure of the gas over the solution and x is the solubility of the gas in terms of its mole fraction in the solution; K is a constant, characteristic of the specific combination of the solvent and the gas. It is called Henry's law constant. The partial pressure is expressed in terms of pascal (Pa).

From Eq. 1.7, the Henry's law constant is given as

$$K = \frac{p}{x} \qquad \ldots (1.8)$$

K has the dimensions of pressure. Here, K is not constant, as expected from Eq. 1.8 because of non-ideality of the solution. Its value is obtained by plotting the ratio p / x vs x and extrapolating to $x = 0$. Such a graph is shown in Fig. 1.2.

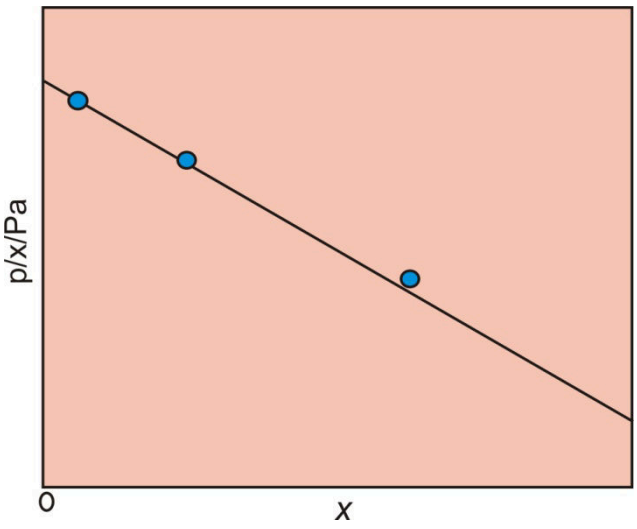


Fig. 1.2: Evaluation of Henry's law constant.

Henry's law constant for some gases are given in Table 1.3.

Table 1.3: Henry's Law Constant at 298 K

	$K/10^9$ Pa	$K/10^9$ Pa
Gas	**In water**	**In benzene**
H_2	7.12	0.37
N_2	8.68	0.24
O_2	4.40	-
CO	5.80	0.16
CO_2	0.17	0.01

It has been found that Henry's law is followed most closely by dilute solutions of gases that do not react with the solvent. Thus, the law is not valid for the solubility of hydrogen chloride or ammonia in water. Hydrogen chloride ionises in water and ammonia enters into chemical combination with water.

$$H_2O + HCl \rightleftharpoons H_3O^+ + Cl^-$$

$$H_2O + NH_3 \rightleftharpoons NH_4OH \rightleftharpoons NH_4^+ + {}^-OH$$

3. Nature of the gas and the solvent

Generally, gases which react chemically with the solvent are more soluble in it than in other solvents. For example, hydrogen chloride gas is more soluble in water than in benzene. Gases which can be easily liquefied are more soluble in common solvents.

Example 2

The Henry's law constant for O_2 is 4.40×10^9 Pa. Calculate the molarity of oxygen in water at 298 K. The partial pressure of oxygen over the solution is 1.00×10^5 Pa. Assume that 1.00 dm^3 of the aqueous solution weighs 1.00 kg.

Solution

$K = 4.40 \times 10^9$ Pa

$p = 1.00 \times 10^5$ Pa

Mole fraction of oxygen,

$$x_{O_2} = \frac{n_{O_2}}{n_{O_2} + n_{H_2O}} = \frac{n_{O_2}}{n_{O_2} + (1.00/0.018)\ \text{mol}}$$

$$\cong \frac{n_{O_2}}{(1.00/0.018)\ \text{mol}} = \frac{n_{O_2}}{55.6\ \text{mol}}$$

The approximation is done as given above since the number of moles of O_2 is negligible in comparison to the number of moles of H_2O.

Substituting the values in Eq. 1.8, we get

$$4.40 \times 10^9 \text{Pa} = \frac{1.00 \times 10^5\ \text{Pa}}{n_{O_2}/55.6\ \text{mol}} = \frac{1.00 \times 10^5\ \text{Pa}}{n_{O_2}} \times 55.6\ \text{mol}$$

or $n_{O_2} = \frac{1.00 \times 10^5 \text{ Pa}}{4.40 \times 10^9 \text{ Pa}} \times 55.6 \text{ mol} = 1.26 \times 10^{-3} \text{ mol}$

In other words, the solubility of oxygen in water at 298 K is 1.26×10^{-3} mol dm^{-3}, since 1 kg (or 1 dm^3) of the solution contains 1.26×10^{-3} mol of oxygen.

SAQ 3

Why cannot fish live in warm water?

1.6 SOLUTIONS OF LIQUIDS IN LIQUIDS

In the liquid-liquid type solutions, we will consider only binary liquid solutions, i.e., solutions containing two liquids.

When two liquids A and B are mixed, we can have the following possibilities:

i) liquid A is *completely miscible* with liquid B in all proportions (e.g., water and ethanol, toluene and benzene, etc.).

ii) liquids A and B are only *partially miscible* in each other (e.g., water and phenol).

iii) liquids A and B are *completely immiscible* with each other (e.g., water and carbon tetrachloride).

We shall study completely miscible liquid systems in this unit. The other two types will be taken up for study in Unit 2.

Let us now study Raoult'slaw and understand what ideal solutions are.

1.6.1 Raoult's Law and Ideal Solutions

Consider a binary solution containing two liquids A and B which are completely miscible with each other in all proportions. In such solutions, the terms, solute and solvent, can be interchanged for the two components.

In 1880, the French Chemist, Raoult found that when a non-volatile solute is dissolved in a solvent (liquid), the vapour pressure of the solvent decreases. If the solute and the solvent both are volatile, the partial vapour pressures of both the components decreased. Based on these observations, he gave the following generalisation which is called **Raoult's law.**

The partial vapour pressure of any volatile component in a solution is equal to the product of the vapour pressure of the pure component and its mole fraction in the solution.

If x_A and x_B are the mole fractions of the components A and B in the liquid solution and p_A and p_B, the vapour pressures of these components, respectively, then according to Raoult's law.

$$p_A = p_A^0 x_A \qquad \ldots (1.9)$$

Each component of an ideal solution is present in differing amounts in liquid and vapour phases. Remember that Raoult's law talks about the relationship between the partial pressure of a component and its mole fraction in the liquid phase.

and $p_B = p_B^0 x_B$ … (1.10)

where p_A^0 and p_B^0, are the vapour pressures of pure components A and B, respectively.

If the vapours behave like an ideal gas, then according to Dalton's law of partial pressures, the total vapour pressure, p, is given by

$$p = p_A + p_B = p_A^0 x_A + p_B^0 x_B \quad \text{… (1.11)}$$

Note that the partial pressure curves II and III of the components A and B, respectively pass through the respective origins T and Q (where the mole fraction of a particular component and its partial pressure are zero). This is understandable since the partial pressure of a component, p_i as given by Raoult's law is $p_i = p_i^0 x_i$. This resembles the equation $y = mx$ that represents a straight line passing through the origin. The curve I representing the total vapour pressure of an ideal solutions, is a straight line connecting p_A^0 and p_B^0, since the total pressure p as per Eq. 1.11 is given by

$p = p_A^0$, when $x_A = 1$ and $x_B = 0$,

And $p = p_B^0$, when $x_A = 0$ and $x_B = 1$

Ideal Solutions

A solution which obeys Raoult's law at all concentrations and at all temperature is called an ***ideal solution***.

Two liquids A and B on mixing form an ideal solution, if

i) the molecules of A and B have similar structure and polarity, and

ii) the intermolecular attractions between A and A, B and B, and A and B are all alike.

1.6.2 Raoult's Law Curves

According to Raoult's law, the partial vapour pressures of components A and B of an ideal solution are given by Eqs. 1.9 and 1.10, respectively. The partial vapour pressure of each component can be plotted against its mole fraction in the liquid phase. Such vapour pressure curves for an ideal solution are shown in Fig. 1.3.

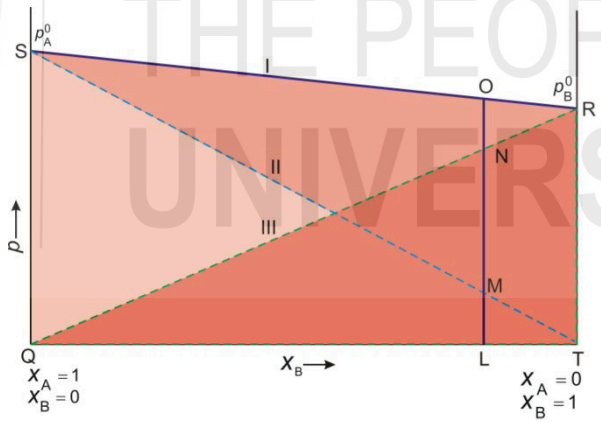


Fig. 1.3: Vapour pressure curves for an ideal solution:
Curve I: Total vapour pressure of solution;
Curve II: Partial vapour pressure of A, $p_A = p_A^0 x_A$
Curve III: Partial vapour pressure of B, $p_B = p_B^0 x_B$

The dotted lines show the variation of partial vapour pressures of the components A and b their mole fractions in the liquid phase. Thus, curve QR (III) shows the variation of partial vapour pressure of B with its mole fraction in liquid solution and curve ST (II) shows the variation of partial vapour pressures of A with its mole fraction in the liquid solution. The points, S and R, represent the vapour pressures (p_A^0 and p_B^0) of the pure components A and B, respectively. The variation of total vapour pressure with respect to the mole fraction of B in the liquid solution is given by the curve SR (I).

From Fig. 1.3, it can be seen that vapour pressure of an ideal solution of composition L is given by the sum of the partial vapour pressure of A and the partial vapour pressure of B (or OL = ML + NL).

1.6.3 Characteristics of Ideal Solutions

You know that a solution which obeys Raoult's law at all concentrations and at all temperature is called an **ideal solution**. Also,two liquids A and B on mixing form an ideal solution, if

i) the molecules of A and B have similar structure and polarity, and

ii) the intermolecular attractions between A and A, B and B, and A and B are all alike.

Thermodynamically, ideal solutions are those in which there is no volume change ($\Delta_{mixing}V$=0)and enthalpy change ($\Delta_{mixing}H$=0) when two liquidsA and B are mixed. Thus, the characteristics of an ideal solution are as follows:

i) It must obey Raoult's law.

ii) ($\Delta_{mixing}H$=0)

iii) ($\Delta_{mixing}V$=0

Some examples of nearly ideal solutions are as follows:

i) ethylene bromide and ethylene chloride

ii) *n*-hexane and *n*-heptane

iii) benzene and toluene

iv) *n*-butyl chloride and n-butyl bromide

v) carbon tetrachloride and silicon tetrachloride

1.7 NON-IDEAL SOLUTIONS

Most of the completely miscible liquid pairs form **non-ideal solutions**. These solutions do not obey Raoult's law. They either show *positive deviation* (when the vapour pressure of the solution is *higher* than that of an ideal solution of the same composition) or *negative deviation* (when the vapour pressure of the solution is *lower* than that of an ideal solution of the same composition). In such solutions, we can say that

$$p_A \neq p_A^0 x_A \quad \ldots (1.12)$$

$$p_B \neq p_B^0 x_B \quad \ldots (1.13)$$

When the components of a non-ideal solution are mixed, a considerable change in volume and enthalpy is noticed. Thus, the characteristics of non-ideal solutions are as follows:

i) They do not obey Raoult's law.

ii) ($\Delta_{mixing}H \neq 0$)

iii) ($\Delta_{mixing}V \neq 0$

Examples of non-ideal solutions showing positive and negative deviations are given in Table 1.4.

Table 1.4: Liquid pairs showing deviation from Raoult's law

Positive deviation	Negative deviation
$H_2O + C_2H_5OH$	$H_2O + HCl$
$CH_3COCH_3 + C_2H_5OH$	$H_2O + HNO_3$
$C_2H_5OH + C_6H_{12}$	$H_2O + H_2SO_4$
$CH_3COCH_3 + CS_2$	$CH_3COCH_3 + CHCl_3$

Let us work out an example illustrating the application of Raoult's law.

Example 3

Two liquids A and B form an ideal solution at 300 K. The vapour pressure of a solution containing 1.0 mol of A and 2.0 mol of B at 300 K is 2.0 x 10^5 Pa. When one more mole of B is added to the solution, the vapour pressure of the solution is 2.1 x 10^5 Pa. Calculate the vapour pressures of A and B in the pure state.

Solution

According to Eq. 1.11, total vapour pressure of the solution is given by,

$$p = p_A^0 x_A + p_B^0 x_B$$

Substituting the values, we get

$$2.0\times10^5\ \text{Pa} = p_A^0\left(\frac{1.0}{1.0+2.0}\right) + p_B^0\left(\frac{2.0}{1.0+2.0}\right)$$

or $\quad 2.0 \text{ x } 10^5 \text{ Pa} = p^0_A/\ 3.0 + 2.0\ p^0_B/\ 3.0$

or $\quad p^0_A + 2.0\ p^0_B = 6.0 \text{ x } 10^5 \text{ Pa} \qquad \ldots (1)$

Also, $\quad 2.1\times10^5\ \text{Pa} = p_A^0\left(\frac{1.0}{1.0+3.0}\right) + p_B^0\left(\frac{3.0}{1.0+3.0}\right)$

or $\quad p_A^0 + 3.0\,p_B^0 = 8.4\times10^5\ \text{Pa} \qquad \ldots (2)$

From Eqs. (1) and (2), we get

$$p_B^0 = 2.4\times10^5\ \text{Pa}$$

$$p_A^0 = 1.2\times10^5\ \text{Pa}$$

You can now attempt the following SAQ.

SAQ 4

0.100 mol of acetone and 0.100 mol of chloroform are mixed at 308 K. At this temperature, the total vapour pressure of the solution is 3.47×10^4 Pa. The vapour pressures of pure acetone and pure chloroform at 308 K are 4.60×10^4 Pa and 3.92×10^4 Pa, respectively. Verify whether this solution is ideal or not.

1.7.1 Raoult's Law Curves

Let us now study Raoult's law curves of non-ideal solutions i.e. solutions exhibiting positive and negative deviations from Raoult's law.

i) Vapour Pressure Curves of Solutions Showing Positive Deviation

If the molecular interactions between A and B are weaker than the A-A or B-B molecular interactions, then the escaping tendency of the molecules of A and B from the solution becomes more than that from the pure liquids. As a result, the vapour pressure of the solution will be greater than that of an ideal solution of the same composition. Such solutions are said to show positive deviation from Raoult's law.

Mathematically,

$$p_A = p_A^0 \times x_A \quad \ldots (1.14)$$

$$p_B = p_B^0 \times x_B \quad \ldots (1.15)$$

and $$p > p_A^0 x_A + p_B^0 x_B \quad \ldots (1.16)$$

In Fig. 1.4, the dotted lines are theoretical curves showing the ideal behavior, the solid lines are curves drawn as per experimental values and show positive deviation from the ideal behavior. When ethanol and cyclohexane are mixed, the curves as shown in Fig. 1.4 are obtained.

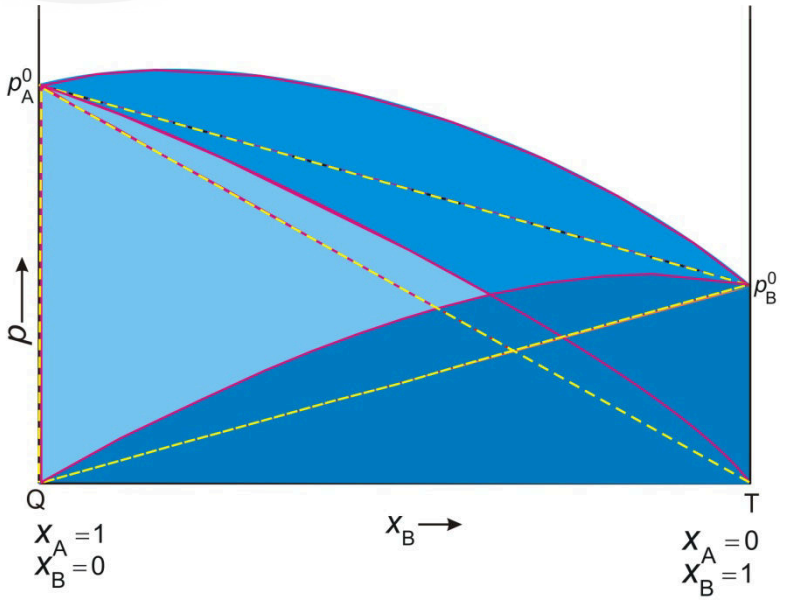


Fig. 1.4: Curves showing positive deviation from Raoult's law.

The increase of molecular attraction causes a decrease in vapour pressure of liquids.

In ethanol, there is a strong intermolecular hydrogen bonding. When cyclohexane is added to it, the cyclohexane molecules get in between the ethanol molecules; thereby decreasing the intermolecular interactions. During the formation of such solutions, heat is absorbed and there is a slight increase in volume.

ii) Vapour Pressure Curves of Solutions Showing Negative Deviation

If the intermolecular forces between A and B are stronger than those of A-A and B-B, the solution formed by mixing A and B shows negative deviation from Raoult's law. Due to stronger A-B interactions, the escaping tendency of A and B from the solution becomes less than that from the pure liquids. The vapour pressure of such as a solution will be less than an ideal solution of the same composition.

This behavior is shown in Fig. 1.5.

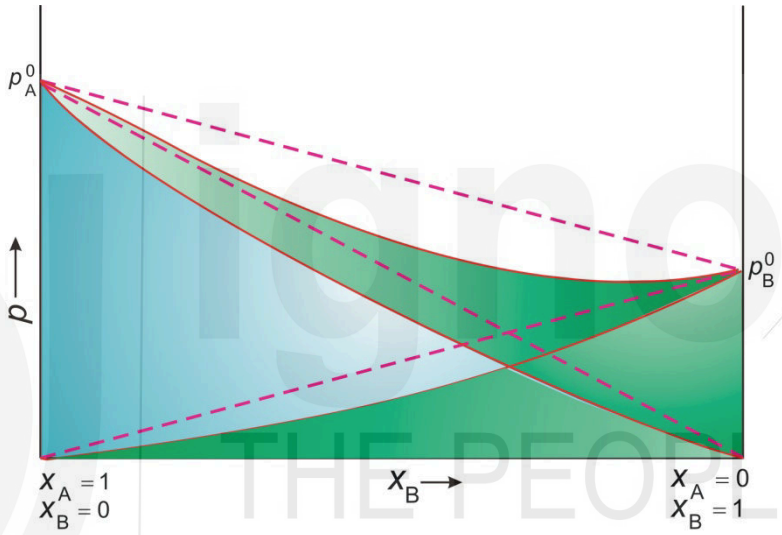


Fig. 1.5: Curves showing negative deviation from Raoult's law.

The dotted lines are the theoretical curves representing the ideal behavior, whereas the solid lines are the curves drawn as per experimental values and show negative deviation from ideal behaviour. When acetone and chloroform are mixed, they form hydrogen bonds with each other.

As a result, the intermolecular attractions between acetone and chloroform become stronger. The tendency of the molecules to escape from the solution, thus, decreases. The vapour pressure, therefore, decreases. During the formation of such solution, heat is evolved and there is slight decrease in volume.

1.8 VAPOUR PRESSURE VARATION WITH LIQUID AND VAPOUR PHASE COMPOSITIONS

Consider a solution containing one mole of benzene and one mole of toluene so that the mole fraction of each component in the solution is 0.5. The vapour pressures of pure benzene and toluene at 298 K are 1.25×10^4 Pa and 3.70×10^3 Pa, respectively.

According to Raoult's law

$$p_{C_6H_6} = p^0_{C_6H_6} x_{C_6H_6}$$

$$= (1.25 \times 10^4 \text{ Pa} \times 0.5 = 6.25 \times 10^3 \text{ Pa}$$

$$p_{C_7H_8} = p^0_{C_7H_8} x_{C_7H_8}$$

$$= (3.70 \times 10^3 \text{ Pa}) \times 0.5 = 1.85 \times 10^3 \text{ Pa}$$

According to Dalton's law of partial pressures,

$$p_{total} = (6.25 \times 10^3 \text{Pa}) + (1.85 \times 10^3 \text{Pa})$$

$$= 8.10 \times 10^3 \text{Pa}$$

Mole fraction of benzene in the vapour phase,

$$= \frac{6.25 \times 10^3 \text{ Pa}}{8.10 \times 10^3 \text{ Pa}} = 0.77$$

Mole fraction of toluene in the vapour phase,

$$= \frac{1.85 \times 10^3 \text{ Pa}}{8.10 \times 10^3 \text{ Pa}} = 0.23$$

It is quite interesting to compare the mole fractions of benzene in the vapour and liquid phase solutions. From the calculations made above, the mole fraction of benzene in the vapour phase (0.77) is more than that in the liquid phase (0.5). Again, the mole fraction of toluene in the vapour phase (0.23) is less than that in the liquid phase (0.5).

Keeping in mind that benzene is more volatile than toluene, we can arrive at the following generalisation which is one of the forms of **Konowaloff's rule**.

The mole fraction of a more volatile component in an ideal solution is more in the vapour phase than in the liquid phase.

For the purpose of comparing the compositions of the solutions in the liquid and the vapour phases at a given total vapour pressure, it is worth drawing curves of the type I and II shown in Fig. 1.6.

The upper curve i.e.: curve I is called *liquidus* curve as above this curve, under high pressure, only liquid phase exists. Similarly, the curve II is called *vapourous* curve as only vapours exist below this curve at low pressures. In the region between two curves, liquid and vapour both the phases are present.

CurveI shows that variation of total vapour pressure with respect to the mole fraction in the liquid phase. Similarly, curve II shows the variation of the total vapour pressure with respect to the mole fraction in the vapour phase. The line MN is called a **tie line** and it gives *the composition of the liquid and vapour phases in equilibrium at a particular total vapour pressure*.

For **ideal solutions** obeying Raoult's law**,** the curves I and II of the type shown in Fig.1.6 are obtained.

In Figs. 1.6 to 1.15, *V* and L refer to vapour phase and liquid phase curves, respectively.

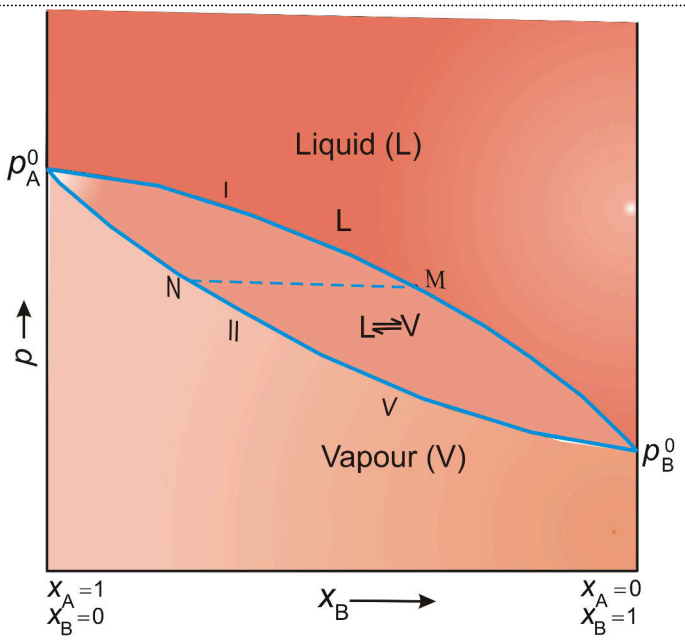


Fig. 1.6: Liquid and vapour phase composition curves for an ideal solution.

For Non-ideal Solutions

In the case of solutions showing positive deviation from Raoult's law, the liquid and vapourphase composition curves are of the type shown in Fig. 1.7. Note that there is a maximum point, M, where both the liquid and vapour phases have the same composition.

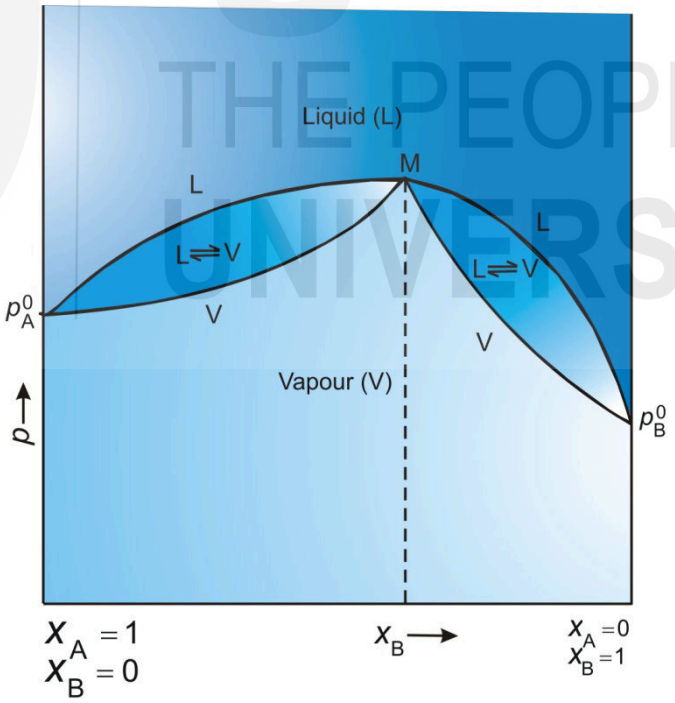


Fig. 1.7: Liquid and vapour phase composition curves for a liquid mixture showing positive deviation.

In the case of a solution showing negative deviation from Raoult's law, the liquid and vapour phase composition curves are of the type shown in Fig. 1.8.

Note that the curves meet at the minimum point M where both the liquid and vapour phases have the same composition.

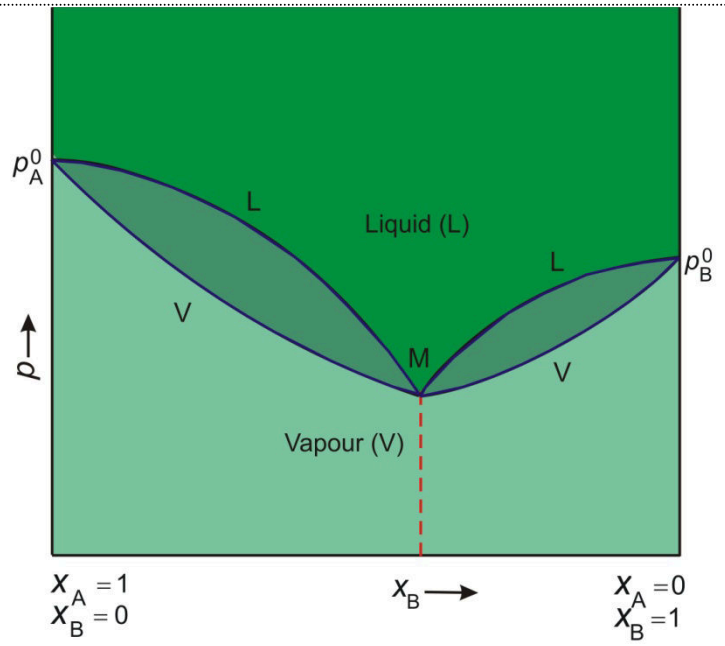


Fig.1.8: Liquid and vapour phase composition curves for a liquid mixture showing negative deviation.

So far we studied the effect of composition on the vapour pressure of the completely miscible liquid systems.

In the next section, we will study the effect of composition on the boiling points of such systems. Such studies are helpful in understanding some of the aspects of separation of components from a binary liquid mixture. In particular, we will study the principle of fractional distillation and azeotropic distillation.

SAQ 5

In a binary solution obeying Raoult's law, can the liquid and the vapour phases have the same composition?

1.9 BOILING POINT DIAGRAMS: TEMPERATURE-COMPOSITION CURVES

Let us consider a binary mixture consisting of two liquids A and B which are completely miscible with each other. On heating under a constant pressure, say, under atmospheric pressure, it will start boiling when the total vapour pressure becomes equal to the atmospheric pressure.

If p represent the atmospheric pressure, then the condition for boiling is

$$p = p_A + p_B \quad \ldots (1.17)$$

where p_A and p_B are the partial pressures of the two components A and B, respectively at the boiling point of the solution.

Since different compositions of a solution have different vapour pressures, the various solutions will not reach a total vapour pressure equal to the atmospheric pressure at the same temperature.Thus, the solutions of different compositions will boil at different temperatures.

In general, solutions having low vapour pressure will boil at temperatures higher than those having high vapour pressures. It is because solutions having high vapour pressure can have the total pressure equal to the atmospheric pressure at relatively lower temperatures as compared to solutions for which vapour pressures are low.

Hence, it is possible to draw temperature-composition diagrams which will correspond to the three general types of vapour pressure-composition diagrams.

First, we shall study boiling point-composition curves of an ideal solution.

1.9.1 Distillation of an Ideal Solution

Let us consider a binary mixture of liquids A and B obeying Raoult's law.

Let the vapour pressure of pure A be higher than that of pure B (Fig. 1.9 a). Consequently at constant pressure, the boiling point of A (T_A) will be lower than that of B (T_B). We can get an idea about the relative composition of the vapour phase over a solution using Konowaloff's rule. Although you have studied one of the forms of this rule in the last section, this rule can also be stated as follows:

In the distillation of a binary liquid mixture, vapours coming out will be richer in that component whose addition to the liquid mixture causes an increase in vapour pressure.

In other words, as compared to the liquid phase , the vapour phase is richer in the more volatile component. In the liquid mixture that we have taken, A is more volatile than B. Hence, the vapour phase composition at any temperature must lie closer to A than the corresponding liquid phase composition.

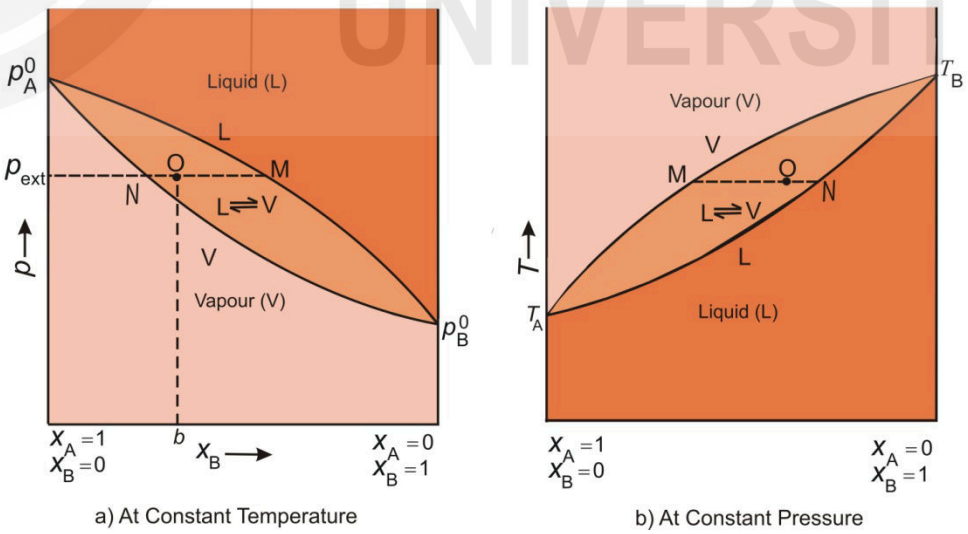


Fig. 1.9: a) Liquid and vapour phase compositions plotted against vapour pressure at constant temperature for an ideal solution, and b) liquid and vapourphase compositions plotted against temperature at constant pressure for an ideal solution.

Thus, in the composition - temperature plots, the vapour phase composition curve must lie above the liquid phase composition curve as shown in Fig. 1.9

b). Note the difference in the relative positions of the liquid and vapour phase curves between Figs.1.9 a) and b).

Before, proceeding to the discussion of various stages of separation of components of an ideal solution, it is worthwhile to understand the lever rule and its use in the determining the relative amounts of the liquid and vapour phases using the tie line.

1.9.2 Lever Rule

You know that a lever is a simple machine. It is a rigid bar that turns on a pivot called fulcrum.

Levers are classified into three types depending upon the positions of fulcrum, load and effort.

In the first type of levers, the fulcrum is in between the effort and the load, see Fig 1.10 a). The common examples of the such levers are scissors and a see saw, Fig 1.10 b).

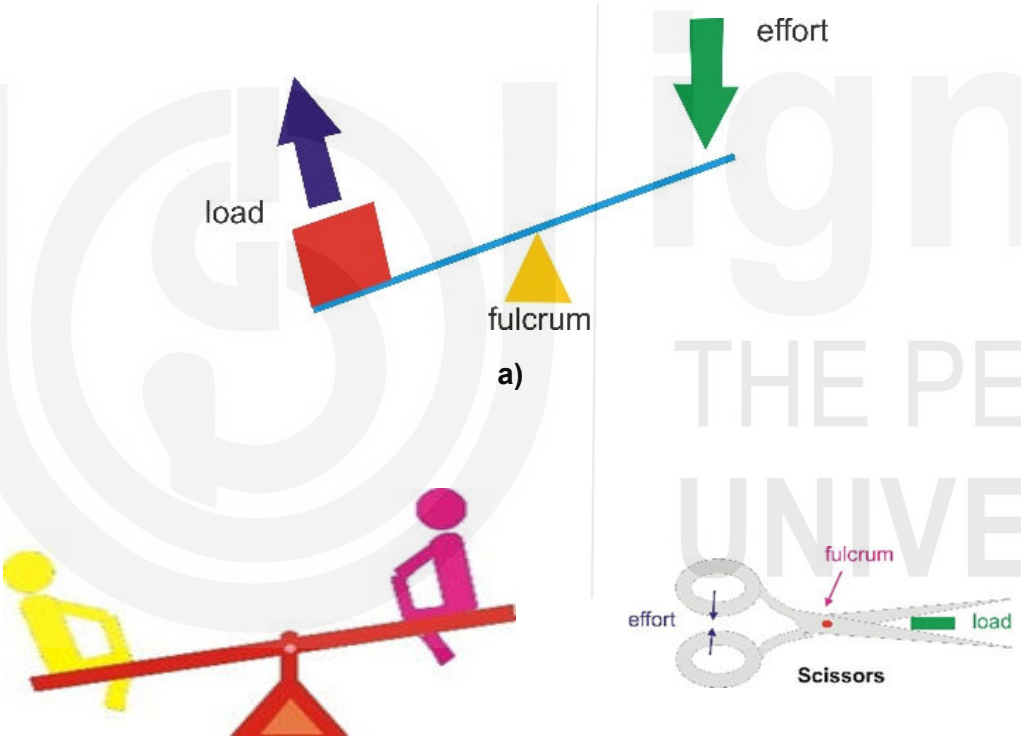


Fig. 1.10: a) A lever, b) Common examples of lever and c) Equilibrium position.

As shown in Fig.1.10 c) above, at equilibrium or at balanced position, the clockwise and the anticlockwise moments should be equal. Thus,

Anticlockwise moment = $d_1 \times w_1 = w_2 \times d_2$ = clockwise moment

or $$\frac{w_1}{w_2} = \frac{d_2}{d_1} \quad \ldots \quad (A)$$

So you can also conclude that a longer distance d_1 can help in lifting a heavier weight w_2 by using much less effort w_1.

This is the principle of lever.

Let us now focus our attention on Fig. 1.9 again. In Fig. 1.9 a),suppose we take a point O on the tie line MN and extend MN to a pressure p_{ext}; then at this pressure, the point M gives the composition of the liquid phase as '*a*' while point N gives the composition of the vapour phase as '*b*'. These compositions are expressed here in terms of mole fraction of B. Similarly, in Fig. 1.9 b), we can draw a tie line MN corresponding to a particular temperature and interpret the points M and N accordingly.

Here, the point O, similar to the fulcrum or the pivot point of the lever, gives the overall composition of the system. The composition and the amounts of the phases are interrelated in the same way as the different weights (w_1 and w_2) and the distances (d_1 and d_2) are related to each other, i.e.

Amount of vapour N $\times$ ON = Amount of liquid M $\times$ OM

$$\frac{\text{amount of vapour N}}{\text{amount of liquid M}} = \frac{\text{OM}}{\text{ON}} \quad \ldots(B)$$

$$\frac{\text{At N (amount of vapour phase)}}{\text{At M (amount of liquid phase)}} = \frac{\text{OM}}{\text{ON}} = \frac{d_2}{d_1}$$

The equation above is called **lever rule**.

You can now go back to Eq. (A) and compare Eqs. (A) and (B). Are these not similar?

Thus, *the relative amounts of material in the two phases is inversely proportional to the lengths of opposite segments in the tie line.*

Using the tie line and the lever rule, we can find out the compositions of liquid and vapour phases and also calculate their relative amounts.

Also note that if position of point O is changed to any other point on the tie line MN, then we will get different lengths OM and ON accordingly. If point O lies near point N, then ON length will be smaller and the system will contain more of vapour and less of liquid. Similarly, if the point O lies nearer to M, i.e. OM length becomes smaller and in this situation, the system will contain more of liquid and less of vapour.

The **smaller** the distance ON, the **greater** is the amount of vapour, and *vice-versa*.

Let us now study the distillation of components of ideal solution.

Using Fig. 1.11 we can understand the various stages in the separation of the components of an ideal solution.

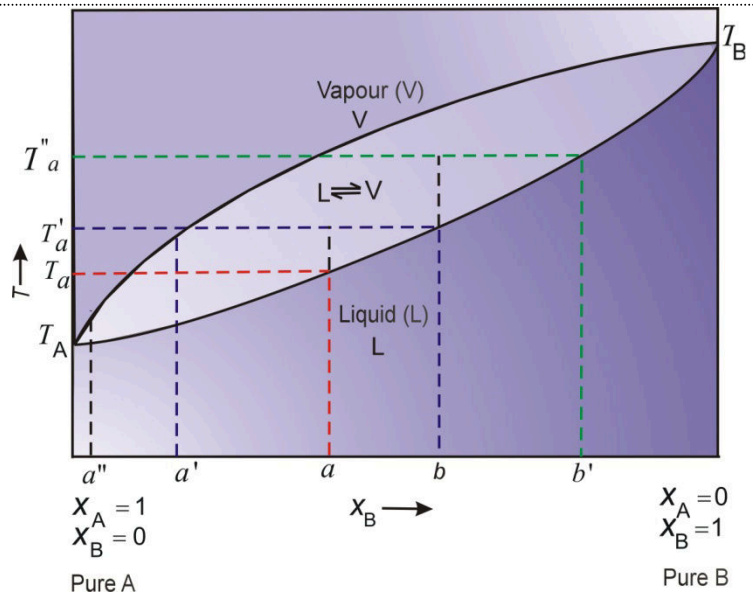


Fig. 1.11: Separation of the components of an ideal solution at constant pressure.

Let us start with a solution of two liquids A and B having composition *a*. The liquid A is more volatile and has a lower boiling point T_A than that of B, T_B, which is less volatile. If this solution is heated, it starts boiling at the temperature T_a when its vapour pressure becomes equal to the atmospheric pressure. The vapour formed in the beginning is very rich in liquid A but its amount is very small. Let the solution be heated to a little higher temperature T'_a. At this temperature, the vapour phase has composition *a*' (which is richer in A than the original solution *a*) and the liquid phase composition changes to *b*. Assume that the vapours of the composition*a*' are condensed to get the condensate with the same composition (*a*'). The residual liquid having composition *b* is richer in liquid B (less volatile liquid).

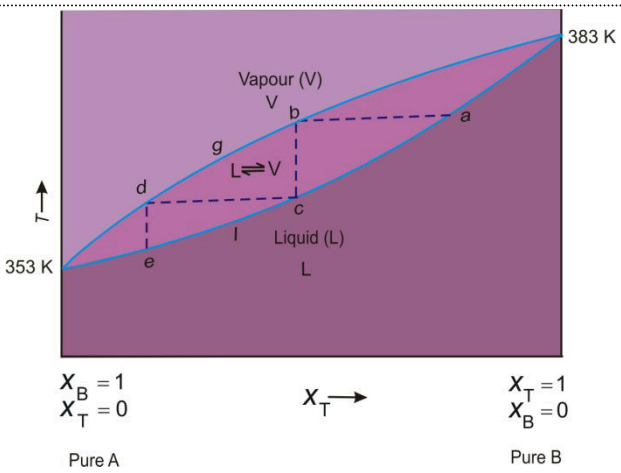
When the condensate (*a*') is heated, it boils at a lower temperature. If it is boiled at the temperature T_a, the vapour formed *a*" are still richer in liquid A, which give new condensate with composition *a*". The residual liquid *b*, obtained earlier has higher boiling than T_a. If it is distilled at a higher temperature T_a", the new residue left *b*' is still richer in liquid B.

Thus, each repeated distillation of condensate would give new condensate which is still richer in more volatile liquid A. On repeating this process, we can obtain pure liquid A as the condensate.

Similarly, after each distillation, the residual liquid becomes richer in less volatile liquid B and finally, only the pure liquid B is left as the residue.

Fractional Distillation

The several stages described for the separation of ideal solution into its pure components can be carried out in the continuous process which is called fractional distillation. In fractional distillation, the process of successive vaporisation and condensation is carried out in a fractionating column. Let us understand it by taking benzene and toluene liquid mixture, having the composition *a* (Fig. 1.12).



x_B and x_T represent respectively, the mole fractions of benzene and toluene.

Fig. 1.12: Liquid and vapour compositions of benzene and toluene; x_B and x_T refer to mole fractions of benzene and toluene, respectively.

The vapours in equilibrium are richer in the more volatile component, benzene, and will have the composition *b*. This vapour may be condensed by lowering the temperature along the line *bc*. If a small fraction of this condensate is vaporised, the vapours formed will have composition *d*. Finally, by repetition of vaporisation and condensation, a vapour fraction of pure benzene can be obtained. As more and more benzene is removed, the residual liquid becomes richer in toluene and finally, only pure toluene is left as the residue in the distillation flask.

Here, each vaporisation and condensation represented by the path (*abcde)* corresponds to a process in which only a tiny fraction of the vapour is condensed and revaporised. Such a process takes a very long time for separation of the two liquids. Practically, efficient fractionating columns are used for making the process fast. Let us now understand the distillation of non-ideal solutions.

1.9.3 Distillation of Solutions Exhibiting Positive and Negative Deviations

i) Distillation of a Solution Exhibiting Positive Deviation

Let us now take up the separation of a mixture of liquids showing positive deviation from Raoult's law, Fig. 1.13 represents the boiling point-composition diagram of such a system.

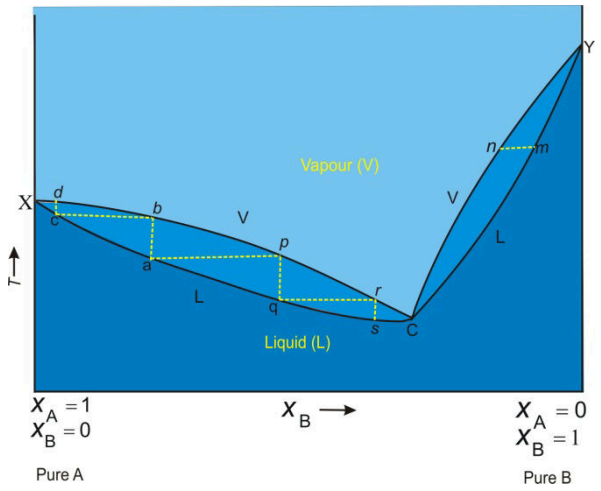


Fig. 1.13: Boiling point-composition diagram of a liquid mixture showing positive deviation.

Note that this system has a minimum point (C) where the liquid and vapour phases have the same composition.

Let us consider the distillation of a solution of composition, *a*, which is between X and C. The vapours coming off will have the composition *p* and will be richer in B than the liquid, *a*. Because of this, the composition of the residue will shift towards A. Hence, the residue will boil at a higher temperature than the original solution, *a*. If the distillation is continued (through the steps *abc, bcd* etc.), finally a residue of pure A, will be obtained.

Now if, the vapours of composition *p* coming out from the original solution, are condensed and redistilled repeatedly (through the steps *pqr, qrs,* etc.), vapours of composition C will eventually be obtained. Such vapours when condensed and redistilled will again yield the vapours of composition C,i.e. vapours will have the same composition as that of liquid solution. Hence, no further separation is possible by distillation. Because of this, the liquid of composition C is called the *constant boiling mixture*. Thus, anymixture having a composition between X and C can be separated by fractional distillation only into a residue of pure A and a final distillate of composition, C, but pure B cannot be recovered.

On the other hand, if a solution of composition *m* which is between C and Y is distilled, then the vapours of composition *n* which are coming out, will be richer in A than the original solution. Hence, on repeated distillation, the residue will tend towards pure B, while the distillate will tend towards C. Such solutions on complete distillation will yield, pure B in the residue and constant boiling mixture C in the distillate. Pure A cannot be recovered by the distillation of a liquid mixture of composition between C and Y.

Thus, in such cases, complete separation of A and B is not possible.

ii) Distillation of a Solution Exhibiting Negative Deviation

Now let us study the distillation behaviour of a mixture of liquids A and B showing negative deviation from Raoult's law. Fig. 1.14 represents the variation of liquid and vapour compositions of such a system at different temperatures.

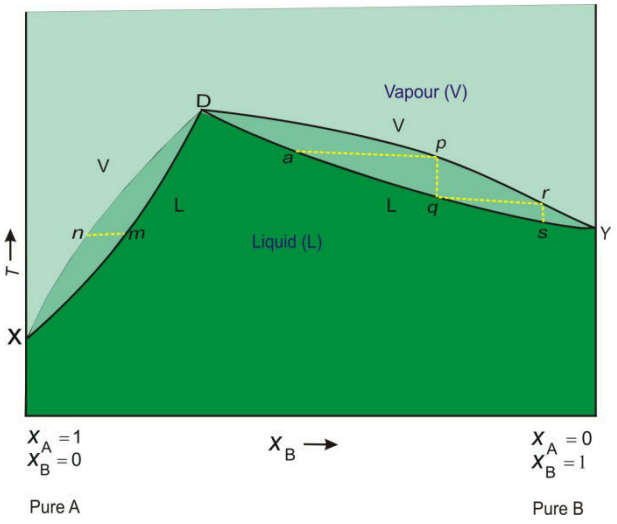


Fig. 1.14: Boiling point-composition diagram of a liquid mixture showing negative deviation.

The behaviour of such a system on distillation is similar to the previous one. The difference is that the residues tend towards the maximum boiling mixture D, while the distillates tend towards the pure constituents. If the starting mixture has a composition *a* which is between Y and D, then the vapours will have composition *p* where the vapours are richer in B than the solution *a*. Hence, the composition of the residue will shift towards D. Repeated distillation of the condensate will finally yield pure B in the vapour form. That is, repeated evaporation and condensation of liquid *a* leads to liquid residue of composition D and vapours of pure B.

Similarly, a mixture of composition *m* between D and X will yield on distillation a vapour of composition *n* richer in A than the solution. Here again, the residue will shift towards D. By redistillation of the condensate, the vapours will tend towards pure A. Finally, we will have a residue of composition D and a distillate of pure A.

In general, we can separate a liquid mixture showing negative deviation from Raoult's law into a residue of composition D, which is the *constant maximum boiling mixture,* and a distillate of either pure A or pure B, depending on whether the starting composition is between X and D or D and Y. But D cannot be separated further by distillation.

Azeotropes are called *constant boiling mixtures*, since these mixtures boil at constant temperature. The vapours coming out of the azeotropic mixture have the same composition as that of the liquid.

The constant boiling mixtures having composition C in solutions exhibiting positive deviation,(Fig. 1.13) and composition D in solutions exhibiting negative deviation, (Fig. 1.14) are called **azeotropes** (i.e., *liquids boiling unchanged*). They resemble pure compounds in their boiling behaviour. However, changes in pressure produce changes in the **composition as well as the boiling point** of the azeotropes, (see Table 1.5).

Table 1.5: Pressure Dependence of H_2O-HCl Azeotropes

Pressure/10^5 Pa	HCl %	Boiling point T_B / K
0.658	20.92	370.7
0.921	20.36	379.5
1.00	20.22	381.7
1.05	20.16	383.1

In Tables 1.5 and 1.6, T_B stands for the boiling point of the azeotrope formed.

The azeotropes are not chemical compounds but are rather mixtures resulting from the interplay of intermolecular forces in solution. Table 1.6 lists some azeotropic mixtures along with their composition and boiling points.

Table 1.6: Azeotropes with Minimum Boiling Points (at 10^5 Pa)

Component-I	Boiling point, $\frac{T_B \text{ of I}}{K}$	Component-II	Boiling point, $\frac{T_B \text{ of II}}{K}$	Azeotrope	
				Mass% of I	Boiling point T_B /K
H_2O	373.1	C_2H_5OH	351.4	4.50	351.3
H_2O	373.1	$CH_3COC_2H_5$	352.7	11.30	346.5
CCl_4	349.9	CH_3OH	337.8	79.44	328.8
CS_2	319.4	CH_3COCH_3	329.6	67.00	312.4
$CHCl_3$	334.3	CH_3OH	337.8	87.40	326.5

SAQ 6

Can azeotropes be separated into pure components by fractional distillation? Explain.

1.10 SUMMARY

In this unit, we have studied about the solutions and their various properties.

We have learnt the following:

- A solution is a homogeneous mixture of two or more substances.
- Solutions can be formed in all the three phase, *viz*., solid, liquid and gaseous.
- Solutions can be divided into nine types depending upon the physical state of the solute and the solvent.
- A solution which cannot dissolve more amount of a solute at a particular temperature is called a saturated solution.
- Pressure has only a small effect on the solubility of solids in liquids.
- The solubility of a gas varies with pressure.
- Completely miscible liquid pairs may form ideal or non-ideal solutions.
- Ideal solutions obey Raoult's law. Non-ideal solutions either show positive or negative deviation from Raoult's law.
- Ideal solution can be separated into pure components by fractional distillation.
- Non-ideal solution can be separated into two fractions by fractional distillation–one, a pure component and, another, a constant boiling azeortropic mixture.

1.11 TERMINAL QUESTIONS

1. Fill in the blanks in the following:

   i) The solubility of a solute …… with increase in temperature when the dissolution is accompanied by absorption of heat.

   ii) One molal solution contains a mole of a solute dissolve in ….. of the solvent.

   iii) In an ideal solution, partial vapour pressure of a component of a solution = mole fraction x ……

   iv) The constituents of …….. solution can be separated by fractional distillation into pure components.

2. Explain why we cannot prepare absolute alcohol by fractional distillation.

3. If 0.100 kg of an aqueous solution of potassium chloride contains 7.45×10^{-3} kg of the solute, then calculate the molality of the solution.

4. The vapour pressures of pure liquids A and B at 300 K are 2.6×10^4 Pa and 6.4×10^4 Pa, respectively. Calculate the mole fractions of A and B in vapour and liquid phases of a solution when the equilibrium total vapour pressure of the binary liquid solution is 4.5×10^4 Pa at 300 K. Assume that the solution and the vapour behave ideally.

5. At 298 K , solubility of carbon dioxide in water is 3.40×10^{-2} mol dm^{-3}. The partial pressure of carbon dioxide over the solution is 1.00×10^5 Pa. Assuming that one dm^3 of the solution contains 1.00 kg of water, calculate the Henry's law constant for carbon dioxide.

6. State whether the following statements are true or false:

   i) Azeortopes are compounds and not mixures.

   ii) Molality is the number of moles of solute dissolved in one kilogram of the solvent.

   ii) Raoult's law for ideal solutions is applicable both to the liquid and the vapour phase compositions.

   iv) The solubilities of all substances, i.e., solids, liquids and gases, in liquids increase with rise in temperature.

7. State Konowaloff's rule.

8. Which of the following liquid pairs can be completely separated into its pure components?

   i) Ethanol – water

   ii) Ethylene chloride – ethylene bromide

   iii) Nitric acid – water

   iv) Acetone – carbon disulphide

   v) Carbon tetrachloride – silicon tetrachloride.

9. An azeotropic mixture of hydrochloric acid and water contains 20.2% hydrochloric acid. Calculate its molality.

1.12 ANSWERS

Self Assessment Questions

1. i) Solid in solid

   ii) Liquid in solid

   iii) Gas in liquid

2. The mass of ethanol and water are 0.100kg each.

   No. of moles of ethanol = $\frac{0.100 \text{ kg}}{0.046 \text{ kg mol}^{-1}} = 2.17 \text{ mol}$

   No. of moles of water = $\frac{0.100 \text{ kg}}{0.018 \text{ kg mol}^{-1}} = 5.56 \text{ mol}$

   Mole fraction of ethanol in the solution

   $$= \frac{2.17 \text{ mol}}{(2.17 \text{ mol} + 5.56 \text{ mol})}$$

   $$= \frac{2.17 \text{ mol}}{7.73 \text{ mol}} = 0.28$$

   Mole fraction of water in the solution = (1 – 0.28) = 0.72

3. The solubility of oxygen is less in warm water and hence, the amount of oxygen is not enough for the fish to survive.

4. Mole fraction of acetone (x_A) = 0.500

   Mole fraction of chloroform (x_C) = 0.500

   Partial vapour pressure of acetone (p_A) = $0.500 \times 4.60 \times 10^4$ Pa

   $= 2.30 \times 10^4$ Pa

   Partial vapour pressure of chloroform (p_C) = $0.500 \times 3.92 \times 10^4$Pa

   $= 1.96 \times 10^4$ Pa

   If this solution were to behave ideally, the total vapour pressure should be $(2.30 \times 10^4$ Pa) + $(1.96 \times 10^4$ Pa) = 4.26×10^4 Pa. The observed value $(3.47 \times 10^4$ Pa) which is less than the value for an ideal solution. Therefore, acetone-chloroform mixture exhibits negative deviation from Raoult's law.

5. Not possible.

6. Azeotropes are constant boiling mixtures. They cannot be separated into pure components by fractional distillation because the liquid and the vapour phases have the same composition.

Terminal Questions

1. i) increases

   ii) 1 kg

   iii) vapour pressure of the pure component

   iv) an ideal

2. When an aqueous solution of ethyl alcohol is fractionated, it forms a constant boiling mixture (containing 95.5% ethyl alcohol and 4.5% water).

3. Mass of solute (KCl) = 7.45×10^{-3} kg

Mass of solvent = $(100 - 7.45) \times 10^{-3}$ kg = 92.55×10^{-3} kg

$$\text{No. of moles of the solute} = \frac{\text{Mass of the solute}}{\text{Molar mass of the solute}}$$

$$= \frac{7.45 \times 10^{-3}\,\text{kg}}{7.45 \times 10^{-2}\,\text{kg mol}^{-1}} = 0.1\,\text{mol}$$

$$\text{Molality of solution} = \frac{\text{Number of moles the solute}}{\text{Mass of the solvent}}$$

$$= \frac{0.1\,\text{mol}}{92.55 \times 10^{-3}\,\text{kg}} = 1.08\ \text{m}$$

4. From the given data, $p^0_A = 2.6 \times 10^4$ Pa and $p^0_B = 6.4 \times 10^4$ Pa.

Let the mole fractions of A and B in the liquid phase be x_A and x_B, respectively.

Applying Raoult's law,

$$p_A = p^0_A x_A \text{ and } p_B = p^0_B x_B$$

Total vapour pressure,

$$p = p_A + p_B = p^0_A x_A + p^0_B x_B$$

or $\quad 4.5 \times 10^4\,\text{Pa} = (2.6 \times 10^4\,\text{Pa}) x_A + (6.4 \times 10^4\,\text{Pa}) x_B$

But, $x_A + x_B = 1$ or $x_B = 1 - x_A$

$$4.5 \times 10^4\ \text{Pa} = (2.6 \times 10^4\ \text{Pa})\, x_A + (6.4 \times 10^4\ \text{Pa})(1 - x_A)$$

$$= 6.4 \times 10^4\ \text{Pa} - (3.8 \times 10^4\ \text{Pa})\, x_A$$

Mole fraction of A in liquid phase

$$x_A = \frac{(6.4 \times 10^4\,\text{Pa}) - (4.5 \times 10^4\,\text{Pa})}{3.8 \times 10^4\,\text{Pa}} = \frac{1.9 \times 10^4\,\text{Pa}}{3.8 \times 10^4\,\text{Pa}} = 0.5$$

Mole fraction of B in liquid phase

$$x_B = 1 - x_A = 1 - 0.5 = 0.5$$

$$p_A = p^0_A x_A = 2.6 \times 10^4\ \text{Pa} \times 0.5 = 1.3 \times 10^4\ \text{Pa}$$

$$p_B = p^0_B x_B = 6.4 \times 10^4\ \text{Pa} \times 0.5 = 3.2 \times 10^4\ \text{Pa}$$

$$\text{Mole fraction of A in vapour phase} = \frac{p_A}{p} = \frac{1.3 \times 10^4\ \text{Pa}}{4.5 \times 10^4\ \text{Pa}} = 0.29$$

Mole fraction of B in vapour phase = 1-0.29 = 0.71.

5. According to Henry's law, Henry's constant, K, is given by

$$K = \frac{p}{x_{CO_2}}$$

Number of moles of carbon dioxide in 1 dm^3 of the solution

$= 3.40 \times 10^{-2}$ mol

Number of moles of water present in 1 dm^3 of the solution

$$\frac{1.00 \text{ kg}}{0.018 \text{ kg mol}^{-1}} = 55.6 \text{ mol}$$

Mole fraction of CO_2(x_{CO_2}) = $\frac{3.40 \times 10^{-2} \text{ mol}}{(3.40 \times 10^{-2} + 55.6) \text{ mol}} \cong \frac{3.40 \times 10^{-2}}{55.6}$

$= 6.12 \times 10^{-4}$

$$K = \frac{p}{x_{CO_2}} = \frac{1.00 \times 10^5 \text{ Pa}}{6.12 \times 10^{-4}} = 1.63 \times 10^8 \text{ Pa}$$

6. i) False ii) True iii) False iv) False.

7. See Secs. 1.8 and 1.9.

8. ii) and v)

9. Let us consider 0.100 kg of the azeotropic mixture.

Mass of water in 0.100 kg of the solution = (0.100 – 0.0202) kg

= 0.0798 kg

No. of moles of HCl dissolved in 0.0798 kg H_2O = $\frac{\text{Mass of HCl}}{\text{Molar mass of HCl}}$

$$= \frac{0.0202 \text{ kg}}{0.0365 \text{ kg mol}^{-1}}$$

$$= 0.553 \text{ mol}$$

Molality of the solution = $\frac{\text{No. of moles of HCl}}{\text{Mass of water}} = \frac{0.553 \text{ mol}}{0.0798 \text{ kg}}$ = 6.93 m.

UNIT 2

SOLUTIONS-II

Structure

2.1 INTRODUCTION

In Unit 1, we have discussed the *completely miscible liquid systems*. In this unit, we shall study the *partially miscible* and *completely immiscible* liquid systems.

Under partially miscible liquid systems, we will describe the variation of their miscibility with temperature and explain critical solution temperature. In completely immiscible systems, we will discuss about the vapour pressure of such systems as well as steam distillation and its principle.

We shall then explain Nernst distribution law and illustrate the calculation of distribution constant. We will also consider the situations where the solute dissociates or associates in one or both the liquids.

Finally, we will highlight the applications of the distribution law and illustrate its use in calculating the amount of the substances left un-extracted after a given number of extractions. This will help us in understanding the principle of extraction by the solvents.

In the next two units of this Block, you shall study important aspects of phase equilibrium.

Expected Learning Outcomes

After studying this unit, you should be able to:

- describe the effect of temperature on the miscibility of partially miscible liquid pairs;
- define critical solution temperature or consolute temperature;
- explain the effect of impurities on the consolute temperature;
- discuss the principle of steam distillation;
- state distribution law and write the expression for distribution coefficient;
- arrive at the expression of distribution coefficient when the solute dissociates or associates in one/both the liquids;
- discuss the applications of distribution law; and
- explain the principle of solvent extraction.

2.2 PARTIALLY MISCIBLELIQUID SYSTEMS

Some liquid pairs do not form solutions in all compositions. Such liquid pairs are said to be *partially miscible liquids*. However, due to increased solubility with increase or decrease of temperature, these may become completely miscible.

We can understand such a system by using the example of a system containing phenol and water. When a very small amount of phenol is added to water at room temperature, it dissolves completely to give a *single liquid phase*. However, when the addition of phenol is continued, a point is reached when phenol does not dissolve anymore. At this point, *two phases*, i.e., two liquid layers are formed–one consisting of water saturated with phenol and the other containing phenol saturated with water. Further addition of phenol causes water to shift from water–rich layer to phenol–rich layer.

If the addition of phenol is continued, a point is reached when phenol acts as a solvent for all the water present and the two phases merge with each other to form a single phase, i.e., solution of water in phenol. Thus, on shaking equal volumes of phenol and water, two layers are formed–one of saturated solution phenol in water and the other of saturated solution water in phenol.

2.2.1 Critical Solution Temperatures

It has been experimentally found that at a constant temperature, the composition of the two layers, although different from each other, remains constant as long as the two phases are present. Such *solutions of different compositions coexisting with each other* are termed as **conjugate solutions**.

The addition of small amounts of phenol or water changes the volumes of the two layers and not their compositions. As the temperature is increased, the behaviour remains the same except that the mutual solubility of the two increases. When the temperature reaches 338.8 K, the composition of the two

layers becomes identical and thereafter, the two liquids are completely miscible; i.e., at and above 338.8K, phenol and water dissolve in each other in all proportions and yield only a single liquid layer on mixing. The variation of mutual solubility of water and phenol with temperature is shown in Fig. 2.1

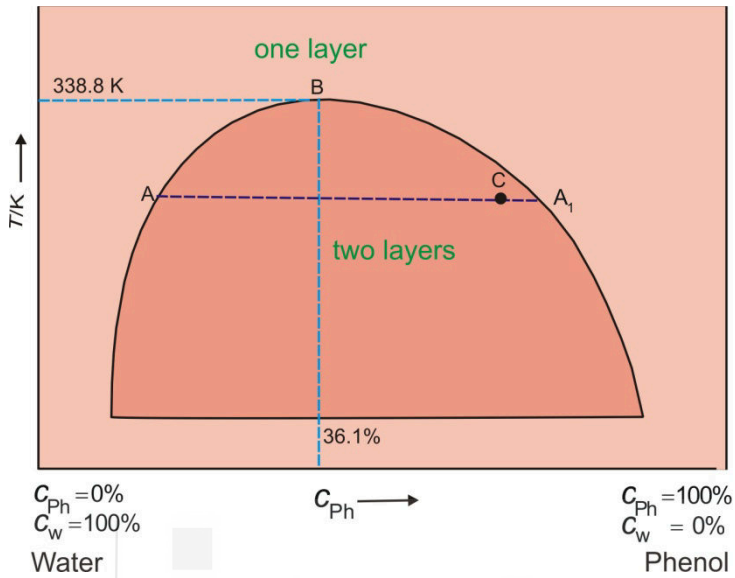


Fig. 2.1: Phenol-water system; c_{Ph} stands for composition of phenol and c_w for composition of water.

At a particular temperature, say 325 K point A represents the composition of water-rich layer and point A_1, represents the composition of phenol-rich layer in equilibrium with the first layer. Between these two compositions, all mixtures will yield two layers of compositions A and A_1. Outside these compositions, the two liquids are soluble mutually at 325 K. Similar behaviour is seen at other temperatures below 338.8 K. We can conclude that the dome-shaped area represents the range of existence of two liquid phases and the area outside the dome represents a single liquid phase. The temperature corresponding to the point B, i.e., the temperature at which the solubility becomes complete is called the **critical solution temperature** or the **consolute temperature.**

Since the *mutual solubility of phenol and water increases with rise in temperature*, the critical solution temperature (CST) lies on top of the dome. Hence, such liquid systems are said to possess an *upper critical solution temperature* or *upper consolute temperature*. Thus, the critical solution temperature, for phenol-water system is 338.8 K. At and above 338.8K, phenol and water are completely miscible with each other in all proportions. At this temperature, the composition of the solution is 36.1% phenol and 63.9% water.

Here, you can consider the line formed by joining the points A and A_1 as the *tie line* and consider a point C on it. Similar to the interpretation of lever rule for liquid–vapour equilibrium studied in Unit 1, here also we can use lever rule as the two layers are in equilibrium. Thus, at any point C, the relative amounts of the two separate layers are given by the relationship,

$$\frac{\text{Mass of the layer A}}{\text{Mass of the layer A}_1} = \frac{A_1C}{AC} \qquad \text{...(2.1)}$$

There are some liquid pairs (e.g., triethylamine-water) for which *mutual solubilities decrease with rise in temperature.* As the temperature is decreased, the mutual solubilities increase and *below the consolute temperature*, the two liquids become miscible in all proportions. Such systems possess *lower consolute temperature*. The variation of mutual solubility of triethylamine and water with temperature is shown in Fig. 2.2.

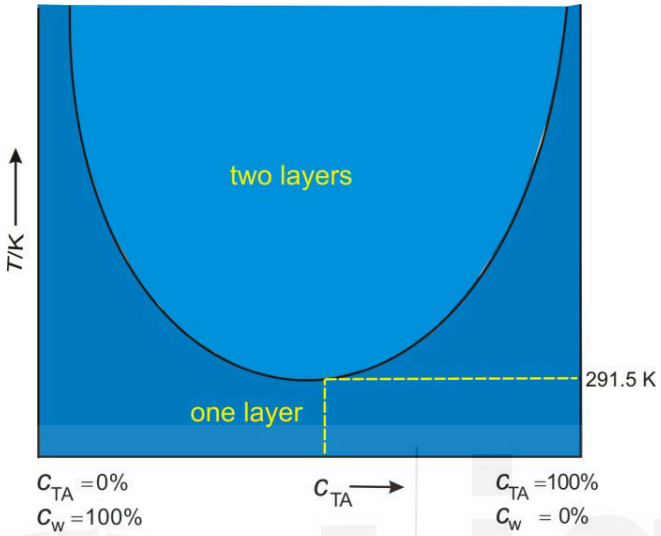


Fig. 2.2: Triethylamine-water system; c_{TA} stands for the composition of triethylamine.

Above 291.5 K, on shaking triethylamine and water two layers are formed; but below 291.5 K, triethylamine and water are completely miscible with each other in all proportions.

There are a few liquids pairs, e.g., nicotine and water which show *both* the upper and lower consolute temperatures. These liquid pairs are completely miscible above a certain temperature (upper consolute temperature) and also below a certain temperature (lower consolute temperature). The variation of mutual solubilities of nicotine and water with temperature is shown in Fig. 2.3.

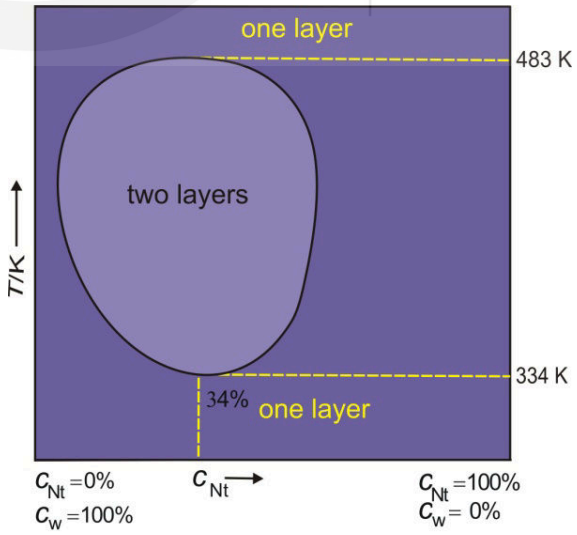


Fig. 2.3: Nicotine-water system; c_{Nt} stands for the composition of nicotine.

Within the enclosed area, the two liquids are only partially miscible, while outside the enclosed area, they are completely miscible. The composition

corresponding to both the upper and the lower consolute temperatures is the same, viz., 34% nicotine.

Table 2.1 lists the consolute temperatures of some liquid pairs. The two liquid components are denoted as A and B.

Table 2.1: Consolute Temperatures of Some Liquid Pairs

Components		Consolute temperature / K	
A	**B**	**Upper**	**Lower**
Water	Phenol	338.8	—
Aniline	Hexane	333.6	—
Methanol	Carbon disulphide	323.5	—
Water	Diethylamine	—	316
Water	Triethylamine	—	291.5
Water	Nicotine	483	334
Water	*m*-Toluidine	393	280

2.2.2 Effect of Impurities on CST Values

The presence of an impurity, dissolved in one or both of the phases, changes the CST values as well as the liquid composition at CST. Substance soluble in only *one* of the liquids *raises the upper CST* and *lowers the lower CST*. For example, one percent solution of sodium chloride raises the upper CST of phenol-water system by 12^0 . About 0.12 molar solution of naphthalene (insoluble in water) in phenol raises the upper CST of phenol-water system by about 30^0. Substances which are soluble in *both* the liquids tend to *lower the upper CST* and *raise the lower CST*. For example, sodium oleate is soluble in both water and phenol. Addition of 1% solution of sodium oleate to phenol-water system lowers the CST value by 45^0.

As seen above, the presence of small amounts of impurities produces a very large change in the CST value. The change in CST values is usually a linear function of concentration of impurities. Traces of water present in alcohol are estimated by measuring their CST values with cyclohexane.

As mentioned above a very small amount of sodium oleate lowers the CST value of phenol-water system considerably. Thus, by making phenol completely miscible with water (adding appropriate amounts of sodium oleate), lysol-like disinfectants are made.

SAQ 1

Give one example each for liquid pairs with

a) lower critical solution temperature.

b) upper critical solution temperature.

c) both upper and lower critical solution temperatures.

SAQ 2

What is the effect of adding 0.1 molar KCl on the CST of phenol-water system?

SAQ 3

What would happen when potassium carbonate is added to a solution of water and alcohol?

2.3 IMMISCIBLE LIQUID PAIRS

In Sec. 2.2, we studied properties of the partially miscible liquid pairs. In this section, we will discuss the characteristics of the completely immiscible liquid pairs. We should, however, understand that there is always some solubility of a substance into the other. But this is so low that we can call it insoluble or completely immiscible.

According to Raoult's law, the vapour pressure of a liquid is lowered on the addition of another liquid, if the latter is soluble in the former. Otherwise, the vapour pressure of each component remains unaffected and each liquid exerts its own vapour pressure independent of the other. Thus, when two completely immiscible liquids A and B are mixed, the total vapour pressure (p) above the mixture will be the sum of the vapour pressures of the pure liquids at that temperature, i.e.,

$$p = p_A^0 + p_B^0 \qquad \ldots(2.2)$$

where p_A^0 and p_B^0 are respectively, the vapour pressures of pure A and B. You also know that a system starts boiling when its total vapour pressure becomes equal to the atmospheric pressure. The mixture of two immiscible liquids A and B will thus start boiling at a temperature (T) at which,

$$p_A^0 + p_B^0 = \text{atmospheric pressure} \qquad \ldots(2.3)$$

This temperature will be lower than the normal boiling point of either A or B. The mixed vapours thus obtained and condensed will have a composition dependent on the partial pressures of A and B at temperature T. Since the number of moles of each component present in the vapour phase is proportional to its vapour pressure, the mole ratio of A to B (n_A/n_B) in the condensate is given by

Condensate or distillate is the liquid obtained by condensing the vapours.

$$\frac{n_A}{n_B} = \frac{p_A^0}{p_B^0} \qquad \ldots(2.4)$$

If w_A and w_B are the masses of A and B in the condensate, and M_A and M_B their respective molar masses, then

$$\frac{n_A}{n_B} = \frac{w_A / M_A}{w_B / M_B} = \frac{w_A M_B}{w_B M_A} = \frac{p_A^0}{p_B^0} \quad \ldots(2.5)$$

or

$$\frac{w_A}{w_B} = \frac{p_A^0 M_A}{p_B^0 M_B} \quad \ldots(2.6)$$

Having understood the above concepts, let us see how these are useful in the technique of steam distillation.

2.3.1 Principle of Steam Distillation

The fact, that a system of immiscible liquids starts boiling at temperatures less than the normal boiling points of both the liquids, is made use of in steam distillation. The steam distillation is a process of purifying organic liquids which have high boiling points and are immiscible with water. For purification by steam distillation, an impure compound

i) must be immiscible in water,

ii) should not decompose at the temperature of steam,

iii) should have a fairly high vapour pressure at 373 K, and

iv) should have non-volatile impurities.

For example, chlorobenzene has a boiling point of 405 K. A mixture of water and chlorobenzene distils at a constant temperature of 363.3 K, when the external pressure in 9.8×10^4 Pa, by passing steam through it.

Let us explain the procedure for purifying an organic liquid using steam distillation. The apparatus used for steam distillation is as shown in Fig. 2.4.

A water condenser has a water inlet (D) and an outlet (E). This condenser is used for cooling the vapours (below 373 K) to get the liquid.

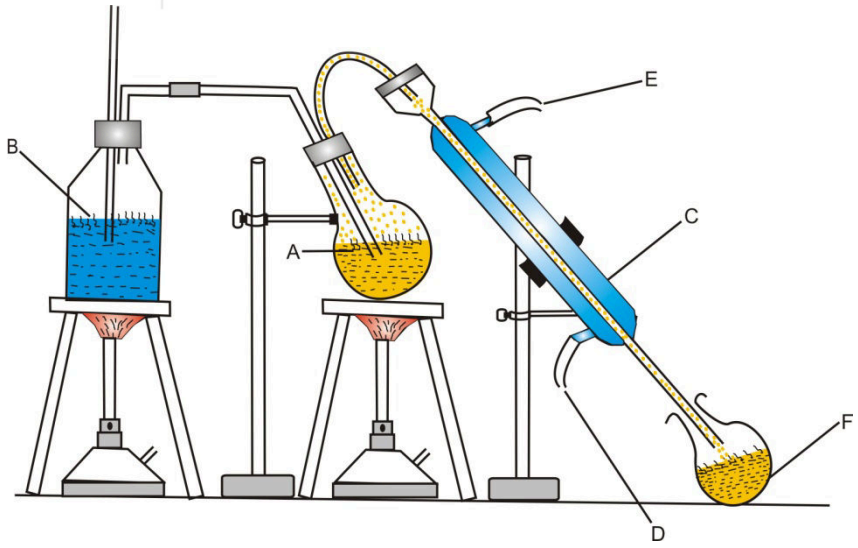


Fig. 2.4: Steam Distillation.

The impure organic compound is taken in a round-bottomed flask (A) and a small quantity of water is added. The flask must be kept in a slanting position

to prevent the impure liquid from splashing up into the condenser. The flask A is then heated gently. Now, steam from container B is bubbled through the contents of the flask A. The vapours of the organic compound mix with steam and escape into the water condenser C. The condensate thus obtained in the flask F is a mixture of water and the organic compound. This mixture can then be separated by means of a separating funnel.

Let us now understand the application of Eq. 2.6 with the help of the following example.

Example 1

A mixture of water and an organic liquid A, which is immiscible in water, distils at 368 K when the external pressure is 1.00 ×10^5 Pa. The vapour pressure of water at 368 K is 8.35 × 10^4 Pa. Calculate the relative molecular mass of A if the distillate contains40% of water by weight.

Solution

Let us represent the vapour pressures of pure water and the organic liquid A at 368 K as $p^0_{H_2O}$ and p^0_A, respectively. At a total pressure of 1.00 × 10^5 Pa, the liquid mixture boils; therefore,

$$p^0_{H_2O} + p^0_A = 1.00 \times 10^5 \text{ Pa}$$

At the distillation temperature, $p^0_{H_2o}$ = 8.35 × 10^4 Pa

Hence, p^0_A = (1.00 × 10^5 Pa - 8.35 × 10^4 Pa) = 1.65 ×10^4 Pa

Using Eq. 2.6,

$$\frac{w_{H_2O}}{w_A} = \frac{p^0_{H_2O} \times M_{H_2O}}{p^0_A \times M_A}$$

But water is 40% by weight; hence, we can write

$$\frac{40}{60} = \frac{8.35\times10^4 \text{ Pa}}{1.65\times10^4 \text{ Pa}} \times \frac{0.018 \text{ kg mol}^{-1}}{M_A}$$

or

$$M_A = \frac{8.35\times10^4 \text{ Pa}}{1.65\times10^4 \text{ Pa}} \times 0.018 \text{ kg mol}^{-1} \times \frac{60}{40}$$

$$= 0.137 \text{ kg mol}^{-1}$$

The relative molecular mass of A = 137

SAQ 4

Why does a mixture of two immiscible liquids boil at a temperature which is lower than the boiling point of any of the pure liquids?

2.4 NERNST DISTRIBUTION LAW AND ITS APPLICATIONS

In this section, we will discuss the distribution of a solute when added to a pair of immiscible liquids. Let us take the example of distribution of iodine when added to two immiscible liquids-water and carbon tetrachloride and understand what is Nernst distribution law.

2.4.1 Nernst Distribution Law

Water and carbon tetrachloride are practically immiscible with each other but iodine dissolves both in water and carbon tetrachloride. When iodine is added to a mixture of water and carbon tetrachloride at a certain temperature, iodine distributes itself between the two immiscible layers-water and carbon tetrachloride. Let the concentrations of iodine in water and carbon tetrachloride be c_{I} and c_{II}, respectively, at a particular temperature. Then ,we have

$$\frac{c_{\text{I}}}{c_{\text{II}}} = K \qquad \ldots(2.7)$$

where K is a constant at a constant temperature.

If more of iodine, is added to this system, it again distributes itself between the two layers. Now, the concentration of iodine in both the layers will be more than that in the previous case. Let the concentrations be c'_{I} and c'_{II} in water and CCl_4 layers, respectively. Though $c'_{\text{I}} > c_{\text{I}}$ and $c'_{\text{II}} > c_{\text{II}}$, the ratio $c'_{\text{I}} / c'_{\text{II}}$ is again equal to the constant, K, i.e.,

$$\frac{c_{\text{I}}}{c_{\text{II}}} = \frac{c'_{\text{I}}}{c'_{\text{II}}} = K \qquad \ldots(2.8)$$

It is evident that, in each case, I_2 distributes itself between the two immiscible layers in such a way that the ratio of its concentration in the two layers is a constant at a certain temperature. It was pointed out by Nernst that the ratio, $c_{\text{I}} / c_{\text{II}}$ is constant only when the solute exists in the same molecular form, i.e., the relative molecular mass of the solute is the same in two layers. The Nernst distribution law may be stated as follows:

At a fixed temperature, a substance X distributes itself between the two immiscible solvents A and B in equilibrium with each other in such a way that the ratio of the concentration of X in the two solvents is constant, provided that the solute X is in the same molecular state in both the solvents.

Mathematically,

$$K = \frac{\text{Concentration of X in solvent A}}{\text{Concentration of X in solvent B}} \qquad \ldots(2.9)$$

The constant K is called the *distribution coefficient or partition coefficient* of the solute between the two solvents. You can see from the data given in Table 2.2 that the value of K is fairly constant in dilute solutions. But, as the concentration increases, there is a deviation.

Table 2.2: Distribution of I_2 between H_2O and CCl_4

$\frac{10^4 \times C_{H_2O}}{\text{mol dm}^{-3}}$	$\frac{10^4 \times C_{CCl_4}}{\text{mol dm}^{-3}}$	$K = \frac{C_{H_2O}}{C_{CCl_4}}$
3.22	2.745	1.17×10^{-2}
5.03	4.29	1.17×10^{-2}
7.63	6.54	1.17×10^{-2}
11.5	10.1	1.14×10^{-2}
13.4	11.96	1.12×10^{-2}

The distribution coefficient *K* depends upon

- nature of the solute,
- nature of the solvents and
- temperature.

The distribution law can be derived taking into account thermodynamic considerations.

Thermodynamic Derivation of Distribution Law

In BCHCT-133 course, Block 2, Unit 5 on Chemical Equilibrium-I, Eq. 5.4 stated the relation of the chemical potential of an ideal gas to its partial pressure in a mixture of gases. Similar expressions can be written when the concentration and the mole fraction are considered in a mixture of gases. Here, we are going to use the modified form of Eq. 5.4 to denote the chemical potentials of a solute (such as iodine) in the two immiscible liquids. Instead of mole fraction used in a similar situation, we are going to use activity (*a*) which is an 'effective' mole fraction. In the case of an infinitely dilute solution, activity becomes equal to mole fraction; hence, similar to Eq. 5.4.The chemical potentials of iodine, μ_1 and μ_2, respectively in water and carbon tetrachloride are given by following equations.

$$\mu_1 = \mu_1^0 + RT \ln a_1 \quad \text{.... (2.10)}$$

$$\mu_2 = \mu_2^0 + RT \ln a_2 \quad \text{.... (2.11)}$$

where μ_1^0 and μ_2^0 are standard chemical potentials of iodine in water and carbon tetrachloride at unit activity; also, a_1 and a_2 are the activities of iodine in water and carbon tetrachloride, respectively.

At equilibrium, $\mu_1 = \mu_2$

Hence, $\mu_1^0 + RT \ln a_1 = \mu_2^0 + RT \ln a_2$

or $\mu_2^0 - \mu_1^0 = RT \ln a_1 - RT \ln a_2$

$= RT \ln a_1 / a_2$

At constant temperature, μ_1^0 and μ_2^0 are constants.

Also, *R* is constant. Therefore, it follows that

$$a_1 / a_2 = \text{constant} \qquad \ldots(2.12)$$

This is another form of the distribution law. At low concentrations, activities can be replaced by concentration, and we get

$$\frac{a_1}{a_2} = \frac{c_1}{c_2} = \text{constant}$$

or

$$\frac{a_1}{a_2} = \frac{c_1}{c_2} = K$$

Nernst first gave attention to the fact that the above statement of the distribution law is valid only when the solute undergoes *no change such as dissociation* or *association* in either of the solvents. If a solute dissociates into simple molecules or ions or if it associates to form complex molecules, then the distribution law does not apply to the total concentration of the solute in each of the two phases. It is applicable to the *concentration of a particular species common to both the layers*. Let us look at this in some detail by considering the following cases.

2.4.2 Dissociation of a Solute in One of the Solvents

Eqs. 2.13 to 2.21 are written following the principle of chemical equilibrium.

Let us take a solute X which remains undissociated in phase I. We assume that its concentration in phase I is c_1. In phase II, let it undergo dissociation into A and B. If c_2 is the total concentration in phase II beforedissociation, and α is the degree of dissociation, then we can write

$$\underset{c_2(1-\alpha)}{X} \rightleftharpoons \underset{c_2\alpha}{A} + \underset{c_2\alpha}{B} \qquad \ldots(2.13)$$

Evidently, the concentration of the undissociated molecules of X in phase II is $c_2(1-\alpha)$. So as per distribution law, the distribution coefficient is given by

$$K = \frac{\text{Concentration of X in phase I}}{\text{Concentration of undissociated X in phase II}}$$

or $K = c_1/c_2\,(1-\alpha)$ …(2.14)

The following example illustrates the application of Eq. 2.14

Example 2

An organic acid A, distributes between 1.0 dm^3 each of an organic solvent, S, and water. The concentration of the acid in aqueous layer is 1.20×10^{-2} kg dm^{-3} and in the organic layer, it is 1.44×10^{-3} kg dm^{-3}. If the distribution coefficient of the acid between the organic solvent and water is 0.16, calculate the degree of dissociation of the organic acid in water. Assume that the acid does not undergo any change in its molecular state in the organic solvent, S.

Solution

Let the concentration of the acid in the organic and water layer be c_1 and c_2, respectively. Hence,

$c_1 = 1.44 \times 10^{-3}$ kg dm^{-3}

and $c_2 = 1.20 \times 10^{-2}$ kg dm^{-3}

Using Eq. 2.14, we have

$$0.16 = \frac{1.44 \times 10^{-3}\ \text{kg dm}^{-3}}{1.20 \times 10^{-2}\ \text{kg dm}^{-3} \times (1-\alpha)} = \frac{0.12}{(1-\alpha)}$$

Or $$(1-\alpha) = \frac{0.12}{0.16} = 0.75$$

$$\alpha = 1 - 0.75 = 0.25$$

The percentage dissociation of the acid in water in 25%.

Let us next consider what will happen if the solute associates in one of the solvents.

2.4.3 Association of the Solute in one of the Solvents

Let X be a solute that does not undergo dissociation or association in phase I. Let its concentration be c_i in phase I. And, it associates in phase II as given in Eq. 2.15 to give the molecules, X_n.

Let us assume that c_2 is the concentration of the solute in phase II, if there is no association, Let α be the fraction of the molecules that is associated in phase II to give the molecules X_n.

$$\begin{array}{ccc} n\,X & \rightleftharpoons & X_n \\ c_2(1-\alpha) & & c_2\alpha/n \end{array} \qquad \ldots(2.15)$$

Then, the concentration of the associated molecules can be calculated as follows:

The concentration of the unassociated X = $c_2(1-\alpha)$

The concentration of X used for forming associated molecules = $c_2\alpha$

Since n moles of X give one mole of the associated species, X_n

Concentration of the associated species, $X_n = c_2 \frac{\alpha}{n}$ …(2.16)

Then, $$K = \frac{\text{Concentration of X in phase I}}{\text{Concentration of undissociated species in phase II}}$$

or $$K = \frac{c_1}{c_2(1-\alpha)} \qquad \ldots(2.17)$$

Also, it is possible to calculate the equilibrium constant, K_{eq}, for equilibrium represented by Eq. 2.15, if α is known.

$$K_{eq} = \frac{c_2 \frac{\alpha}{n}}{[c_2(1-\alpha)]^n} \qquad \ldots (2.18)$$

or $$[c_2(1-\alpha)]^n = \frac{c_2 \frac{\alpha}{n}}{K_{eq}} \quad \ldots (2.19)$$

$$[c_2(1-\alpha)] = \left[\frac{c_2\alpha/n}{K_{eq}}\right]^{1/n}$$

$$[c_2(1-\alpha)] = \left[\frac{c_2\alpha}{nK_{eq}}\right]^{1/n} \quad \ldots (2.20)$$

Substituting Eq. 2.20 in Eq. 2.17,

$$K = \frac{c_1}{\left[\frac{c_2\alpha}{nK_{eq}}\right]^{1/n}} = \frac{c_1}{c_2^{1/n}}\left[\frac{nK_{eq}}{\alpha}\right]^{1/n}$$

At constant temperature, n, K_{eq} and α are constants.

$$K = \frac{c_1}{c_2^{1/n}} \text{.constant}$$

$$K' = \frac{K}{\text{constant}} = \frac{c_1}{c_2^{1/n}} \quad \ldots (2.21)$$

Hence, if c_1, c_2 and n are known, K'could be found out. The value of n could help us in finding out whether the solute remains as a dimer, trimer etc. in a particular solvent.

With the help of Eq. 2.21, it is possible to determine approximate values of n. Two important methods for this purpose are illustrated below:

1) Method of Trial and Error

In Eq. 2.21, integer values starting with 1 and above are given to n. The value for which Eq. 2.21 gives a constant value for $K'$is adopted.

2) Graphical Method

n is called the order of association.

Eq. 2.21 can also be written as follows,

$$c_1 = K'(c_2)^{1/n}$$

Taking logarithms on both sides, we get

$$\log c_1 = \log K' + \frac{1}{n}\log c_2$$

$$\log c_1 = \frac{1}{n}\log c_2 + \log K \quad \ldots (2.22)$$

Eq. 2.22 is of the type $y = mx + c$ which is an equation for a straight line. If a graph is plotted between log c_1 and log c_2, a straight line is obtained as shown below in Fig. 2.5. The slope of the line gives the value of $1/n$ from which n can be calculated. The intercept on the y-axis gives the value of log $K'$and henceK'can be calculated.

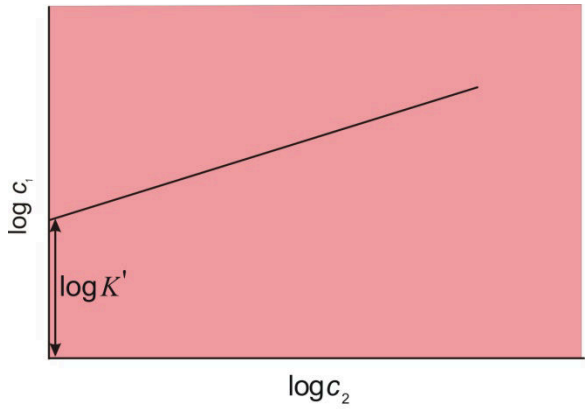


Fig. 2.5: log c_1 plotted against log c_2.

Example 3

The following results were obtained for the distribution of benzoic acid between water and benzene at 298 K:

Concentration in H_2O (c_1) / (mol dm^{-3})	0.0033	0.0058	0.0075
Concentration in C_6H_6 (c_2) / (mol dm^{-3})	0.0156	0.0495	0.0835

What conclusion can be drawn from these results regarding the molecular form of benzoic acid in benzene? Assume that c_1 represents the concentration of the undissociated benzoic acid in water.

Solution

It is known that benzoic acid is dissociated in water into its ions. The concentration c_1 of the benzoic acid given above is that of the undissociated acid. If benzoic acid remains as normal molecules in benzene, then $\frac{c_1}{c_2}$ must be constant. Let us see whether it is so?

$$\frac{c_1}{c_2} = \frac{0.0033 \text{ mol dm}^{-3}}{0.0156 \text{ mol dm}^{-3}} = 0.211$$

$$\frac{c_1}{c_2} = \frac{0.0058 \text{ mol dm}^{-3}}{0.0495 \text{ mol dm}^{-3}} = 0.117$$

$$\frac{c_1}{c_2} = \frac{0.0075 \text{ mol dm}^{-3}}{0.0835 \text{ mol dm}^{-3}} = 0.090$$

As $\frac{c_1}{c_2}$ varies considerably, benzoic acid in benzene is not present as normal molecules. We can find the value of *n* using trial and error method. Substituting $n = 2$ in Eq. 2.21, let us see whether we get a constant value for $\frac{c_1}{c_2^{1/2}}$.

$$\frac{c_1}{c_2^{1/2}} = \frac{0.0033 \text{ mol dm}^{-3}}{\left(0.0156 \text{ mol dm}^{-3/2}\right)^{1/2}} = \frac{0.0033 \text{ mol dm}^{-3}}{0.0125(\text{ mol dm}^{-3})^{1/2}} = 0.0264 \text{ (mol dm}^{-3})^{1/2}$$

$$\frac{c_1}{c_2^{1/2}} = \frac{0.0058 \text{ mol dm}^{-3}}{(0.0495 \text{ mol dm}^{-3})^{1/2}} = \frac{0.0058 \text{ mol dm}^{-3}}{0.223(\text{ mol dm}^{-3})^{1/2}} = 0.0260 \text{ (mol dm}^{-3})^{1/2}$$

$$\frac{c_1}{c_2^{1/2}} = \frac{0.0075 \text{ mol dm}^{-3}}{(0.0835 \text{ mol dm}^{-3})^{1/2}} = \frac{0.0075 \text{ mol dm}^{-3}}{0.289(\text{ mol dm}^{-3})^{1/2}} = 0.0260 \text{ (mol dm}^{-3})^{1/2}$$

It is clear from the above calculations that the values of $\frac{c_1}{c_2^{1/2}}$ are fairly constant.

Hence, benzoic acid in benzene exists as a dimer, $(C_6H_5COOH)_2$.

To understand the application of distribution law, when the solute undergoes association in one solvent and dissociation in another, let us consider the distribution of benzoic acid between water and chloroform as given in Table 2.3.

Table 2.3: Distribution of Benzoic Acid between Water and Chloroform at 313 K

In Table 2.3, c_{w1} is the concentration of un-dissociated benzoic acid in aqueous layer and c_{c1} is the concentration of unassociated benzoic acid in chloroform layer.

$\frac{10^3 \times c_W}{\text{mol dm}^{-3}}$	$\frac{10^3 \times c_C}{\text{mol dm}^{-3}}$	$\frac{c_W}{c_C}$	$\frac{10^3 \times c_{W1}}{\text{mol dm}^{-3}}$	$\frac{10^3 \times c_{C1}}{\text{mol dm}^{-3}}$	$K = \frac{c_{w1}}{c_{C1}}$
2.11	7.21	0.293	1.78	4.04	0.441
2.68	10.8	0.248	2.31	5.23	0.442
3.53	16.8	0.210	3.10	7.01	0.442
7.25	57.0	0.127	6.62	15.0	0.441
12.7	167.0	0.076	11.8	26.9	0.439

In Example 3, the concentrations of un-dissociated benzoic acid in aqueous layer (c_1) have been given. But in Table 2.3, c_w gives the total concentration of benzoic acid in the aqueous layer and it includes the dissociated and un-dissociated forms. Also, c_C is the total concentration of benzoic acid in chloroform layer. You see that c_w/c_C is not constant. The observed results can be explained on the basis that the acid is partially dissociated in water into hydrogen ion and benzoate ion and partially associated in chloroform into dimers.

Since, the distribution law can be applied to the common species present in both the phases (i.e., un-dissociated or unassociated benzoic acid), correction must be applied for association and dissociation. After applying these corrections, you see that $\frac{c_{w1}}{c_{C1}}$ is constant as given in the last column.

Now, you have a good understanding of using distribution law in different

situations. At this stage, it is worthwhile to discuss some applications of this law.

2.4.4 Applications of the Distribution Law

The study of the distribution of a solute between two immiscible solvents is quite useful in a number of ways. A few of these applications are given below:

1. By studying the distribution of acetic acid and benzoic acid between water and benzene, it is possible to show that acetic acid and benzoic exist as dimers in benzene.
2. If a solute dissociates in one of the solvents, then knowing the distribution coefficient, the degree of dissociation of the solute can be calculated at a particular temperature.
3. The distribution law has also been used in the study of many problems e.g., solvent extraction, analysis and determination of equilibrium constants. Let us study the principle of solvent extraction in detail.

Solvent Extraction

Solvent extraction is used both at laboratory and industrial scale in various processes. An organic compound can often be extracted economically from an aqueous solution or a suspension by,

- adding an organic solvent,
- shaking and separating the two layers, and
- finally, distilling off the organic solvent to recover the separated compound.

In the process of extraction, we make use of the fact that the distribution coefficient of most of the organic compounds is very large in favour of organic solvents. It can be shown that with a given volume of an extracting liquid, the organic compound extracted is more if the given volume of the extracting liquid is used in a number of smaller lots than if the whole of it is used in one lot. Let us derive a general formula which enables the calculation of the amount that is left unextracted after a given number of extractions.

If the distribution coefficient of a solute between ether and water is 3 in favour of the ether, it means that the solute in three times more soluble in ether as compared to that in water.

Let us consider an aqueous solution of volume V. Let the mass of an organic compound dissolved in it be w. Let us use volume v of the organic liquid for each extraction and let the mass of the organic compound that remained unextracted in water one extraction be w_1.

After the First Extraction

Concentration of the organic compound in the aqueous layer = $\frac{w_1}{V}$

Mass of the organic compound in the organic layer = $w - w_1$

Concentration of the organic compound in the organic layer = $\frac{w - w_1}{v}$

Distribution coefficient, K, is given by the following expression:

$$K = \frac{\text{Concentraton of the compund in the aqueous layer}}{\text{Concentraton of the compund in the organic layer}}$$

or $$K = \frac{\frac{w_1}{V}}{\frac{(w - w_1)}{v}} = \frac{w_1 v}{(w - w_1)V}$$

or $$K(w - w_1)V = w_1 v$$

or $$KwV = w_1 v + Kw_1 V = w_1(v + KV)$$

or $$w_1 = \frac{KwV}{(v + KV)} = w\frac{KV}{v + KV}$$

After the Second Extraction

Similarly, after the second extraction, the mass of the organic compound that remains unextracted is,

$$w_2 = w_1 \frac{KV}{(v + KV)} = w\left(\frac{KV}{v + KV}\right)^2$$

After *n* Extractions

In general, the mass of the organic compound that remains unextracted after *n* extractions is given by,

$$w_n = w\left(\frac{KV}{v + KV}\right)^n \quad \ldots(2.23)$$

Applications of Solvent Extraction

1. Often we have to recover the organic compounds from an aqueous solution using extraction method.

Desilverisation means removal of silver. Argentiferrous galena is an ore of lead containing silver.

2. Desilverisation of Argentiferrous Lead

Argentiferrous galena contains small quantities of silver which could be extracted quite economically by Parkes process. In this process, molten zinc is used for extracting silver from molten argentiferrous lead as it is immiscible with molten lead. The distribution coefficient of silver between molten Zn and molten Pb is 300 at 1073 K. Therefore, when molten zinc is added to molten argentiferrous lead, practically the whole of silver present passes into the molten zinc layer. On cooling, Zn-Ag alloy solidifies before lead. The solid layer can be remove easily. As zinc is volatile, it can be separated from silver by distillation.

2.5 SUMMARY

In this Unit, you have learnt the following:

- When two liquids are mixed, they may be completely miscible, partially miscible or completely immiscible.
- The miscibility of partially miscible liquid pairs varies with temperature.

- The miscibility of some partially miscible liquid pairs, e.g., phenol-water increases with rise in temperature.
- The temperature at which a pair of partially miscible liquids becomes completely miscible iscalled critical solution temperature or consolute temperature. Thus, phenol-water system possesses an upper CST.
- Some liquid pairs possess lower CST, i.e., their mutual solubility decreases with rise in temperature. Below a certain temperature, such liquid pairs are completely miscible.
- Some liquid pairs possess both lower and upper CST.
- The presence of an impurity in one or both the phases changes the CST values.
- Substances soluble in one of the liquids raise the upper CST and lower the lower CST.
- Substances soluble in both the liquids tend to lower the upper CST and raise the lower CST.
- A pair of immiscible liquids boil at a temperature lower than the boiling points of any of the liquids. This fact is made use of in steam distillation.
- When a solute is added to a pair of immiscible liquids, it distributes itself between the two liquids in such a way that the ratio of the concentrations of the solute in the two phases remains constant. This is called the distribution law.
- The distribution law can be used to study the state of association or dissociation of the solute in one or both the phases.
- The distribution law also helps in determining the degree of dissociation of a solute. The order of association of a solute can also be determined using distribution law.
- The distribution law has applications in solvent extraction, analysis and determination of equilibrium constants.

2.6 TERMINAL QUESTIONS

1. Two liquids A and B are completely immiscible with each other. Their normal boiling points are T_A and T_B, respectively, and T_A is less than T_B. The two liquids taken together will boil at

   i) T_A

   ii) T_B

   iii) $\frac{T_A + T_B}{2}$

   iv) a temperature less than T_A.

   v) a temperature more than T_B.

2. An immiscible mixture of an organic liquid, Aand water on steam distillation boils at 372 K at pressure 1.00×10^5 Pa. At this temperature, the vapour pressure of water is 9.60×10^4 Pa. The ratio of the mass of water to the mass of A in the distillate is 4:1. Calculate the relative molecular mass of liquid A.

3. Explain the behaviour of partially miscible liquid systems with respect to change of temperature.

4. Derive distribution law thermodynamically.

5. When 1.00 dm^3 of an aqueous solution containing 5.00×10^{-3} kg of a solute is shaken with 5.00×10^{-2} dm^3 ether, it is found that 8.50×10^{-4} kg of the solute passes into ether. How much of the solute will be left unextracted, if the same aqueous solution is shaken with a second installment of 5.0×10^{-2} dm^3 ether? The solute exists in the same molecular state in both water and ether.

6. Succinic acid is associated in benzene. Find the order of association (n) from the following data on the distribution of succinic acid between water and benzene. Assume that c_1 is the concentration of undissociated succinic acid in water and c_2 is the total concentration of succinct acid in benzene.

$10^3 \times c_1$ in water/ (kg dm^{-3})	1.10	1.95	2.90
$10^3 \times c_2$ in benzene/ (kg dm^{-3})	14.2	41.2	96.5

2.7 ANSWERS

Self-Assessment Questions

1. See Table 2.1.

2. Raises the critical solution temperature of phenol-water system.

3. Since potassium carbonate is highly soluble in water but not in ethanol, the solubility of ethanol in water decreases and two layers and formed.

4. The sum of the vapour pressures of the two liquids becomes equal to the atmospheric pressure at a lower temperature.

Terminal Questions

1. iv)

2. Given that,

$$\frac{\text{Mass of water}}{\text{Mass of A}} = \frac{4}{1}$$

Vapour pressure of water $(p^0_{H_2O}) = 9.60 \times 10^4$ Pa

Vapour pressure of liquid A $(p^0_A) = 1.00 \times 10^5$ Pa - 9.60×10^4 Pa

$= 4.00 \times 10^3$ Pa

Using Eq. 2.6,

$$\frac{w_{H_2O}}{w_A} = \frac{p^0_{H_2O} \times M_{H_2O}}{p^0_A \times M_A}$$

or $$M_A = \frac{p^0_{H_2O} \times M_{H_2O}}{p^0_A} \times \frac{w_A}{w_{H_2O}}$$

$$= \frac{9.60 \times 10^4 \text{ Pa} \times 0.018 \text{ kg mol}^{-1}}{4.0 \times 10^3 \text{ Pa}} \times \frac{1}{4}$$

$$= 0.108 \text{ kg mol}^{-1}$$

Hence, the relative molecular of mass A = 108

3. See Sec. 2.2.

4. See Sec. 2.4.

5. Concentration of the solute in aqueous layer

$$(c_1) = (5.00 - 0.850) \times 10^{-3} \text{ kg} / 1.00 \text{ dm}^3$$

$$= 4.15 \times 10^{-3} \text{ kg dm}^{-3}$$

Concentration of the solute in ether layer

$$(c_2) = \frac{8.50 \times 10^{-4} \text{ kg}}{5.00 \times 10^{-2} \text{ dm}^3} = 1.70 \times 10^{-2} \text{ kg dm}^{-3}$$

Distribution coefficient between water and ether,

$$K = \frac{c_1}{c_2} = \frac{4.15 \times 10^{-3} \text{ kg dm}^{-3}}{1.70 \times 10^{-2} \text{ kg dm}^{-3}} = 0.244$$

Using Eq. 2.23, the amount of the solute left after the second extraction is

$$w_2 = w\left(\frac{KV}{v + KV}\right)^2 = 5.00 \times 10^{-3} \text{ kg} \left[\frac{0.244 \times 1.00 \text{ dm}^{-3}}{5.00 \times 10^{-2} \text{ dm}^{-3} + (0.244 \times 1.00 \text{ dm}^3)}\right]^2$$

$$= 3.44 \times 10^{-3} \text{ kg}$$

6. By trial and error method, let us try whether $\frac{c_1}{c_2}$ is constant by keeping n = 1 in Eq. 2.21.

$$\frac{c_1}{c_2} = \frac{1.10 \times 10^{-3} \text{ kg dm}^{-3}}{14.2 \times 10^{-3} \text{ kg dm}^{-3}} = 0.077$$

$$= \frac{1.95 \times 10^{-3} \text{ kg dm}^{-3}}{41.2 \times 10^{-3} \text{ kg dm}^{-3}} = 0.047$$

$$= \frac{2.90 \times 10^{-3} \text{ kg dm}^{-3}}{96.5 \times 10^{-3} \text{ kg dm}^{-3}} = 0.030$$

As the value of $\frac{c_1}{c_2}$ is not constant, $n \neq 1$.

Let us now try for $n = 2$.

$$K = \frac{c_1}{\sqrt{c_2}} = \frac{1.10 \times 10^{-3} \text{ kg dm}^{-3}}{\sqrt{14.2 \times 10^{-3} \text{ kg dm}^{-3}}} = 9.23 \times 10^{-3} (\text{kg dm}^{-3})^{\frac{1}{2}}$$

$$= \frac{1.95 \times 10^{-3} \text{ kg dm}^{-3}}{\sqrt{41.2 \times 10^{-3} \text{ kg dm}^{-3}}} = 9.61 \times 10^{-3} (\text{kg dm}^{-3})^{\frac{1}{2}}$$

$$= \frac{2.90 \times 10^{-3} \text{ kg dm}^{-3}}{\sqrt{96.5 \times 10^{-3} \text{ kg dm}^{-3}}} = 9.34 \times 10^{-3} (\text{kg dm}^{-3})^{\frac{1}{2}}$$

As the value of $\frac{c_1}{c_2^{\frac{1}{2}}}$ is constant, the order of association is 2. Hence, succinic acid exists as a dimer in benzene.

UNIT 3

Phase Equilibrium–I

Structure

3.1 INTRODUCTION

In the Course BCHCT-133 you have learnt in detail about energetics; chemical equilibrium and ionic equilibrium and are familiar with the meaning and importance of equilibrium studies. Further, in the first two units of this block you have learnt about solutions. In all these, you have learnt primarily about the characteristics of the systems that are homogeneous, that is, the systems in which the properties of the system are uniform throughout. You have also come across cases of heterogeneous equilibrium like vapourisation, sublimation, fusion, phase transformation, distribution of solutes between phases etc. In these cases, we used different rules (laws) suitable for the systems to understand them.

In this and the next unit we would take up equilibrium in heterogeneous systems in a unified manner by using phase rule that applies to all kinds of heterogeneous equilibria. The phase rule serves to identify and fix the number of variables for a heterogeneous system. A study of phase equilibrium is important in various domains like, chemistry, physics, metallurgy, chemical engineering, material science and geology etc.

We will begin the unit by defining and explaining the terms such as true, metastable, and unstable equilibrium; phase, component, degrees of freedom; and phase transition. Thereafter, we would take up the criterion for phase equilibrium followed by the deduction of Gibbs phase rule. Then, we would discuss about the stability of different phases of a pure substance in terms of chemical potential (μ). In this context we would explain the nature of μ versus T curves and their pressure dependence. This will be followed by the derivation of Clapeyron and Clausius-Clapeyron equations and a discussion on their importance in phase equilibria. In the next unit, we would take up the applications of phase rule to one and two component systems.

Expected Learning Outcomes

After studying this unit, you should be able to:

- define and differentiate between true and metastable equilibrium;
- define and explain the terms like, phase, component, and degrees of freedom in the context of phase equilibrium using suitable examples;
- calculate the number of phases, components and degrees of freedom for a given heterogeneous system;
- state and explain the criterion for phase equilibrium in a heterogenous system;
- define phase transition and describe the changes occurring during different phase transitions;
- state phase rule; deduce the same and outline its significance;
- explain the stability of different phases of a pure substance in terms of μ versus T curves;
- explain the effect of pressure on the μ versus T curves for a pure substance; and
- derive Clapeyron and Clausius-Clapeyron equations and apply them to heterogeneous systems in equilibrium.

3.2 BASIC TERMINOLOGY

You have learnt about the nature and characteristics of chemical and ionic equilibria in the course BCHCT-133. However, in case of phase equilibrium there are certain new terms, which need to be understood before taking up phase rule and its application to phase equilibrium.

3.2.1 True, Metastable and Unstable Equilibrium

In your earlier studies in the context of chemical equilibrium you have learnt equilibrium to be a state of *apparent no change* in the concentration of different species as a function of time. If the state of equilibrium can be achieved from either direction, i.e., from the reactants or from the products then, it is referred to as **true equilibrium**. For example, we can have a

A true equilibrium is achieved when the Gibbs energy of the system is at a minimum for the given set of variables operating on the system.

system containing ice and water to be at equilibrium at 0ºC and 1 atm. This equilibrium can be achieved either by heating a sample of ice to partially melt it to give some water or by cooling a sample of water to partially freeze it to give some ice. Similarly, we can establish equilibrium between a liquid and its vapours in a closed system either by heating the liquid or by partially condensing the vapours by cooling. Thermodynamically speaking, in such cases the Gibbs energy of the system is at its minimum when the system is at the equilibrium.

Let's take another example say we take a sample of clean water that is free of dust in a smooth container and cool it slowly without any disturbance. What do we expect? We expect that as the temperature approaches 0°C, the freezing point of water then water would freeze. However, it is possible that the water does not freeze, and the temperature continues to decrease and goes below 0°C and the water stays to be in the liquid state even at $-5^{\circ}C$. Now, if we leave the water at $-5^{\circ}C$ undisturbed then it can continue to stay to be in liquid state at $-5^{\circ}C$. Now, since we do not observe any change can we say that we have got the system at equilibrium. The answer is no; let us see why?

If we disturb the water at $-5^{\circ}C$ by shaking it a bit or by stirring it or by adding a small crystal of ice to it (i.e., we do seeding), we observe that the water at $-5^{\circ}C$ immediately freezes and the temperature increases to 0°C. Now, if we take a sample of ice at say $-20^{\circ}C$ and warm it gradually, we find that we do not get water when the temperature becomes $-5^{\circ}C$; the ice melts only when the temperature becomes 0°C. What do we conclude from this example? We conclude that water at $-5^{\circ}C$ is *not* in a state of true equilibrium because we could obtain it only in one direction by gradually cooling water but not by warming ice at a lower temperature. The liquid water at $-5^{\circ}C$ is called **super cooled water** and such equilibrium that can be obtained only from one direction is called **metastable equilibrium**.

Let us take another system in which we dissolve just sufficient amount of sodium chloride in water to prepare a nearly saturated solution such that there are a few crystals of sodium chloride along with the solution. If we observe the system for some time, we find no change-the crystals stay along with the solution. Since we do not observe any change, can we say that the system in state of equilibrium? To find answer to this, we need to leave such a system for long time, say overnight. We may be surprised to note that the crystals of sodium chloride have disappeared (dissolved). In such a case since initially we observed the system for an insufficient time it appeared to be in equilibrium (apparent no change) however, the process of dissolution of salt to achieve true saturation was slow and was still continuing. Such a system may be termed as ***unstable equilibrium*** or **non-equilibrium**. In fact, it does not involve any equilibrium at all, it is just a case of very slow process.

A state of unstable equilibrium exists when the approach to equilibrium in a system is so slow that the system appears to undergo no change over a short period of time.

3.2.2 Phases (*P*)

The word phase is derived from the Greek meaning "appearance". Gibbs defined a phase as *a homogenous system that is "uniform throughout, not only in chemical composition, but also in physical state".* Alternatively, a phase may be seen as "*a homogeneous, physically distinct, and mechanically separable portion of a system".* Mechanically separable here means that each phase can

be separated from every other phase of the system by mechanical means of separation like, filtration, sedimentation, decantation etc. Further, a phase is separated from other homogeneous parts of the system by boundary surfaces. In phase rule, which we would take up a little later a phase, is denoted as *P*. Let us take some examples to understand the term, phase.

- A mixture of gases say air is a single phase as all gases mix in all proportions and are not separable by mechanical means as given above. However, one must remember that the gases in the mixture should not react with one another for it to be a one-phase system. For example, if we mix unequal amounts of NH_3 and HCl gas then the two would react to form solid ammonium chloride that would settle down and some of the gas (in excess) would also remain. Thus, there would be two phases; solid phase (ammonium chloride) and gaseous phase (the gas in excess).

- Any true solution by definition is a homogeneous mixture of two or more substances irrespective of their physical state (solid/liquid/gas) or their relative amounts in the mixture. A dilute solution of sodium chloride in water or a mixture of alcohol and water that form true solutions are examples of one-phase systems. We cannot separate the constituents of a true solution by mechanical means. Thus, *a true solution is a single phase*.

- Just breaking the system into smaller parts does not form new phases. A large block of ice or crushed ice; both are examples of one phase systems.

- A system may consist of a number of solid or liquid phases but can have only one gaseous phase. For example, two or more miscible liquids constitute a single phase. However, if one or more of these liquids are volatile then their vapours in equilibrium also constitute a phase. For example, a system containing a mixture of alcohol and water in equilibrium with their vapours will be a two-phase system; one liquid phase and one vapour (or gas phase). Thus, *two miscible liquids in equilibrium with their vapours constitute a two-phase system*.

- An aqueous solution of sodium chloride (or any other soluble substance) is a one-phase system as it is a true solution. However, a saturated solution of sodium chloride in contact with excess solid sodium chloride forms two-phase system.

- Mixtures of two allotropes say monoclinic and rhombic sulphur constitutes two phases because a phase must have the same physical and chemical properties. Two allotropes are chemically identical but differ in their physical properties.

- A heterogeneous mixture of different solid substances would have as many phases as there are substances present in the system. However, if we have a mixture of two solids and a solid solution is formed between them then it becomes a one-phase system, as a solid solution is homogeneous.

3.2.3 Components (*C*)

It is immaterial which of the constituents are chosen as components; it is their number that is important.

The concept of phases in a system is relatively straightforward but the idea of components in the context of phase equilibrium (also phase rule) is a little involved. The number of components of a system can be defined as, "*the smallest number of independently variable chemical constituents of the system in terms of which composition of each phase in equilibrium can be completely defined either directly or in the form of an equation*". It is important to note the distinction between the components and constituents. The components are not same as constituents of the system i.e., the elements or compounds present in the system. Alternatively, we can say components are those chemically distinct *constituents whose concentrations may be independently varied in the various phases of the system*.

The requirement of smallest number is crucial in this definition. If the concentrations of the chosen components are stated for each phase, then the concentrations of any and all substances present in each phase of the system are uniquely fixed. Let us understand it with the help of some examples of different types of systems. We begin with systems where constituents do not react.

All the constituents need not be components, but all the components must be the constituents in the system.

a) Systems in which the constituents do not react

- Let's take one of very simple systems in which ice, water and water vapours are in equilibrium. In this case there are three phases viz., solid, liquid and gas however, the composition of each phase can be expressed in terms of only one component viz., water. You may note here that in this system there is only one constituent so the components have to be one; it can't be lesser (you cannot have zero components) or greater (a component has to be a constituent of the system and we have only one constituent here). You may note here that hydrogen and oxygen, the constituents of water, are not to be regarded as components. It is so because, they are not present in the system as such, but they are combined in definite proportions to form water, and their amounts cannot be varied independently.

- In a system containing sugar and water there are two possibilities. First, if the solution is unsaturated it will be a homogeneous system i.e., it will have only one phase. It has two constituents, sugar and water and we need to specify both of them to express the composition of the solution as

  x Sugar + y H_2O

  i.e., the number of components is two. Secondly, if the amount of sugar in the system is more than its solubility in given amount of water then the system would become a heterogeneous system having two phases: homogeneous sugar solution and undissolved sugar. Here again, we would need two components to specify the composition of each phase as

  Aqueous phase: x Sugar + y H_2O

  Solid phase: Sugar + 0 H_2O

Thus, it is a two-component system. In general, we can say that *in systems where the constituents do not react, the number of components is equal to the number of constituents.*

b) **Systems in which constituents undergo chemical reaction**

In such cases the number of components, C is given as $C = C' - R$; where C' is the number of constituents in the system and R is the number of reactions actually taking place in the system or the restrictions (or constraints) on independent variability of the concentration of the constituents. Let's take some examples to understand it.

- Thermal decomposition of calcium carbonate as given below

  $CaCO_3 \rightleftharpoons CaO + CO_2$

  In this case there are three distinct constituents viz., calcium carbonate, calcium oxide and carbon dioxide between which the equilibrium exists. However, all of these are not to be taken as the components, as they are not mutually independent, there is one restriction on their concentration to be varied independently. This restriction happens to be the equilibrium constant because of which if we specify the concentrations of any two of the constituents, that of the third automatically gets fixed. Therefore, the number of components in this case would be; $C = 3 - 1 = 2$. That is, it is a two-component system. Now, the question comes up is that which of the three constituents of the system are the components? In principle, the choice of components of the system out of the constituents is arbitrary i.e., we can choose any two constituents. However, in this particular case the choice makes a difference let's see how?

  If we choose $CaCO_3$ and CaO as the components; then the composition of each phase can be expressed by the following equations:

Phase		Composition in terms of components		
$CaCO_3$	=	$CaCO_3$	+	$0\,CaO$
CaO	=	$0\,CaCO_3$	+	CaO
CO_2	=	$CaCO_3$	−	CaO

  You may note here that we have used both zero and negative quantities of the components to express the composition of different phases as equations. We will get similar equations if we choose $CaCO_3$ and CO_2 as the components.

Phase		Composition in terms of components		
$CaCO_3$	=	$CaCO_3$	+	$0\,CO_2$
CaO	=	$CaCO_3$	−	CO_2
CO_2	=	$0\ CaCO_3$	+	CO_2

  However, if we choose CaO and CO_2 as the components then the use of negative quantities can be avoided as shown below.

An aqueous solution of sodium chloride contains three species (constituents) i.e., water, Na^+ ions, and Cl^- ions. Now since the number of Na^+ ions, and Cl^- ions must be equal (it is a constraint) the number of components would be $C = 3 - 1 = 2$

Phase		Composition in terms of components		
$CaCO_3$	=	CaO	+	CO_2
CaO	=	CaO	+	$0\,CO_2$
CO_2	=	$0\,CaO$	+	CO_2

Therefore, as a matter of convention, in this case we use CaO and CO_2 as the components for the system though other two choices are also correct.

- Let us consider sublimation of ammonium chloride as the next example of the type of systems where the constituents can react. We know that on sublimation, ammonium chloride decomposes into ammonia gas and HCl gas and an equilibrium exists as given below.

$$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$$

In this case there are three constituents in the system viz., solid ammonium chloride, ammonia gas and HCl gas. Further, there are two restrictions also; first of these restrictions is the equilibrium constant (as in case of decomposition of calcium carbonate) and the second restriction being the requirement that the concentrations of ammonia gas and HCl gas must be equal. This is so because the decomposition of $NH_4Cl(s)$ gives a molecule each of $NH_3(g)$ and $HCl(g)$.

$$[NH_3(g)] = [HCl(g)]$$

therefore, the number of components in this case would $C = 3 - 2 = 1$ That is, it is a one-component system.

If at equilibrium, 'a' moles of $NH_4Cl(s)$ has decomposed then the amounts of $NH_3(g)$ and $HCl(g)$ in the gas phase would be 'a' moles each. The composition of the two phases can be expressed in terms of $NH_4Cl(s)$ as follows

Phase	**Constituents**		**Composition in terms of components**
Gas	$NH_a(g)^*$ + $HCl(g)^*$	=	a NH_4Cl
Solid	NH_4Cl	=	NH_4Cl

* in equal amounts ('a' moles each)

However, you should remember that this is true only if $NH_3(g)$ and $HCl(g)$ are produced from the sublimation of $NH_4Cl(s)$ only. In case we add some $NH_3(g)$ (or $HCl(g)$) from outside, the equilibrium gets disturbed; the amounts of $NH_3(g)$ and $HCl(g)$ are no more equal (i.e., the second restriction is lifted) and it becomes a two-component system

$$C = 3 - 1 = 2$$

To understand it, let us say we begin with solid $NH_4Cl(s)$, on sublimation a part of it gets decomposed to give equal amounts of $NH_3(g)$ and $HCl(g)$

and an equilibrium is established. Now, if we add some $HCl\,(g)$ from outside to this system at equilibrium, this will suppress the equilibrium. Some $HCl\,(g)$ molecules will combine with $NH_3(g)$ molecules to give back some solid $NH_4Cl(s)$ and a new equilibrium would set up. If we assume that at this stage effectively 'a' moles of $NH_4Cl(s)$ have decomposed, then in the gas phase the amounts of $NH_3(g)$ and $HCl\,(g)$ would be 'a' moles and '(a+b)' moles respectively, where 'b' is the number of moles of $HCl\,(g)$ added from outside. The equilibrium and equilibrium concentrations of different species can be represented as

Components	$NH_4Cl(s)$	+ $HCl\,(g)$	$\rightleftharpoons$	$NH_3(g)$	+ $HCl\,(g)$
Conc. (in moles)				a	(a+ b)

The composition of the two phases now would be expressed as follows

Phase	Constituents		Composition in terms of components
Gas	$NH_3(g)^*$ + $HCl\,(g)^*$	=	a NH_4Cl + b HCl
Solid	$NH_4Cl(s)$	=	NH_4Cl + 0 HCl

* in unequal amounts ('a' moles and (a+b) moles respectively)

In case we had added ammonia instead of $HCl\,(g)$ to the system then again it would have been a two-component system and the components would be $NH_4Cl(s)$ and $NH_3(g)$.

- Let us take a system obtained by mixing ethanol and acetic acid and allowing it to react. How many components are there in the system? Let's analyse. You know from your earlier studies that ethanol and acetic acid would react to give ethyl acetate and water. The following equilibrium would exist.

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

We see that the system would have four constituents and there is one restriction due to equilibrium. We may promptly say that the number of components to be $C = 4 - 1 = 3.$ However, there is one more restriction i.e., the amounts of ethyl acetate and water formed in the reaction would be equal and the number of components would be $C = 4 - 2 = 2.$

Degrees of freedom
"*the smallest number of independent variables such as temperature, pressure, composition etc. which must be* ***fixed*** *in order to completely define the state of the system at equilibrium*".

3.2.4 Degrees of Freedom (*F*)

A system is said to be defined completely if we specify different variables of the system such that the system retains the same state of equilibrium. Alternatively, we can say that same state of equilibrium in the given system can be reproduced using the specified variables. The variables used to define the system are chosen from the state functions of the system, such as pressure, temperature, volume, energy, entropy, and the concentrations of the various components in different phases. However, we do not need to specify all of these variables as specifying some of these variables, automatically determines the values of the other variables. However, there is a minimum number of variables that need to be specified and this number is called the

degrees of freedom or **variance** of the system and is denoted as *F*. So, we can define the number of degrees of freedom as, "*the smallest number of independent variables such as temperature, pressure, composition etc. which must be specified (fixed) in order to completely define the state of the system at equilibrium*". In the context of phase equilibrium, we consider only three variables viz., pressure, temperature and the concentration.

In an alternative definition the number of degrees of freedom can be defined as, "*the number of intensive variables that can be varied independently without changing the number of phases present in the system*". Let's take some examples to understand the meaning of degrees of freedom.

- If the system consists of a certain amount of a pure gas, its state can be specified completely by using any two of the variables viz., pressure, temperature, and the volume. This is so because if any two of these are known, the third can be calculated from gas equation. We say that the system has two degrees of freedom, or the system is **bivariant**.
- In the system having equilibrium between water and water vapor, at any given temperature, the pressure of vapor in equilibrium with liquid water i.e., its vapour pressure is fixed in value. So, we need to specify only one variable say temperature to determine the state of the system. Thus, the system has only one degree of freedom, or is said to be **univariant**.
- Going further, if we take a system in which ice, water and water vapour are in equilibrium. It happens precisely at a temperature of 0.0075°C and pressure of 4 mm of Hg. Any change in pressure, temperature or concentration will destroy the equilibrium and generally two of the phases will be lost. This implies that we cannot change any of the variables i.e., the degree of freedom (*F*) is zero i.e., the system is **invariant**.

Degrees of freedom

"*the number of intensive variables that can be **varied** independently without changing the number of phases present in the system*"

Having learnt about the basic terminology for studying phase equilibrium why don't you solve the following simple questions to assess your understanding.

SAQ 1

Calcium carbonate on heating in a closed vessel decomposes as per the following equation. How many phases are there in the system?

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

SAQ 2

Calculate the number of components in a system containing a mixture of $PCl_5(s)$, $PCl_3(g)$ and $Cl_2(g)$. Consider that the following equilibrium exists in the system

$$PCl_5(s) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

SAQ 3

A certain amount of solid ammonium chloride was heated in a closed container where it undergoes sublimation. In the vapour phase ammonium chloride decomposes to give $NH_3(g)$ and $HCl(g)$. The following equilibrium is established.

$$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$$

To this system at equilibrium, 'b' moles of ammonia was added. Once the equilibrium was reestablished, 'a' moles of ammonium chloride had sublimed. Express the system in the form of equation and express the composition of the phases in terms of the components.

SAQ 4

What is the number of degrees of freedom of the system containing a solid substance and its vapour in equilibrium?

3.3 CRITERION FOR PHASE EQUILIBRIUM

In order to have different phases in a heterogenous system to be in equilibrium they must meet the requirements of thermal, mechanical and chemical equilibrium. Let's outline the requirements for these equilibria so as to establish criterion for phase equilibrium. You are aware that two systems are said to be in thermal equilibrium if they are at same temperature. If different phases are not in thermal equilibrium, then there will be heat flow from one phase to another. Further, for mechanical equilibrium the pressure of all the phases should be the same else one phase would increase in volume at the expense of the other.

The criterion of chemical equilibrium can be expressed in terms of equality of chemical potential of various components in different phases. In order to establish this criterion, let us recall that for a process to be spontaneous it must be accompanied by a decrease in Gibbs energy and for any infinitesimal change at equilibrium, the Gibbs energy change, dG should be zero. You would also recall from Unit 4 of BCHCT-133 course that Chemical potential of species i in a system, is the rate of change of Gibbs energy of the system with the number of moles of the component i when the temperature, pressure and the number of moles of all other components is kept constant i.e.,

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} \qquad \ldots(3.1)$$

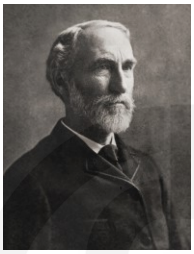
Further, the molecules of a component spontaneously move from regions of high chemical potential to the regions of low chemical potential in a mixture. This continues till the chemical potential of the component becomes same throughout the system. In other words, the chemical potential of the component should be the same in and throughout every phase present in the system for them to be in equilibrium. Thus, we can summarise the

requirements for equilibrium for say component 1 between two phases (say phase α and β) in a system as

Equilibrium	Criterion
Thermal equilibrium	$T_\alpha = T_\beta$
Mechanical equilibrium	$p_\alpha = p_\beta$
Chemical equilibrium	$\mu_1(\alpha) = \mu_1(\beta)$

Thus, we can conclude that for a heterogeneous system at constant pressure and temperature the criterion for phase equilibrium is that *"chemical potential of all the components is same in and throughout every phase present in the system"*.

3.4 GIBBS PHASE RULE


Josiah Willard Gibbs

Josiah Willard Gibbs established in 1876 that there is a definite relationship between the number of degrees of freedom, the number of components, and the number of phases present in a heterogeneous system at equilibrium. This relationship is known as the **Gibbs phase rule** or just as the **Phase rule** and states that, "*if the equilibrium of a heterogeneous system is not affected by electrical or magnetic forces or by gravity then the degrees of freedom (F), number of components (C) and number of phases (P) are connected by means of the equation*,

$$F = C - P + 2 \qquad \ldots(3.2)$$

Later, Ostwald, Roozeboom, van't Hoff, and others worked extensively and demonstrated how this highly generalised rule could be utilized in the study of problems in heterogeneous equilibrium. Further, it is important to note that the validity of phase rule is not dependent on any model of atomic or molecular structure. Our understanding of atomic and molecular structure has changed drastically in the twentieth century, but the phase rule has withstood the test of time. There has not been any exception or modification to the rule. However, there is one disadvantage with the phase rule that it does not give quantitative information about the equilibrium. It just fixes the number of variables involved in the equilibrium. The quantitative relationships between the variables are established through equations like Clausius - Clapeyron equation about which you would learn in the next section. For now, let's deduce Gibbs phase rule by calculating the degrees of freedom of a heterogeneous system consisting of *C* components present in *P* phases.

3.4.1 Deducing Gibbs Phase Rule

Let's take a heterogeneous system in which *C* components exist in *P* phases. We need to calculate the degrees of freedom for such a system to deduce Gibbs phase rule.

As discussed above, the degrees of freedom of a heterogeneous system in equilibrium refers to the number of independent variables that are required to

completely define the state of the system. This number equals the total number of variables for the system minus the number of variables that are fixed by virtue of the system being in equilibrium. That is,

F = (Total number of variables)−(Number of variables fixed due to equilibrium)

Let's first calculate the total number of variables of the system.

As the state of all the systems depend on the temperature and the pressure, so every system would have p and T as variables.

Next, we need to calculate the concentration variable for all the phases. For this we assume that each phase has all the C components.

Now, for a given phase the composition can be defined by specifying the concentrations (mole fractions) of $C-1$components; the concentration of the remaining component would be known by difference. Thus, for one phase there will be $C-1$concentration variables.

Sum of mole fractions of all the components is equal to 1.

For P phases the number of concentration variables would be $P(C-1)$

The total number of variables for the system would be $P\,(C-1)+2$ …(3.3)

Now, let us calculate the number of restrictions on the system. As discussed above, condition of equilibrium requires that the chemical potentials of each component should be the same in every phase. For a given component 1 to be in equilibrium in two phases (α and β) the following must be true (i.e., a restriction)

$$\mu_1(\alpha) = \mu_1(\beta) \qquad \ldots(3.4)$$

Similarly, for component 1 to be in equilibrium in three phases (α, β and γ) the requirement is

$$\mu_1(\alpha) = \mu_1(\beta) \quad \text{and} \quad \mu_1(\alpha) = \mu_1(\gamma) \qquad \ldots(3.5)$$

Thus, we see that the equilibrium of a given component between two phases puts one restriction and for three phases we have two restrictions. Therefore, for P phases we would have $P-1$ restrictions. This is for one component. For C components the number of restrictions would become $C(P-1)$.

=> Total number of restrictions imposed by equilibrium= $C(P-1)$ …(3.6)

Thus, the degrees of freedom for the system would be:

F = (Total number of variables) – (number of variables fixed due to equilibria)

Substituting from Eq. (3.3) and Eq. (3.6)

$$F = [P(C-1)+2] - [C(P-1)] \qquad \ldots(3.7)$$

Simplifying, we get

$$F = [\cancel{PC} - P + 2] - [\cancel{CP} - C] = C - P + 2$$

$$F = C - P + 2 \qquad \text{or} \qquad P + F = C + 2 \qquad \ldots(3.8)$$

This is the desired expression for the **Gibbs phase rule.**

In our arguments we have assumed that each component is present in all the phases. However, if some component is missing from a given phase, then what will happen? Will the equation change? The answer is NO. In such a case the number of concentration variables would decrease by one. At the same time, the number of restrictions would also decrease by one and our phase rule equation would remain the same. This means that the phase rule is generally valid under all conditions of distribution of components provided that equilibrium exists in the system. Having learnt about the meaning of equilibrium in heterogeneous systems and the Gibbs phase rule answer the following simple question to assess your understanding.

SAQ 5

Give the criteria for phase equilibrium in a one-component system containing three phases in equilibrium at constant temperature and pressure.

3.5 STABILITY OF THE PHASES OF A PURE SUBSTANCE

As discussed above, for a heterogeneous system in equilibrium the chemical potential (μ) of each component must be the same in every phase in which that component appears. For one component system we can say that Gibbs energy per mole or molar Gibbs energy, $G_m = \frac{G}{n}$. Further, you would recall from thermodynamics that for small change in Gibbs energy we could write

$$dG = -S\,dT + V\,dp \qquad \ldots(3.9)$$

Dividing throughout by n (number of moles) we get

$$dG_m = d\mu = -S_m dT + V_m dp \qquad \ldots(3.10)$$

where, S_m and V_m are the molar entropy and molar volume, respectively. We can write

$$\left(\frac{\partial \mu}{\partial T}\right)_p = -S_m \quad \text{and} \quad \left(\frac{\partial \mu}{\partial p}\right)_T = V_m \qquad \ldots(3.11)$$

The derivatives in Eq. (3.11) give the slopes of the μ versus T and μ versus p curves, respectively. Let us take up the μ versus T curves first.

As the entropy increases with increasing temperature, the μ versus T curves should be slightly concave downwards. However, these are approximated as straight lines for simplicity.

3.5.1 μ versus T curves

You would recall from the third law of thermodynamics, that the entropy of a substance is always positive which means that the slope of μ versus T curve will be negative. For the three phases of a single substance we can write

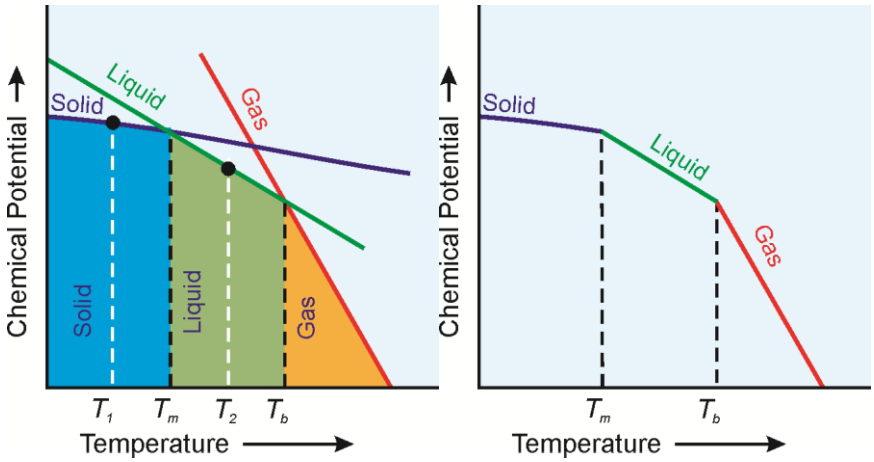
$$\left(\frac{\partial \mu_{solid}}{\partial T}\right)_p = -S_m(\text{solid}) \qquad \ldots(3.12)$$

$$\left(\frac{\partial \mu_{liquid}}{\partial T}\right)_p = -S_m(\text{liquid}) \qquad \ldots(3.13)$$

$$\left(\frac{\partial \mu_{gas}}{\partial T}\right)_p = -S_m(\text{gas}) \quad \ldots(3.14)$$

Further, you know that

$$S_m(\text{gas}) > S_m(\text{gas}) > S_m(\text{gas}) \quad \ldots(3.13)$$



(a) (b)

Fig. 3.1: Chemical potential versus temperature curves for a substance in different phases and (b) overall nature of the curve

This means that the slope of μ versus T curve for gas phase would be more negative (i.e., the chemical potential will fall more sharply with increase in temperature) than that for liquid phase, which in turn would be more negative than that for the solid phase as shown in Fig. 3.1.

You would once again recall from thermodynamics that any system spontaneously goes from higher chemical potential to a lower chemical potential where it is more stable. In other words, at a given temperature that phase of the substance would be stable which has lower chemical potential. If we see the μ versus T curve at temperature T_1 marked on Fig 3.1 (a) we find that here solid phase would be more stable. Similarly, at temperature T_2 liquid phase would be more stable. Suppose we take a liquid at a temperature T_1 it would spontaneously freeze as it is accompanied by a decrease in Gibbs energy. Similarly, a solid at temperature T_2 would spontaneously melt.

At a given temperature the phase with the lowest value of the chemical potential is the stable phase.

Now if we take the system at temperature T_1 i.e., in solid phase and increase its temperature we can see from the figure that its chemical potential would decrease. You can note that for liquid phase (if it could exist at this temperature) the decrease in chemical potential is steeper. At a certain temperature the μ versus T curves for solid phase and liquid phase would intersect. At this temperature the chemical potentials of the solid phase and the liquid phase would be equal i.e., they will be in equilibrium. In other words, the solid and liquid phase can coexist. This temperature is called the **melting point** of the solid. Similarly, if we increase the temperature of the system initially at temperature T_2 (i.e., in liquid phase) at a certain temperature, the liquid and gas phase can coexist in equilibrium, as their chemical potentials are equal. This is the **boiling point** of the substance.

The overall nature of the μ versus T curve for a pure substance is shown in Fig. (3.1 (b)). There are two transitions, from solid to liquid and from liquid to

vapour. These are called **phase transitions** because the phase of the substance gets changed here. You may observe that these phase transitions at T_m and T_b are accompanied by a change in slope of the curve. Such transitions are called **first order phase transitions**. The phases on the two sides of the transition temperature have different entropies. Such phase transitions e.g., conversion of ice into water require latent heat for the transition. This means that when these transitions occur, the heat is absorbed but there is no observable temperature change. You would recall from your earlier studies that the ratio of heat absorbed and the corresponding change in temperature is called **heat capacity**. Since here the heat is being absorbed but the temperature does not change, we can say that in a first order phase transitions the heat capacity is infinitely large.

In some cases, for example in sudden appearance of superconductivity in certain metals on cooling them to very low temperatures. The phase transition (conducting to superconducting) does not require any latent heat. Such transitions are called **second order phase transitions** and such transitions are accompanied by finite heat capacity changes. Let us now take up the pressure dependence of μ versus T curves

3.5.2 Pressure Dependence of μ Versus T Curves

We have discussed about the μ versus T curves at constant pressure and have observed phase transition at characteristic temperatures. Let's now take up pressure dependence of these curves and see how pressure change affects these phase transitions. We can see from Eq. (3.11) that,

$$\left(\frac{\partial \mu}{\partial p}\right)_T = V_m \qquad \ldots(3.14)$$

As the molar volume is always positive this means that at a given temperature the chemical potential of the system would vary directly with pressure i.e., it will decrease with a decrease in p. Further, the molar volume of a gas is much more than that of the liquid, which is roughly equal or slightly more than that of the solid. As a result, on decreasing the pressure on the system the value of μ for gas would decrease much more than that for the liquid whereas for solid the value will decrease slightly. Schematic μ versus T curves for the solid, liquid and gaseous state of a substance at two different pressures are given in the Fig. 3.2; the ones at lower pressure are indicated by the dotted lines.

On reducing the pressure the range of temperature over which the liquid is the stable phase gets reduced.

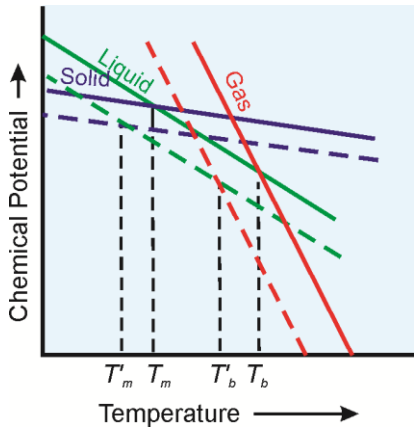
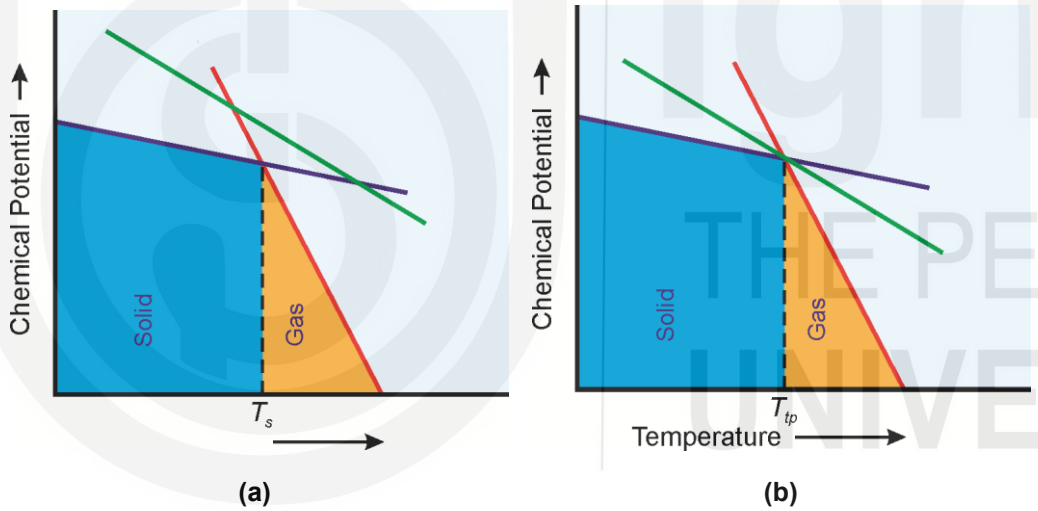


Fig. 3.2: Chemical potential versus temperature curves for a substance in different phases at pressure p_1 (bold line) and p_2 ($p_2 < p_1$) (dotted line).

You may note that at lower pressure the solid and liquid curves intersect at a lower temperature i.e., the melting point decreases. Similarly, the curves for gaseous state and the liquid state also intersect at lower temperature indicating the decrease in the boiling point. We are familiar with this observation that the boiling point decreases on decreasing the pressure. You may note here, that the effect of pressure on the boiling point is much greater than that on the melting point because the molar volume of gas is much more than that of the liquid.

Now if we decrease the pressure sufficiently then it may so happen that at a certain pressure the μ versus T curves for the solid phase meets that of the gas phase at a temperature lower than that at which it meets the liquid phase curve; Fig 3.3 (a). This means that there will be equilibrium between solid and the gas phase i.e., the solid would undergo **sublimation**.

Similarly, we may have a combination of temperature and pressure at which the solid, liquid, and vapour curves intersect at a point i.e., the solid, liquid and vapour phase coexist and are in equilibrium; Fig 3.3 (b). Such a combination of temperature and pressure is called the **triple point** for the system. This combination of p and T for a given system is unique; if any of these parameters were changed some of the phases would disappear.



(a) (b)

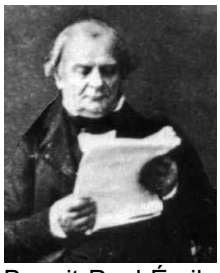
Fig. 3.3: Schematic representation of chemical potential versus temperature curves for a substance in different phases indicating a) sublimation and b) triple point.

The phase rule that we deduced in section 3.4 gives qualitative information about the relationship between the numbers of phases, components and degrees of freedom for a system. We would elaborate more on it in the next unit when we will discuss about the phase diagrams of different one and two component systems. For now, we need to discuss about another important equation called Clapeyron equation that provides information on the quantitative understanding of phase equilibria. However, before that answer the following simple question to assess your understanding of stability of different phases of a pure substance and the factors involved.

SAQ 6

How would the increase in pressure affect the μ versus T curves for a pure substance? Draw a schematic diagram indicating the same.

3.6 CLAPEYRON and CLAUSIUS-CLAPEYRON EQUATIONS


Benoit-Paul-Émile Clapeyron

In our discussion on the variation of chemical potential with temperature and the effect of pressure on the μ versus T curves we have seen that the chemical potential of a given system depends on temperature as well as the pressure. The question comes up is 'are the equilibrium temperature and pressure of a system related?' The answer is yes and such a relationship was developed by French engineer Benoit-Paul-Émile Clapeyron in 1834 and is known as **Clapeyron equation**. This was later put on firm thermodynamic basis by Clausius therefore it is called **Clausius-Clapeyron equation**. Let's begin by deriving Clapeyron equation.

3.6.1 Clapeyron Equation

Let us take a one-component system having two phases (α and β) in equilibrium. As we know that for the two phases to be in equilibrium the pressure, temperature and the chemical potential of the component in the two phases should be equal. Under conditions of constant temperature and pressure the chemical potential of two phases must be the same i.e.,

$$\mu_\alpha(T,p) = \mu_\beta(T,p) \qquad \ldots(3.15)$$

If we either change the temperature keeping the pressure constant, or change the pressure keeping the temperature constant, one of the phases will disappear. However, if we appropriately change both the pressure as well as the temperature the two phases can be kept in equilibrium i.e., the two phases would coexist. The Clapeyron equation essentially provides this dp/dT relationship. A pressure versus temperature plot along which the two phases coexist is called **coexistence curve** as shown in Fig. (3.4)

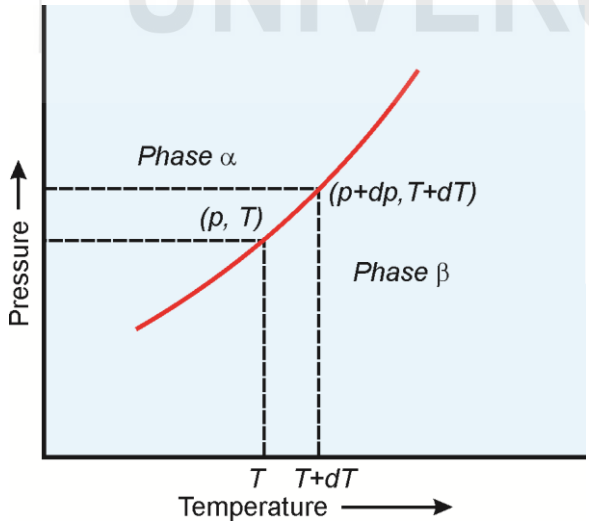


Fig. 3.4: The simultaneous variation of pressure and temperature for one component system gives coexistence curve. The chemical potential of the two phases remains same along this curve.

Now, if we change the pressure from p to $(p+dp)$ the equilibrium temperature will change from T to $(T+dT)$. The corresponding chemical potentials would

be $(\mu_\alpha + d\mu_\alpha)$ and $(\mu_\beta + d\mu_\beta)$ respectively. Therefore at $(p + dp)$ and $(T + dT)$ the equilibrium condition would become

$$\mu_\alpha(T,p) + d\mu_\alpha = \mu_\beta(T,p) + d\mu_\beta \quad \ldots(3.16)$$

On subtracting Eq. (3.15) from Eq. (3.16) we get the following expression,

$$(d\mu_\alpha = d\mu_\beta) \text{ as } \mu_\alpha(T,p) = \mu_\beta(T,p) \ldots(3.17)$$

Using Eq. (3.10) we can write

$$d\mu_\alpha = -S_{m(\alpha)}dT + V_{m(\alpha)}dp \quad \ldots(3.18)$$

$$d\mu_\beta = -S_{m(\beta)}dT + V_{m(\beta)}dp \quad \ldots(3.19)$$

Using Eq. (3.17) to Eq. (3.19) we get

$$-S_{m(\alpha)}dT + V_{m(\alpha)}dp = -S_{m(\beta)}dT + V_{m(\beta)}dp \quad \ldots(3.20)$$

Rearranging, we get

$$(S_{m(\beta)} - S_{m(\alpha)})dT = (V_{m(\beta)} - V_{m(\alpha)})dp \quad \ldots(3.21)$$

$$\Delta S_m dT = \Delta V_m\, dp \Rightarrow \frac{dT}{dp} = \frac{\Delta V_m}{\Delta S_m} \quad \ldots(3.22)$$

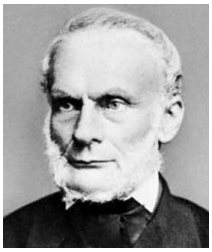
or $$\frac{dp}{dT} = \frac{\Delta S_m}{\Delta V_m} \quad \ldots(3.23)$$

Eq. (3.22) and Eq. (3.23) are two variants of **Clapeyron equation**. It may be that in these equations we have used molar quantities i.e., molar entropy and molar volume. As these quantities are for the same substance, we can have equivalent equations wherein these quantities are used per unit mass i.e.,

$$\frac{dp}{dT} = \frac{\Delta S}{\Delta V} \quad \text{or} \quad \frac{dT}{dp} = \frac{\Delta V}{\Delta S} \quad \ldots(3.24)$$

The significance of Clapeyron equation is that it

- gives the quantitative dependence of the equilibrium temperature on pressure, and /or the variation in the equilibrium pressure with temperature.
- relates the ratio of the change in pressure to the change in temperature with readily measurable quantities like molar volume and molar entropy change for the process.
- can be used to generate schematic plots of the equilibrium pressure versus temperature for different phase transformations like vaporization, fusion, sublimation, or the transition between two allotropic forms of a pure substance.


Rudolf Julius Clausius

3.6.2 Clausius-Clapeyron Equation

German physicist **Rudolf Julius Clausius** simplified and expressed the Clapeyron equation for vaporization and sublimation equilibria in a convenient approximate form. Let us take up the case of vapourisation equilibrium i.e., equilibrium between the liquid and vapour phase of substance A.

$$\text{A (liquid)} \rightleftharpoons \text{A (vapour)} \qquad \ldots(3.25)$$

For such equilibrium we can write the Clapeyron equation as

$$\frac{dp}{dT} = \frac{\Delta_{vap}S}{\Delta_{vap}V} \qquad \ldots(3.26)$$

As at the equilibrium temperature, the transformation is reversible we can write,

$$\Delta_{vap}S = \frac{\Delta_{vap}H}{T} \qquad \ldots(3.27)$$

Where, $\Delta_{vap}H$ is the molar enthalpy of vaporisation and T is the equilibrium temperature. Substituting in Eq. (3.26), the Clapeyron equation takes the form

$$\frac{dp}{dT} = \frac{\Delta_{vap}H}{T\Delta_{vap}V} \qquad \ldots(3.28)$$

Clausius made the following two assumptions

- the molar volume of the vapour is much larger than that for the liquid phase,
- the vapour behave as ideal gas

In light of these assumptions we can write

$$\Delta_{vap}V_{m(vap)} = V_{m(vap)} - V_{m(l)} \qquad \ldots(3.29)$$

and

$$V_{m(vap)} = \frac{RT}{p} \qquad \ldots(3.30)$$

Substituting these in Eq. (3. 28) we get,

$$\frac{dp}{dT} = \frac{\Delta_{vap}H_m}{TV_{m(vap)}} = \frac{p\Delta_{vap}H_m}{T.RT} = \frac{p\Delta_{vap}H_m}{RT^2} \qquad \ldots(3.31$$

$$\Rightarrow \qquad \frac{dp}{dT} = \frac{p\Delta_{vap}H_m}{RT^2} \qquad \ldots(3.32)$$

Rearranging, we get

$$\Rightarrow \qquad \frac{dp}{p} = d\ln p = \frac{\Delta_{vap}H_m dT}{RT^2} \qquad \ldots(3.32)$$

This is the **Clausius-Clapeyron equation** and can be rewritten as

$$d\ln p = \frac{\Delta_{vap}H_m}{R} \times \frac{dT}{T^2} \qquad \ldots(3.33)$$

Integrating Eq. (3.33) in the limits of p_1 to p_2 and T_1 to T_2 and assuming $\Delta_{vap}H_m$ to be constant in the range of temperature, we get

$$\int_{p_1}^{p_2} d\ln p = \frac{\Delta_{vap}H_m}{R}\int_{T_1}^{T_2}\frac{dT}{T^2} \quad \ldots(3.34)$$

Integrating

$$ln\frac{p_2}{p_1} = -\frac{\Delta_{vap}H_m}{R}\left[\frac{1}{T}\right]_{T_1}^{T_2} \quad \ldots(3.35)$$

On applying limits

$$ln\frac{p_2}{p_1} = -\frac{\Delta_{vap}H_m}{R}\left[\frac{1}{T_2}-\frac{1}{T_1}\right] \quad \ldots(3.36)$$

Simplifying

$$2.303\log\frac{p_2}{p_1} = -\frac{\Delta_{vap}H_m}{R}\left[\frac{1}{T_2}-\frac{1}{T_1}\right] \quad \ldots(3.37)$$

$$2.303\log\frac{p_2}{p_1} = -\frac{\Delta_{vap}H_m}{R}\left[\frac{T_1-T_2}{T_1T_2}\right] \quad \ldots(3.38)$$

$$2.303\log\frac{p_2}{p_1} = \frac{\Delta_{vap}H_m}{R}\left[\frac{T_2-T_1}{T_1T_2}\right] \quad \ldots(3.39)$$

This is the integrated form of the Clausius–Clapeyron equation for vapourisation of a liquid and shows that the vapour pressure of a liquid increases exponentially with increase in temperature. We can consider the sublimation equilibrium also on exactly the same lines and obtain the corresponding Clausius –Clapeyron equation for sublimation of a solid. The equation would be as follows.

$$2.303\log\frac{p_2}{p_1} = \frac{\Delta_{sub}H_m}{R}\left[\frac{T_2-T_1}{T_1T_2}\right] \quad \ldots(3.40)$$

Where, $\Delta_{sub}H_m$ is the molar enthalpy of sublimation of the substance undergoing sublimation. If we take indefinite integral of Eq. (3.33) i.e., without any limits we get the following equation.

$$\ln p = \frac{\Delta_{vap}H_m}{RT} + C \quad \ldots(3.41)$$

where C is the constant of integration. According to this equation, if we take the molar enthalpy of vapourisation ($\Delta_{vap}H_m$) to be constant then a plot between $\ln p$ and 1/T would be a straight line with a negative slope equal to $-\frac{\Delta_{vap}H_m}{R}$.

Let us take an example to see an application of Clausius-Clapeyron equation.

Example 3.1: The vapour pressure of water is found to be 3167 pascals at 25° C and 101325 pascals at 100° C. Calculate the enthalpy of vaporisation for water.

Solution: We are given the following data

$T_1 = 298\text{K}$ $p_1 = 3167\text{Pa}$

$T_2 = 373\text{K}$ $p_2 = 101325\text{Pa}$

We assume that the enthalpy of vaporisation, $\Delta_{vap}H_m$ is constant in this temperature range and write the Clausius-Clapeyron equation as

$$2.303\log\frac{p_2}{p_1} = \frac{\Delta_{vap}H_m}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

This can be rearranged to get $\Delta_{vap}H_m$ as follows

$$\Delta_{vap}H_m = 2.303\ R\left[\frac{T_1 T_2}{T_2 - T_1}\right]\log\frac{p_2}{p_1}$$

substituting the values

$$\Delta_{vap}H_m = 2.303 \times 8.314\text{JK}^{-1}\,\text{mol}^{-1}\left[\frac{373\times 298}{75}\right]\text{K}\,\log\frac{101325}{3167}$$

$$\Delta_{vap}H_m = 2.303 \times 8.314\,\text{JK}^{-1}\text{mol}^{-1}\,[1482]\text{K}\,\log 32$$

Simplifying, we get

$$=> \Delta_{vap}H_m = 42.71\,\text{kJ mol}^{-1}$$

In the discussion above we have shown that the boiling point of a substance depends on the pressure. Let us take an example to learn how does the Clapeyron equation helps us in determining the magnitude of this effect.

Example 3.2: The normal boiling point of water at a pressure of 1.013025 bar is 373.15 K. By what value would the boiling point change on increasing the pressure by 1 pascal?

(Given: $\Delta_{vap}H_m = 40.69$ kJ mol^{-1}; molar volumes of steam and liquid water at this temperature and pressure respectively are $30.199\times10^{-3}\text{m}^3\text{mol}^{-1}$ and $0.019\times10^{-3}\text{m}^3\text{mol}^{-1}$.)

Solution: From Eq. (3.28) we know that $\frac{dp}{dT} = \frac{\Delta_{vap}H_m}{T\,\Delta_{vap}V_m}$

Reversing both sides of the equation we get $\frac{dT}{dp} = \frac{T\,\Delta_{vap}V_m}{\Delta_{vap}H_m}$

Using the given data, we calculate the value of $\Delta_{vap}V_m$

$$\Delta_{vap}V_m = (30.199 - 0.019)\times10^{-3}\text{m}^3\text{mol}^{-1} = 30.180\times10^{-3}\text{m}^3\text{mol}^{-1}$$

Substituting the values in the expression we get

$$\frac{dT}{dp} = \frac{373.15\text{K}\times30.180\times10^{-3}\ \text{m}^3\ \text{mol}^{-1}}{40{,}690\,\text{J mol}^{-1}}$$

Simplifying we get

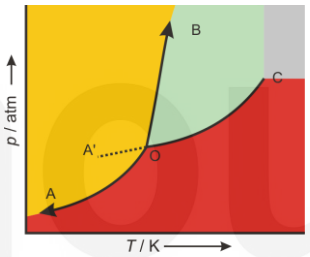
$$\frac{dT}{dp} = 2.768\times10^{-4}\text{KPa}^{-1}$$

This implies that the boiling point decreases by 2.768×10^{-4}K per Pa change in the pressure.

3.6.3 What is a Phase Diagram?

You have learnt above that the stability of different phases of a given system consisting of a pure substance depends on the physical variables of the system. Further, you have also learnt about relationships between the pressure and temperature for heterogeneous systems in terms of Clapeyron and Clausius-Clapeyron equations and their significance. A **phase diagram** is basically *a graphical representation of the number of phases that exist at a given set of values of pressure and temperature for a system of a pure substance*. Although we can use any two of the macroscopic variables viz., pressure, temperature and volume to construct a phase diagram, generally pressure and temperature are used.

A typical phase diagram consists of regions, lines (or curves) and points. The *regions* are that part of the phase diagram where the pressure as well as the temperature can be varied. The *lines* in the phase diagram represent the coexistence curves of two phases and permit variation of any one of the physical properties (p or T). The *points* on the other hand have unique values of p and T , and none of these can be varied. These can be explained by applying phase rule. A schematic representation of the typical phase diagram of one component system is given in the margin. We will take up the application of phase rule to one and two component systems in the next unit.



For now, let us sum up what all we have discussed in this unit. However, before that assess your learning by solving the following simple question

SAQ 7

The normal boiling temperature of ethanol is found to 78.4°C. If the molar enthalpy of vaporization for ethanol is 40.5 kJ mol^{-1} calculate the vapour pressure of ethanol at $50.0^{\circ}C$.

3.7 SUMMARY

In this introductory unit on phase equilibrium we have taken up the basic aspects of equilibrium in heterogeneous systems and have laid down the requisite foundation to take up application of phase rule in understanding heterogeneous equilibria in different one and two-component systems. We began the unit by discussing different types of equilibria encountered in heterogeneous systems. In this context we defined and differentiated between true, metastable and unstable equilibria. A true equilibrium can be achieved either from forward or from the reverse direction whereas a metastable equilibrium can be obtained only in one of the directions. On the other hand, the unstable equilibrium is apparently observed due to a shorter span of observation though the system is not at equilibrium.

The discussion on different types of equilibrium was followed by a detailed account of terms like, phase, components, and degrees of freedom. These terms have been defined explicitly and clarified using a wide range of examples for each term. Then we laid down the criteria for the existence of equilibrium in heterogeneous systems. A system must be in thermal, mechanical, and chemical equilibria. For this the temperature, pressure and the chemical potential need to be same throughout the system. Thereafter we stated and deduced the Gibb's phase rule by inductive reasoning. The next issue we took up was the stability of different phases of a substance. It was stated that at a given temperature the phase with lower value of chemical potential is the stable phase. If a given system at a given temperature is in a phase having higher value of chemical potential, then it would spontaneously change over to the phase with lower chemical potential. In this context we discussed and clarified the concepts of melting point, and boiling point in terms of μ versus T curves. A discussion on the effect of pressure on μ versus T curves provided an insight into decrease in melting point and boiling points on decreasing the pressure and also the conditions for sublimation and observance of triple point.

This was followed by discussion on two important equations viz., the Clapeyron and Clausius-Clapeyron equation. In this context the equations were derived and their application to heterogeneous systems was explained with the help of examples.

3.8 TERMINAL QUESTIONS

1. How many phases are there in
   a) a mixture of graphite and diamond?
   b) A system containing five ice cubes of volume 1 cm^3 each in 100 cm^3 of water?
2. Calculate the number of components in an aqueous solution of sodium acetate
3. What is the maximum number of phases possible in a two-component system?
4. Using phase rule calculate the degree of freedom for a system containing ice in a mixture of alcohol and water.
5. A certain amount of pure $PCl_5(s)$ was kept in a closed vessel. Calculate the number of components in a system containing a mixture of $PCl_5(s)$, $PCl_3(g)$ and $Cl_2(g)$ obtained because of partial dissociation of $PCl_5(s)$.
6. Calculate the number of components in a dilute aqueous solution prepared by dissolving NaCl, LiCl and KBr in water.
7. Write the Clausius–Clapeyron equation for sublimation of a solid and outline its significance.
8. The vapour pressure of a liquid at $50^\circ C$ is equal to 12330 Pa. If the average value of the enthalpy of vaporization between $50^\circ C$ and the

normal boiling point of the liquid is $42.74\,kJ\,mol^{-1}$, estimate the boiling point of the liquid.

3.9 ANSWERS

Self-Assessment Questions

1. In the decomposition of calcium carbonate giving solid calcium oxide and carbon dioxide gas there are three phases. $CaCO_3$ and CaO constitute two distinct solid phases and carbon dioxide forms the gaseous third phase

2. As given, the following equilibrium exists in a system containing a mixture of $PCl_5(s), PCl_3(g)$ and $Cl_2(g)$.

   $$PCl_5(s) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

   There are three distinct constituents in the system i.e., $PCl_5(s)$ and $PCl_3(g)$ and $Cl_2(g)$, So $C = 3$. However, there is one restriction on the system i.e., the presence of equilibrium. Therefore, the number of components in the system would be $C = 3 - 1 = 2$ Thus, it is a two-component system.

3. If at the end 'a' moles of NH_4Cl undergo sublimation and there is an excess of 'b' moles of ammonia then we can write the equilibrium and the concentrations of different species at equilibrium as

	$NH_4Cl(s)$	+ $NH_3(g)$	$\rightleftharpoons$	$NH_3(g)$	+ HCl(g)
Conc. (in moles)				(a+ b)	a

   The composition of the two phases now would be expressed as follows

Phase	Constituents		Composition in terms of components
Gas	$NH_3(g)^*$ + $HCl(g)^*$	=	a NH_4Cl + b $NH_3(g)$
Solid	$NH_4Cl(s)$	=	NH_4Cl + 0 $NH_3(g)$

   * in unequal amounts ((a+b) and 'a' mole respectively)

4. For such a system we need to specify only one of the variables i.e., ether the temperature or the pressure to describe the system. So, the degrees of freedom would be one. We can arrive at the answer by using phase rule also. As the system has one component and two phases, we can write from phase rule, $P + F = C + 2$

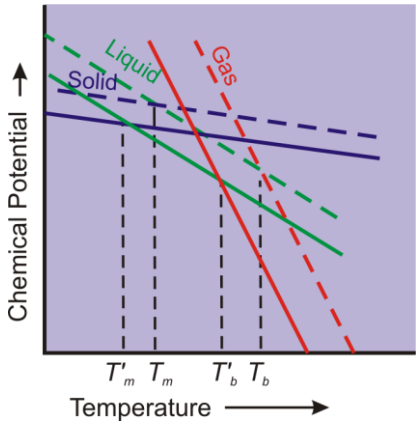
   $$\Rightarrow F = C + 2 - P = 1 + 2 - 2 = 1$$

5. If we represent the three phases in equilibrium as α, β and γ, then the condition for phase equilibrium at constant temperature and pressure would be

   $$\mu(\alpha) = \mu(\beta) = \mu(\gamma)$$

6. At a given temperature the chemical potential of the system would increase with an increase in pressure p. Further, the value of μ for gas

would increase much more than that for the liquid whereas for solid the value will increase slightly. The schematic μ versus T curves for the solid, liquid and gaseous state of a substance at two different pressures are given below; the curves at higher pressure are indicated by the dotted lines. You may note that the melting point and boiling point are higher at higher pressure.



7. We are given the following data

$T_1 = 323\ \text{K}$ $p_1 = ?\,\text{Pa}$

$T_2 = 351.4\text{K}$ $p_2 = 101325\text{Pa}$

$\Delta_{\text{vap}}H_{\text{m}} = 40.5\,\text{kJ mol}^{-1}$

We assume that the enthalpy of vaporisation, $\Delta_{\text{vap}}H_{\text{m}}$ is constant in this temperature range and write the Clausius-Clapeyron equation as

$$2.303\log\frac{p_2}{p_1} = \frac{\Delta_{vap}H_m}{R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

This can be rearranged as follows

$$\log\frac{p_2}{p_1} = \frac{\Delta_{\text{vap}}\text{H}_{\text{m}}}{2.303\text{R}}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

substituting the values

$$\log\frac{p_2}{p_1} = \frac{40500\,\text{J mol}^{-1}}{2.303\times 8.314\,\text{JK}^{-1}\text{mol}^{-1}}\left[\frac{28.4}{113502}\right]\text{K}^{-1}$$

solving, we get

$$\log\frac{p_2}{p_1} = 0.5293 \Rightarrow \frac{p_2}{p_1} = 3.383 \Rightarrow p_1 = \frac{\text{p}_2}{3.383}$$

Substituting for p_2, we get

$$p_1 = \frac{101325\,\text{Pa}}{3.383} = 29951\,\text{Pa}$$

Terminal Questions

1. a) As graphite and diamond are two distinct solids and can be physically separated from their mixture therefore, there are two phases in the system.

b) In this case there are two phases. One is the solid phase (ice) and second is the liquid phase (water). The number of ice cubes and their size is superfluous, it does not affect the number of phases. Similarly, the volume of water also does not matter.

2. An aqueous solution of sodium acetate (a salt) will have three species or constituents i.e., the sodium and acetate ions and water. However, there is one restriction i.e., the concentration of sodium ions and acetate ions must be equal as these are obtained from the dissociation of the salt. Therefore, the number of components would be

$C = C' - R = 3 - 1 = 2$

3. We know that according to the phase rule,

$F = C - P + 2$

It can be rearranged to give

$P = C - \mathrm{P} + 2$

We are given number of components, C = 2. Now since the minimum degrees of freedom can be zero, substituting in the above equation we get

$P = 2 - 0 + 2 = 4$

Thus, the number of phases would be 4.

4. We know that according to the phase rule,

$F = C - P + 2$

In this system there will be two phases viz., ice (solid phase) and mixture of alcohol and water (liquid phase) i.e., P=2

The number of components would also be two because the composition of the solid as well as the liquid phase can be expressed in terms of alcohol and water as follows

Solid phase: water + 0 alcohol

Liquid phase: x water + y alcohol

Substituting in the phase rule expression we get,

$F = 2 - 2 + 2 = 2$

Thus, the degrees of freedom would be 2.

5. We know that $PCl_5(s)$ decomposes to give $PCl_3(g)$ and $Cl_2(g)$, and the following equilibrium exists in the system.

$\rightleftharpoons PCl_3(g) + Cl_2(g)$

There are three distinct constituents in the system i.e., $PCl_5(s)$, $PCl_3(g)$ and $Cl_2(g)$, So $C' = 3$. However, there are two restrictions on the system. The first one is the presence of equilibrium and the second, that the amounts of $PCl_3(g)$ and $Cl_2(g)$ should be equal as these are formed from the decomposition of $PCl_5(s)$ only. Therefore, the number of components in the system would be $C = 3 - 2 = 1$ Thus, it is a one-component system. You should note here that this problem is different from that in SAQ 2. In this problem we began with solid phosphorus pentachloride that

decomposed to give equilibrium mixture whereas in SAQ 2 the system was prepared by mixing the three components. In this case the second restriction does not apply, that is why the number of components was 2.

6. There is a total of six constituents in this system; five ions, and water. The ions are Na^+, K^+, Li^+, Cl^- and Br^-. Also, there are two restriction on the system. The first restriction is that the system should be electrically neutral i.e.,

$$[Na^+] + [K^+] + [Li^+] = [Cl^-] + [Br^-]$$

And secondly, since potassium and bromide ions come from same source, so their concentrations should also be equal, i.e.,

$$[K^+] = [Br^-]$$

We know that $C = C' - R$

$$\Rightarrow \quad C = 6 - 2 = 4$$

Thus, the number of components would be 4.

7. The Clausius –Clapeyron equation for sublimation of a solid can be written as

$$2.303 \log \frac{p_2}{p_1} = \frac{\Delta_{sub} H_m}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

It shows that the vapour pressure of a solid undergoing sublimation increases exponentially with increase in temperature.

8. We are given the following data

$T_1 = 323\ K \qquad p_1 = 12330\ Pa$

$T_2 = ?K \qquad p_2 = 101325\ Pa$

$\Delta_{vap} H_m = 42.74\ kJ\ mol^{-1} = 42740\ J mol^{-1}$

The enthalpy of vapourisation, $\Delta_{vap} H_m$ is given to be constant from 50°C to the boiling point. We can write the Clausius-Clapeyron equation as

$$2.303 \log \frac{p_2}{p_1} = \frac{\Delta_{vap} H_m}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

This can be rearranged as follows

$$\left[\frac{T_2 - T_1}{T_1 T_2} \right] = \frac{2.303 R}{\Delta_{vap} H_m} \log \frac{p_2}{p_1}$$

substituting the values

$$\left[\frac{T_2 - 323}{323 T_2} \right] K^{-1} = \frac{2.303 \times 8.314\ J K^{-1} mol^{-1}}{42740\ J mol^{-1}} \log \frac{101325}{12330}$$

solving, we get

$$\left[\frac{T_2 - 323}{323 T_2} \right] K^{-1} = 0.00041 \Rightarrow T_2 = 373.3 K$$

UNIT 4

Phase Equilibrium–II

Structure

4.1 INTRODUCTION

In the previous unit we had discussed about the basic aspects of equilibrium in heterogeneous systems. In this process you have learnt about different types of equilibria, the criterion for phase equilibrium, phase rule and the meaning and significance of the terms like, phase, components, and degrees of freedom in the context of phase equilibrium. You have also learnt about the stability of different phases of a pure substance and Clapeyron and Clausius-Clapeyron equations and their significance. With this you have acquired the requisite knowledge to take up application of phase rule to heterogeneous systems.

In the present unit we would take up application of phase rule in understanding different one-component and two-component systems. We would begin the unit by discussing the general characteristics of the phase diagram of a one-component system and about the analysis of a typical phase diagram of one-component system. Thereafter, we would describe and analyse the phase diagrams of two specific one-component systems viz., water and sulphur

systems. Both of these systems have specific features, while in water system the solid state is lighter than the liquid state, sulphur exists in two allotropic forms in solid state.

Thereafter, we would take up two-component systems. Herein we would highlight the difficulty in representing the phase diagrams of such systems and discuss the way out by reducing such systems to condensed systems. Then we would explain the phase diagrams of two component systems involving formation of simple eutectic, compound with congruent melting point and compound with incongruent melting points. For each case we would take up a representative example. In the next unit we would take up conduction in electrolytic solutions.

Expected Learning Outcomes

After studying this unit, you should be able to:

- outline the general characteristics of the phase diagram of a one component system;
- draw and interpret a general phase diagram for one-component system by applying phase rule;
- draw the phase diagram for water system and identify different equilibria in it;
- explain the slope of different lines and existence of metastable equilibrium in the phase diagram of water system;
- define and explain the significance of critical point in the phase diagram of water;
- enlist different types of equilibria in sulphur system and show them on the phase diagram;
- draw and explain the phase diagram of sulphur system;
- define condensed systems and give the phase rule for the same;
- describe thermal analysis method of studying phase diagrams of two component systems and give significance of breaks and halts in the cooling curves;
- draw and explain the phase diagram for a simple eutectic system and give an industrial application for the same;
- define the terms like isotherm, isopleth and tie-line in the context of phase equilibrium;
- describe the changes along the isotherm and isopleth on the phase diagram for a two-component system;
- draw and explain the phase diagram of a ferric chloride-water system showing formation of congruently melting compounds; and
- draw and explain the phase diagram of a sodium-potassium alloy system showing formation of incongruently melting compound.

4.2 APPLICATION OF PHASE RULE TO ONE-COMPONENT SYSTEMS

The physical systems displaying heterogeneous equilibrium can be of varied complexities containing any number of components in equilibrium in any number of phases. However, to begin with we would take up simple one-component system so as to understand the general nature of its phase diagram and its analysis.

4.2.1 Characteristics of Phase Diagram of One-Component Systems

You would recall from previous unit that a phase diagram is a graphical representation of the number of phases that exist at a given set of values of pressure and temperature for a system. To understand the general nature of phase diagram of a one-component system, let us start by writing the phase rule expression as

$$F = C + 2 - P \qquad \ldots(4.1)$$

Since for a one component system, $C = 1$ the expression becomes

$$F = 1 + 2 - P \Rightarrow F = 3 - P \qquad \ldots(4.2)$$

Let us try to use this expression to draw some general conclusions about one component systems before taking up typical phase diagram and its analysis.

(i) Maximum number of phases that can coexist (P_{max})

From Eq. (4.2), we can write, $P = 3 - F$ Since the minimum value of the degrees of freedom can be zero, the maximum number of phases that can coexist in a one-component system would be

$$P_{max} = 3 - 0 = 3 \qquad \ldots(4.3)$$

For example, in water system, ice, water and water vapour can coexist in equilibrium.

(ii) Maximum number of degrees of freedom (F_{max})

Now, for a system to exist, it must have at least one phase. Therefore, the maximum number of degrees of freedom possible in a one-component system would be

$$F_{max} = 3 - 1 = 2 \qquad \ldots(4.4)$$

The one-component system can show different phase equilibria. Let us understand what all equilibria are possible for a one-component system.

(iii) One phase equilibria

We know that any substance can exist in three possible physical states, i.e., solid, liquid and gas. Accordingly, the one-component system can show three different one phase equilibria namely, solid, liquid and vapour (gas). For such equilibria, according to phase rule, the degrees of freedom for the system would be

$$F = 3 - 1 = 2 \qquad \ldots(4.5)$$

That is, the system would be **bivariant**. This means that both the pressure as well as the temperature could be varied independently without affecting (changing) the phase. This will be represented in terms of a region (or area) in the phase diagram. There will be an area for each of the phases in the phase diagram.

(iv) Two-Phase equilibria

Now, we take a situation such that the system has two different phases in equilibrium. In such a case, the degrees of freedom for the system would be

$$F = 3 - 2 = 1 \qquad \ldots(4.6)$$

i.e., the system would be **univariant**. This means that either the pressure or the temperature could be varied independently. If we vary and bring temperature to a certain value the pressure of the system gets automatically fixed and vice versa. Such an equilibrium is represented in terms of a curve (or line) in the phase diagram. There will be a curve (or line) in the phase diagram for each of the two-phase equilibria. The various two-phase equilibria possible in a one-component system are

1	Solid $\rightleftharpoons$ Liquid	2	Liquid $\rightleftharpoons$ Vapour
3	Solid $\rightleftharpoons$ Vapour	4	$Solid_1 \rightleftharpoons Solid_2$

The two phase equilibria listed at number 4 above, is exihibited by the substances that show polymorphism or allotropy e.g., sulphur system.

(v) Three-Phase equilibria

We take a situation in which the system simultaneously has three phases in equilibrium. In such a case, the degrees of freedom for the system would be

$$F = 3 - 3 = 0 \qquad \ldots(4.7)$$

This means that the system will be **invariant**, i.e., neither the pressure nor the temperature could be varied without changing the equilibrium. The pressure and temperature have fixed characteristic values for a substance under these conditions. The typical three phase equilibrium is

$$\text{solid} \rightleftharpoons \text{liquid} \rightleftharpoons \text{vapour} \qquad \ldots(4.8)$$

Such an equilibrium is represented in terms of a point in the phase diagram and the point is called a **triple point**. Thus, we see that the phase diagram for a one-component system would consist of areas (regions), curves (or lines) and point (s). A typical phase diagram of a one component system is given in Fig. (4.1).

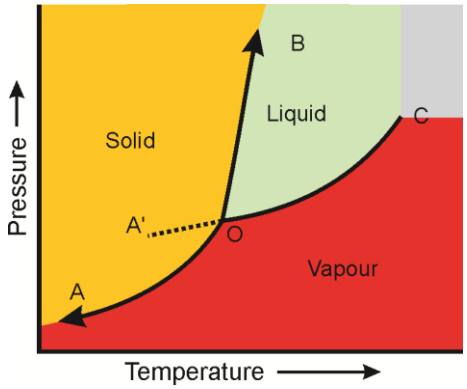


Fig. 4.1: A schematic phase diagram of a typical one-component system.

As discussed above, the phase diagram of a one-component system consists of areas, curves (or lines) and points. Let us learn about their significance.

I. Areas

The phase diagram of one-component system is divided into three distinct areas. You would recall that an area in phase diagram represents a one-phase equilibrium $(P = 1)$ and has two degrees of freedom $(F = 2)$. The three areas of typical phase diagram are:

(i) The area above the curve OA and to the left of the curve OB.

This area lies in low temperature and high-pressure region. You would recall from your school chemistry that solid state of a substance exists under these conditions. Thus, this area represents the temperature and pressure conditions under which the solid phase of the given substance is stable. As the system has two degrees of freedom, the temperature and pressure both can be changed independently. As long as the new state point lies in this region, no change in phase is observed.

(ii) The area below the curves OA and OC

This area lies in the region of low pressure and high temperature-the conditions under which **gas** (or **vapour) phase** is stable. The system is again bivariant as $F = 2$

(iii) The area above the curve OC and to the right of OB

This area lies in the region of high pressure and intermediate temperature where the **liquid phase** is stable. The system is bivariant here too.

II. CURVES (or LINES)

You would recall from previous discussion that a curve (or line) represents a two-phase equilibrium $(P = 2)$ and is univariant $(F = 1)$. The given phase diagram Fig. (4.1) consists of the three curves. Let us learn about the phases in equilibrium along each of these curves along with the name and significance of each curve.

(i) Curve OA

This curve separates the regions of stability of solid and vapour phases. Therefore, it represents the $\text{solid} \rightleftharpoons \text{vapour}$ equilibrium. Each point on this curve gives the vapour pressure of the solid at the given temperature. Since the phenomenon of conversion of solid to vapour is called sublimation. This curve is called as the **sublimation curve.** The curve is extendable to the absolute zero temperature, where, according to the third law of thermodynamics we expect a pure and perfectly crystalline solid.

(ii) Curve OB

The equilibrium represented by this curve is $\text{solid} \rightleftharpoons \text{liquid}$. The phenomenon occurring here is fusion, hence, this curve is called the **fusion curve.** It shows the variation of fusion temperature (or melting point) of the solid with external pressure. The slope of the curve is positive which means that the melting point

of a solid increases on increasing the pressure. The behaviour of water (and a few other substances) is exceptional as its solid state is lighter than its liquid state. In such cases, the slope of fusion curve is large but **negative.** You will learn more about the phase diagram of water in section 4.2.3. The curve OB can be extended in the direction O to B to extremely high pressures, which result in the formation of different forms of solids. The types of solids and their nature is beyond the scope of this course so will not be discussed here.

(iii) Curve OC

The curve OC represents the liquid $\rightleftharpoons$ Vapour equilibrium. This curve depicts the variation of vapour pressure of the liquid with temperature and hence is named as **vapour pressure curve.** Here, $P = 2$, $F = 1$ i.e., the degree of freedom is one. We can choose either temperature or pressure of the system, the value of the other variable automatically gets fixed.

If we forcefully change the values of both the parameters, then one of the two phases would disappear. The curve OC is unique in respect that it is not extendable in the direction O to C. The point C is fixed and is called **critical point.** The corresponding temperature and pressure are called the critical temperature and the critical pressure, which are characteristics of the substance taken. We would discuss their significance a little later.

(iv) Curve OA′

This curve is extrapolation of the curve OC in the backward direction. Along this curve, the same equilibrium continues as along OC, i.e., liquid $\rightleftharpoons$ Vapour equilibrium. You may note that this curve is drawn with dotted lines because the equilibrium along the extended portion OA′ is a **metastable equilibrium.** Ordinarily, we would expect the substance to freeze when cooled below its freezing point. However, it is possible to cool a liquid below its freezing point (or triple point) if it is done carefully.

You would recall from the previous unit that metastable equilibria can be achieved from one direction only. The liquid at such low temperatures is called **super cooled liquid.** The curve OA′ is the vapour pressure curve of super cooled liquid. You shall learn more about it a little later.

III. POINTS

A point in a phase diagram represents a three-phase equilibrium and is called a **triple point**. The phase diagram shown in Fig. (4.1) has only one triple point, O. This point lies in all the three areas of the phase diagram and represents the equilibrium $\text{solid} \rightleftharpoons \text{liquid} \rightleftharpoons \text{vapour}$. As the degrees of freedom in such a case is zero; we can neither vary temperature or pressure independently.

If a substance can exist in more than one solid forms (solids with different crystalline structures) and exhibits the phenomenon of polymorphism or allotropy, then more than one three phase equilibria are possible. You would study about one such system (sulphur system) in section 4.2.4. Since, the number of phases is three $P = 3$, $F = 0$ and the system is non-variant; the temperature and pressure have characteristic fixed values for a given system. If an attempt is made to change either temperature or pressure, two of the phases would disappear and only one phase would remain.

4.2.2 Analysing the Phase Diagram of One-Component Systems

Now we shall take up how to interpret the phase diagram of a one component system and what type of information can be obtained from it. Let us consider Fig. (4.2) given below, which is basically Fig. (4.1) given earlier, but marked with a few points and dotted lines to facilitate analysis. The phase diagram can be used to understand or visualise the changes in the system under different conditions. Generally, we see the effect of temperature on the system at constant pressure i.e., **isobaric changes** or the effect of pressure on a system at a given temperature i.e., **isothermal changes**. Let us begin with isobaric changes.

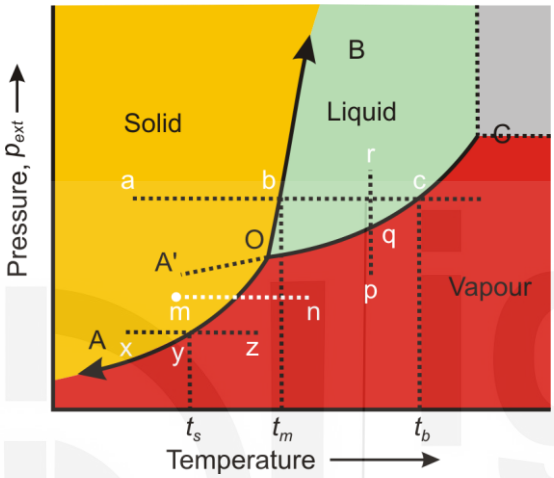


Fig. 4.2: Analysing schematic phase diagram of one component system.

State point

Any point on the phase diagram representing the state of the system at the corresponding *p* and *T* values.

I. Isobaric changes

i) Let us consider the state point 'a' in the phase diagram Fig. (4.2). It represents a solid sample of the substance at a particular temperature and pressure $(p_{ext.})$. What will happen if we start heating the system without changing the pressure? That is, we keep the pressure constant. As this point is in an area, the degrees of freedom here are two but of these two degrees of freedom we have fixed one by keeping the pressure constant so only the temperature can change. The heat supplied would increase the kinetic energy of molecules and the temperature of the solid would increase. The system will move along the isobar represented by the dotted line abc.

At a certain temperature, the dotted line meets the curve OB at point 'b'. This temperature is the melting point (t_m) of the solid. Here the solid starts melting and a two-phase ($\text{solid} \rightleftharpoons \text{liquid}$) equilibrium is established. Here, $P = 2$ and $F = 1$, i.e., degree of freedom is one. Since we have kept the pressure constant, i.e., the available degree of freedom is used, further heating results in the melting of more and more solid *without* any rise in temperature. The temperature would remain constant as long as there are two phases. Thus, the solid has a sharp melting point. The process continues till whole of the solid has melted.

At this stage we will once again have only one phase in equilibrium i.e., liquid and the degrees of freedom would once again become 2. Therefore,

on further heating, the temperature starts rising again and the system moves along the dotted line till it meets the curve OC. Here, the vapour pressure of the liquid becomes equal to the external pressure (p_{ext}) and the liquid start boiling. The temperature at this stage, is the boiling point (t_b) of the liquid. Once again, a two-phase equilibrium (liquid $\rightleftharpoons$ vapour) is established and the degrees of freedom becomes 1. Therefore, further heating does not increase the temperature and the liquid boils at a sharp temperature. Once whole of the liquid has been converted into vapour we would again have a one-phase equilibrium and the temperature would start rising again.

ii) Let us consider another isobar xyz, where the external constant pressure is lower than the triple point O. Here also, the initial state is solid and on heating its temperature rises and the state point moves along the dotted line. This line meets the curve OA at point 'y'. At this point sublimation of the solid begins and vapour is formed without melting of the solid. The corresponding temperature is the sublimation temperature (t_s) of the solid. Here, two –phase equilibrium (solid $\rightleftharpoons$ vapour) is established and the sublimation occurs at the constant temperature. When the process of sublimation is complete, the temperature of the system starts rising again.

II. Isothermal changes

Let us take a state point 'p' on the phase diagram. It represents vapour phase of the substance at a certain temperature and pressure. If we keep the temperature constant and increase the pressure gradually, the state point moves along the dotted line pqr. As the pressure increases, the molecules of the gas come closer and closer. At a certain point 'q' the dotted line meets the vapour pressure curve, OC. Here, the molecules come close enough and intermolecular forces overcome the kinetic energy of molecules and this results in liquefaction of the gas. Once the liquid is formed, a two-phase equilibrium (liquid $\rightleftharpoons$ vapour) is established. As more and more force is applied it results in the formation of more and more liquid. However, the pressure remains constant as long as both the phases are present. After whole of the vapour has been converted into liquid only one phase (liquid) remains, and the pressure starts increasing on further compression.

III. Beyond critical point, C

Lets now take point C, where the liquid-gas equilibrium line ends abruptly, which we called **critical point**. As stated before, the temperature at this point is called critical temperature and the pressure is called critical pressure. What does it mean? This means that if we have a liquid at or above this (critical) pressure it cannot be vaporised no matter how high the temperature goes. Similarly, if we have a gas at or above this (critical) temperature we cannot liquify it no matter how high the pressure is applied. In fact, for the pressure and temperature in the region marked as 'SCF' in the diagram the liquid and gaseous state become indistinguishable and is called 'super critical fluid' (SCF).

Super critical fluid is neither a pure liquid nor a pure gas

Thus, using phase diagram we can get a lot of information about the nature of changes that would occur in the system on changing temperature and/or

pressure of the system. We can also predict the melting and boiling points of the substance under desired external pressure. The phase diagram can also be used to predict whether at a given pressure the substance would directly sublime on heating or first it would melt and then boil. Thus, the study of phase diagram has many practical applications.

Having learnt about the general nature of the phase diagram for one component system and its analysis we can now take up the phase diagram of specific one-component systems. However, before that answer the following simple question to assess your learning.

SAQ 1

Consider a one-component system in a state represented by point 'm' in the typical phase diagram shown in Fig. (4.2). Describe the changes occurring in the system on increasing its temperature along the dotted line 'mo'.

4.2.3 Phase Diagram of Water

Water is one of the simple and important one component systems to study. In order to learn about the phase diagram of water, let us first identify different one, two and three phase equilibria possible in water system. As you know that water can exist in three different one-phase equilibria viz.,

ice (solid phase),	water (liquid phase)	water vapour (gas phase)

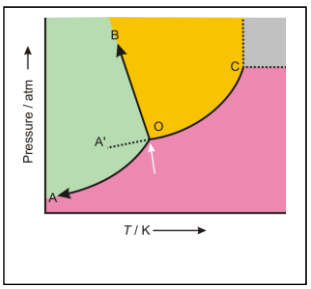
Further, water exibits three different two phase equilibria. These are

ice ⇌ water	water ⇌ water vapour	ice ⇌ water vapour

In addition, all the three phases of water can also coexist in a three phase equilibrium.

ice ⇌ water ⇌ water vapour

A simplified schematic phase diagram of water system is given in the margin. Using what you have learnt above about the general nature of phase diagram of one-component systems mark different equilibria (listed above) of water system in this diagram. Complete the markings before moving ahead.



We are sure that you could correctly identify all the seven possible (one, two and three phase) equilibria for the water system. A suitably labelled schematic phase diagram for the water system is given in Fig.(4.3). Lets analyse it.

One phase equilibria

According to the phase rule the degrees of freedom for one-phase equilibria of water system would be 2 and are represented by the areas marked as ice, water and water vapour in Fig. (4.3). The assignment of these areas is quite straightforward as explained while discussing the typical phase diagram of one-component system. The significance of system being bivariant $(F = 2)$ is that both the temperature and pressure could be varied without changing the nature of the equilibrium. That is, we can keep the pressure constant

anywhere in the region and vary the temperature or vice versa. Ice, water or water vapour remains stable as long as the values of p and T are within the respective areas as indicated in the figure.

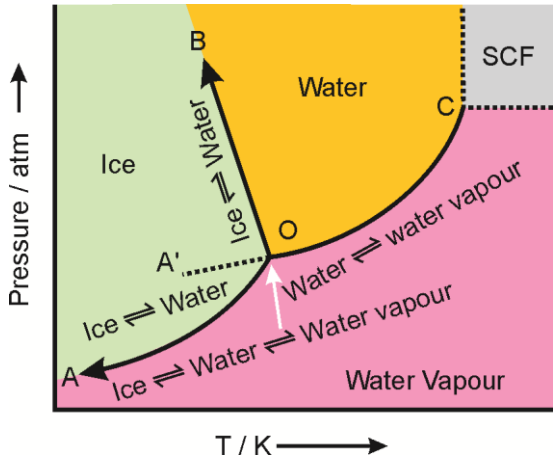
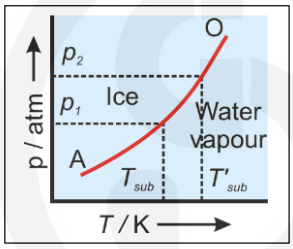


Fig. 4.3: Schematic phase diagram of water (not to scale).

Two phase equilibria

The degrees of freedom for two-phase equilibria would be $(F = 3 - 2 = 1)$ and are represented by the curves; OA, OB and OC as indicated in the diagram. Let us discuss these curves and the nature of their slope.



Curve OA

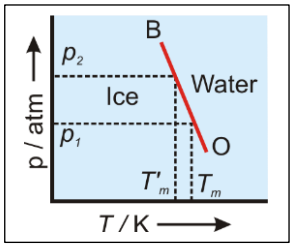
The curve OA represents ice ⇌ water vapour equilibrium and is called **sublimation curve**. We can vary either the pressure or the tempearture along this curve. That is, if we vary the pressure of the system along this curve the temperature gets automatically fixed and vice versa. Further, you would recall from Clausius equation that the slope of the p versus T plot for sublimation is given as,

$$\frac{dp}{dt} = \frac{\Delta_{sub}H_m}{T\Delta_{sub}V_m} \qquad \ldots(4.9)$$

Since T is always positive we can say that the slope depends on the sign of $\Delta_{sub}H_m$ and $\Delta_{sub}V_m$. Since both the enthalpy of sublimation and volume change in the process are positive; the sublimation curve has a positive slope.

$$\frac{dp}{dT} = \frac{\Delta_{sub}H_m}{T\Delta_{sub}V_m} = \frac{+\text{ve}}{+\text{ve}\times+\text{ve}} = +\text{ve} \qquad \ldots(4.10)$$

This means that if we increase pressure the sublimation temperature increases.



Curve OB

The curve OB represents ice ⇌ water equilibrium and is called **fusion curve.** Here again, if we vary the pressure of the system along this curve the temperature gets automatically fixed and vice versa. Again, the slope of this curve is given as,

$$\frac{dp}{dT} = \frac{\Delta_{fus}H_m}{T\Delta_{fus}V_m} \qquad \ldots(4.11)$$

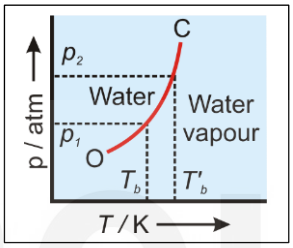
We know that T is always positive; the enthalpy of fusion, $\Delta_{fus}H_m$ is also positive. Therefore, we can say that the slope depends on the sign of $\Delta_{fus}V_m$. You know that ice floats on water, i.e., its density is less than water. This means that when ice melts the volume decreases i.e., $\Delta_{fus}V_m$ is negative so the fusion curve has a negative slope.

$$\frac{dp}{dT} = \frac{\Delta_{fus}H_m}{T\Delta_{fus}V_m} = \frac{+\text{ve}}{+\text{ve}\times-\text{ve}} = -\text{ve} \qquad \ldots(4.12)$$

The significance of the negative slope is that if we increase the pressure the melting point of water decreases ($T'_m < T_m$). *You may note here that the slope of fusion curve is different from that discussed for typical one component system. In fact, the water system is an exception in this regard.*

Curve OC

The curve OC represents water $\rightleftharpoons$ water vapour equilibrium and is called **vapour pressure curve.** It gives the variation of vapour pressure of water as a function of temperature. The slope of this curve is given as,



$$\frac{dp}{dT} = \frac{\Delta_{vap}H_m}{T\Delta_{vap}V_m} \qquad \ldots(4.13)$$

Since T is always positive we can say that the slope depends on the sign of $\Delta_{vap}H_m$ and $\Delta_{vap}V_m$. Since both the enthalpy of vaporisation and volume change in the process are positive; the curve has a positive slope.

$$\frac{dp}{dT} = \frac{\Delta_{vap}H_m}{T\Delta_{vap}V_m} = \frac{+\text{ve}}{+\text{ve}\times+\text{ve}} = +\text{ve} \qquad \ldots(4.14)$$

It means that if we increase the temperature the vapour pressure of water increases.

Three phase equilibrium (point O)

The degrees of freedom for three-phase equilibrium for a one component system would be zero $F = 3-3 = 0$. It is represented by a point in the phase diagram. It is a unique point and for water it (point 'O') is observed at a temperature of 273.16 K (273.1575 K) and a partial vapor pressure of 0.006 atm (0.00603659 atm or 4.58 Torr). Any change in pressure or temperature would disturb the equilibrium and two of the phases would be lost.

1 Torr = 1 mm Hg

Having discussed, the representation of different one, two, and three phase equilibria on the phase diagram, let's discuss two more features of the phase diagram of water. These are the curve OA′ and the critical point (C on the diagram).

Metastable equilibrium, curve OA′

The curve OA′ represents a metastable equilibrium and is called **metastable vapour pressure curve**. This, in fact is the extension of vapour pressure curve,OC below O up to A′ (that is extending below the triple point). Here, we have water in equilibrium with its vapours at temperatures below the freezing point of water. That is, we are able to cool water below its freezing point without letting ice to separate.

You would recall from Unit 3 the metastable equilibrium in water can be obtained by taking a clean, dust free sample of water in a clean and smooth container and cooling without disturbance of any kind. This way we can take the temperature of water down to $-5^{\circ}C$ without any solid ice appearing. Here, the system is in metastable equilibrium and we can preserve such water in liquid state at $-5^{\circ}C$ for any amount of time if we ensure that there is no disturbance. However, if we disturb it in any way by adding a small crystal of ice or by shaking or stirring, it will immediately change it into the ice and the temperature would increase to $0^{o}C$.

As discussed above, the critical temperature is the temperature above which a gas cannot be liquefied and critical pressure is that pressure above which a liquid cannot be vapourised no matter how high is the temperature.

Critical point, C

You would recall from the discussion on the general phase diagram for one-component system that the point C called **critical point** and is that point in the phase diagram where the vapour pressure curve, OC ends abruptly. This is a point where the liquid and the vapour become indistinguishable. For water the critical point is observed at a pressure of 217 atm and a temperature of 647.3 K. These are respectively the critical pressure and critical temperature of water. Here, water and water vapour become indistinguishable and the region is called the super critical fluid (SCF) region.

Having learnt about the phase diagram of water, answer the following simple questions to assess your understanding.

SAQ 2

What is meant by triple point? What is the degree of freedom for a one-component system at triple point?

SAQ 3

How does the boiling point of water depend on the pressure? Explain with the help of vapour pressure curve.

4.2.4 Phase Diagram of Sulphur

Sulphur is another interesting one-component system, slightly more complex than the water system, discussed above. It shows two solid phases (rhombic sulphur and monoclinic sulphur), one liquid phase and a vapour phase. The two different crystalline solid forms are called *allotropic* or *polymorphic* forms. Let us first list out different equilibria possible in sulphur system.

The possible one-phase equilibria for sulphur are

Rhombic sulphur (solid phase); S_R	Monoclinic sulphur (solid phase); S_M
Liquid sulphur (liquid phase); S_L	Sulphur vapour (gaseous phase); S_V

There are six two phase equilibria observed in sulphur system; these are

$S_M \rightleftharpoons S_V$	$S_R \rightleftharpoons S_M$	$S_R \rightleftharpoons S_V$
$S_R \rightleftharpoons S_L$	$S_M \rightleftharpoons S_L$	$S_L \rightleftharpoons S_V$

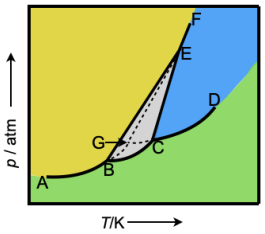
In addition, there could be four three phase equilibria; these are

$S_R \rightleftharpoons S_M \rightleftharpoons S_V$	$S_R \rightleftharpoons S_M \rightleftharpoons S_L$	$S_M \rightleftharpoons S_L \rightleftharpoons S_V$	$S_R \rightleftharpoons S_L \rightleftharpoons S_V$

How about four phase equilibria? Can these be possible? Four phase equilibria are not possible in a one-component system like sulphur. Can you think why? It is so because if we apply phase rule to such a system we find that the degrees of freedom would be

$F = C + 2 - P$

$$F = 1 + 2 - 4 = -1 \qquad \ldots(4.15)$$



Since the degrees of freedom cannot be negative, therefore a four-phase equilibrium is not possible. A simplified schematic phase diagram for sulphur system is given in the margin indicating different areas, curves and points. You may use your understanding of the phase diagram of one-component systems to identify different regions, curves and points listed above before moving ahead.

You might have identified four regions, six curves and four points (B, C, E and G) on the phase diagram. A labelled schematic phase diagram for sulphur system is given in Fig. (4.4). Let's understand it systematically with the help of phase rule.

One phase equilibria

The one-phase equilibria in the sulphur system would have the degrees of freedom, $F = 3 - 1 = 2$ i.e., these are bivariant and are represented by areas. The phase diagram of sulphur (Fig. 4.4) consists of four such areas each representing one-phase. The allocation of regions for the liquid phase (S_L) and vapour phase (S_V) as mentioned in the diagram is straight forward in the light of the general discussion on the phase diagram of one-component system. We are left with two regions corresponding to the two solid phases. The question is which region represents which solid form of sulphur?

In order to decide about the regions (BCE and the area to the left of ABEF) for the two solid phases we use the fact that rhombic sulphur changes to monoclinic sulphur at a temperature of 95.5°C.

$$S_R \overset{95.5^\circ C}{\rightarrow} S_M \qquad \ldots(4.16)$$

This implies that monoclinic sulphur is stable at higher temperature or the monoclinic sulphur is indicated by region BCE while the region on the left of ABEF is for rhombic sulphur. The allocation of different regions in the phase diagram to the respective one-phase equilibria can be summarised as under.

Phase	Region (area)
S_R	To the left of ABEF
S_M	Between BCE
S_L	To the right of FEC and above CD
S_V	Below ABCD

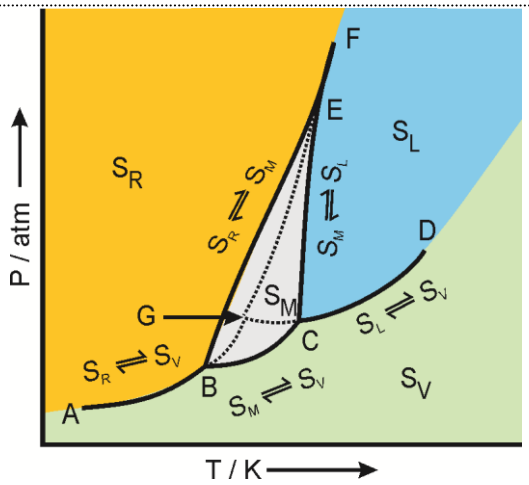


Fig. 4.4: Schematic phase diagram of sulphur system (not to scale).

Two phase equilibria

We have given above that six two-phase equilibria are possible in the sulphur system. As the degrees of freedom for the two-phase equilibria would be 1; these are represented by curves (or lines). The allocation of different curves to the corresponding two-phase equilibria and their description is summarised as under:

Equilibria	Curve	**Description**
$S_R \rightleftharpoons S_V$	AB	Sublimation curve of S_R
$S_M \rightleftharpoons S_V$	BC	Sublimation curve of S_M
$S_L \rightleftharpoons S_V$	CD	Vapour pressure curve of S_L
$S_R \rightleftharpoons S_M$	BE	Transition curve
$S_R \rightleftharpoons S_L$	EF	Fusion curve of S_R
$S_M \rightleftharpoons S_L$	CE	Fusion curve of S_M

You may note here that the nature (slope) of these curves is as per our discussion on the typical phase diagram of one-component system.

Three- phase equilibria

According to the phase rule, the three phase equilibria would be invariant i.e., the degrees of freedom would be zero. The allocation of different points on the phase diagram to the corresponding three-phase equilibria and the characteristic temperature and pressure corresponding to them is given as under:

Equilibria	Point	Pressure / atm	Temperature /K
$S_R \rightleftharpoons S_M \rightleftharpoons S_V$	B	1.32×10^{-5}	368.65
$S_R \rightleftharpoons S_M \rightleftharpoons S_L$	E	1290	424.15
$S_M \rightleftharpoons S_L \rightleftharpoons S_V$	C	3.29×10^{-5}	393.15
$S_R \rightleftharpoons S_L \rightleftharpoons S_V$	G*	3.95×10^{-5}	387.15

* metastable

You may note that the allocation of three points (B, C and E) on the phase diagram of sulphur is simple and straightforward. However, how do we assign the fourth triple point (G) corresponding to the following three-phase equilibrium?

$$S_R \rightleftharpoons S_L \rightleftharpoons S_V \quad \ldots(4.17)$$

These three phases cannot meet each other because region of monoclinic sulphur comes in between the regions of rhombic sulphur and liquid sulphur. This (point G) in fact is a point where three metastable equilibria meet. Let us see what are these metastable equilibria. If we rapidly heat rhombic sulphur beyond 95.5 °C (where it is expected to get converted into monoclinic sulphur) we find that it does not get converted into monoclinic sulphur and the rhombic sulphur remains in metastable state. Its vapour pressure varies as per curve BG. It is the extension of the sublimation curve of rhombic sulphur, AB.

You would recall that in case of water we could cool water to -5°C without letting it get converted into ice

Similarly, if we could supercool liquid sulphur it will be represented by curve CG, it is the extension of the vapour pressure curve CD. The curve EG represents the fusion curve of rhombic sulphur-another metastable equilibrium, which is the extension of the curve FE. These three metastable equilibria meet at point G where rhombic sulphur, liquid sulphur and sulphur vapour coexist. That is, it is the triple point corresponding to the $S_R \rightleftharpoons S_L \rightleftharpoons S_V$ equilibrium.

Having learnt about the phase diagram of sulphur, answer the following simple question to assess your understanding.

SAQ 4

What is meant by a metastable equilibrium? Describe different metastable equilibria observed in sulphur system.

4.3 APPLICATION OF PHASE RULE TO TWO-COMPONENT SYSTEMS

Having learnt about the application of phase rule to one-component system in terms of generating and interpreting the phase diagrams you are now equipped to take up the application of phase rule to two component systems. A two-component system is a heterogeneous system having two independent components. If we apply the phase rule to such a system we get,

$$F = C + 2\text{-}P \Rightarrow F = 2 + 2 - P = 4 - P \quad \ldots(4.18)$$

As the minimum number of phases in a heterogeneous system is one the corresponding degrees of freedom becomes $F = 4 - 1 = 3$. This means we need to specify three different variables to completely define the system. The three chosen variables in such a case are pressure (p), temperature (T) and composition (c). However, this makes constructing the phase diagram quite complicated, because to represent three variables we need three mutually perpendicular coordinate axes. The resulting phase diagram would be a three-dimensional solid figure.

The phase rule can be written as $P+F=C+2$
If the pressure is kept constant, the numeral 2 reduces to 1 on the right-hand side.
If the vapour pressure is ignored (in condensed phase) the number of phases, P is decreased by one, on the left-hand side
This decrease both sides by one and the phase rule changes to
$P+F'=C+1$ or $F'=C+1-P$
While using this we must remember that P includes only the condensed phases (solid or liquid phases) and ignores the vapour phase

As it is difficult to construct such a diagram, one of the ways to resolve the issue is to either take a projection of such a solid diagram on a plane, or take a planar cross section of the diagram for a given constant value of one of the variables. This allows us to represent different equilibria in two-component systems in terms of a two-dimensional plot of any two of the three variables. For example, we can construct a $p-c$ diagram at constant temperature or a T $T-c$ diagram at constant pressure.

Another way out is that we consider different two-phase equilibria like liquid-gas, solid-gas, liquid-liquid, and solid-liquid individually and then combine them to get the overall phase diagram. Some of these equilibria have already been dealt with in Unit 2; here we would focus our attention to the application of the phase rule to solid-liquid equilibria. The study of solid-liquid equilibria is quite important as it provides information about the processes related to alloy formation and crystallisation (purification) etc. Such systems are called as **condensed systems**. Let's see how the phase rule gets modified when applied to such condensed systems.

4.3.1 Phase Rule for Condensed Systems

The behaviour of solid-liquid equilibria is studied under the conditions of constant pressure, generally atmospheric pressure. Accordingly, the pressure can be taken as a constant and it reduces one of the degrees of freedom. In fact, the phase rule equation under the conditions of constant pressure gets modified as

$$F' = C + 1 - P \qquad \ldots(4.19)$$

This is called the **phase rule for condensed systems**. For a two-component system the equation becomes,

$$F' = 3 - P \qquad \ldots(4.20)$$

Now, for a one-phase equilibrium, the modified degrees of freedom become 2 and the system then can easily be represented by a two-dimensional phase diagram. The two variables available (when pressure is constant) are temperature and composition and the phase diagrams for solid-liquid equilibria are called temperature-composition (or $T-c$) diagrams. As the composition in such systems may vary from 100% of component A to 100% of component B, the concentrations are generally presented in terms of mass% or mol %.

In this course we are going to take up solid-liquid equilibrium in such systems where the components are completely miscible in the liquid state and are completely immiscible in the solid state. These systems are further distributed in three types. These are

- Simple eutectic systems
- Systems involving congruent melting point
- Systems involving incongruent melting point

We will now take up these systems individually using suitable examples. We begin with simple eutectic system.

4.4 SIMPLE EUTECTIC SYSTEMS

Let's learn about a system containing lead and silver as a two-component simple eutectic system. As required, this system meets the requirement of condensed systems showing solid-liquid equilibria, that the two components are completely miscible in the liquid state and completely immiscible in the solid state. If we take pure lead; heat it to melt then allow it to gradually cool. What would we observe? We would observe that the melt gradually cools down and when the temperature becomes equal to the melting (or fusion) point of lead, solid lead would separate out. On the other hand, if we take a mixture of lead with a small amount of silver, melt it and allow it to cool. We would observe that the lead would start separating out as a pure solid at a temperature lower than the melting point of the pure lead. The actual temperature would depend on the composition of the mixture. This decrease in temperature at which solid lead crystalises out can be understood in terms of depression in freezing point of a solid on addition of an impurity. You may recall that the mole fraction (χ_A) of a component in a mixture and its melting point (T) are related as

$$\ln \chi_A = -\frac{\Delta H_{fus,A}}{R}\left[\frac{1}{T} - \frac{1}{T_{0,A}}\right] \qquad \ldots(4.21)$$

where, $\Delta H_{fus,A}$ is the enthalpy of fusion of the compound A, and $T_{0,A}$ is the melting point of pure A. The variation of the temperature of crystallisation of lead with the mole fraction can be shown graphically as in Fig. (4.5 (a)). The region above the curve represent liquid states whereas that below it represents states in which pure lead coexists in equilibrium with the solution. The curve is called the **liquidus curve.**

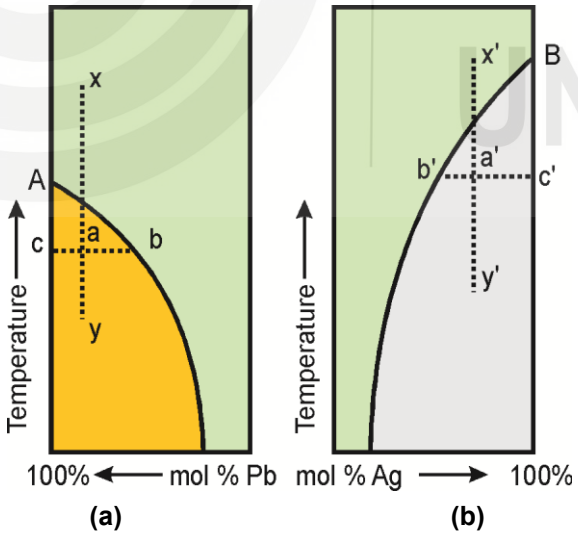


Fig. 4.5: The freezing point curves of a) lead and b) silver.

Suppose we have the system represented by the point x on the graph and we start cooling it, the temperature would decrease along the dotted line xy and when its meets the curve, solid lead starts crystallising out and there would be an equilibrium between solid lead and the solution. On further cooling more and more of the lead would crystallise and the solution would become richer and richer in silver. The composition of solution varies along the liquidus curve. At a point say 'a' the solution of composition 'b' would be in equilibrium

with the solid of composition ‘c’. The line c-a-b is called **tie line**. The ratio of the number of moles of solution to the number of moles of solid lead in the system can be obtained by the **lever rule**. According to lever rule this ratio is equal to the ratio of segments (ac/ab) of the tie line. Lower the temperature, greater the relative amount of solid. However, this trend cannot continue over the whole range of the composition; when the amount of silver is more, it is the silver that would crystallise out. A similar exercise starting with pure silver and adding more and more lead to it is expected to give a curve as given in Fig, (4.5(b)). Can you describe the changes when we move along the line x′y′?

The phase transitions in the solid-liquid equilibria can be followed by using any property which changes significantly at the transition temperature e.g., refractive index, conductivity, specific volume etc. Generally, the solid-liquid equilibria can be studied by two different methods, these are a) solubility measurement and b) thermal analysis. We would be using thermal analysis method to construct or interpret the phase diagrams of two component systems. Let’s first learn about the thermal analysis method also called cooling curve method.

4.4.1 Thermal Analysis Method

Thermal analysis is a convenient method to study solid-liquid equilibria because the phase transitions in such systems are accompanied by significant enthalpy changes and can be followed easily. In this method, the mixtures of two components with different compositions are heated to melt and then allowed to gradually cool down. The temperature of the mixture is followed as a function of time. The observed data is plotted as cooling curves showing the temperatures corresponding to different phase changes. These are then used to construct the phase diagram by plotting these temperatures against the composition of the mixtures. Let us understand this method for a system containing two solids A and B that are immiscible in solid state but are completely miscible in the liquid state.

We start with pure solid, A and heat it to a temperature above its melting point to get a melt and then allow it to cool and monitor temperature as a function of time. The data is then plotted as a cooling curve -a graph between temperature and time as shown by curve I in Fig. (4.6).

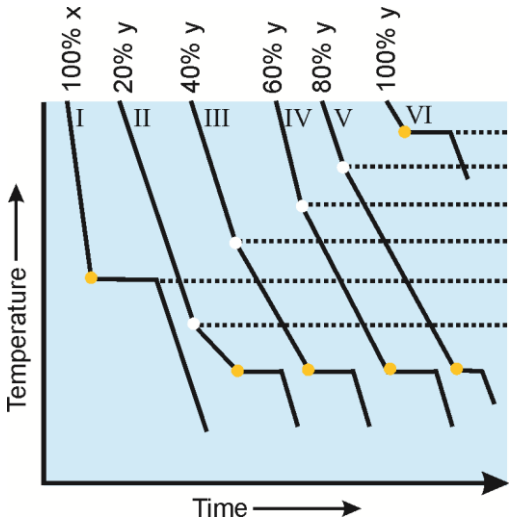


Fig. 4.6: The cooling curves of pure components and their mixtures.

On cooling this melt, the initial slope of the temperature-time curve can be explained in terms of the Newton's law of cooling. Once the temperature reaches the melting point of the solid A the pure solid will start crystallising out. The temperature of the system would remain constant (called **halt**) till the entire solid A separates out. The halt in the cooling curve results from the heat evolved when the liquid solidifies. Further decrease in the temperature would correspond to the cooling of the solid.

We then take a mixture of two solids (A and B) and heat it to get a melt. On cooling this melt, the initial slope of the temperature-time curve again can be explained in terms of the Newton's law of cooling. At a certain temperature (corresponding to the melting point of the solid in excess (say solid A) in the mixture) the solid A would start crystallising out. Remember this temperature would be lesser than the melting point of the pure solid. This process of crystallisation is accompanied by a change in slope of the cooling curve due to the heat evolved during the crystallisation of more and more of the solid. This slows down the cooling rate (the slope of cooling curve would decrease) and the change in slope is called a **break**. After some time when the system reaches a certain temperature called eutectic temperature, both the solids (A and B) start crystallising out and the temperature becomes constant. This is indicated by a **halt** in the cooling curve. Once both the solids get crystalized further cooling decreases the temperature of the solids. This process is indicated by curves II to V in the figure. The cooling curve of the melt of pure solid B (VI) would be similar to curve I, though the temperature of halt would be different (this would correspond to the melting point of the pure solid B).

In order to obtain a phase diagram for a two-component system, a number of their mixtures of varying composition are taken and heated to obtain their melts. These melts are then gradually cooled, and the cooling curves are obtained. The break and/or halt points obtained from the series of cooling curves are then plotted against the corresponding composition to generate the phase diagram as shown in Fig. (4.7) for a eutectic system

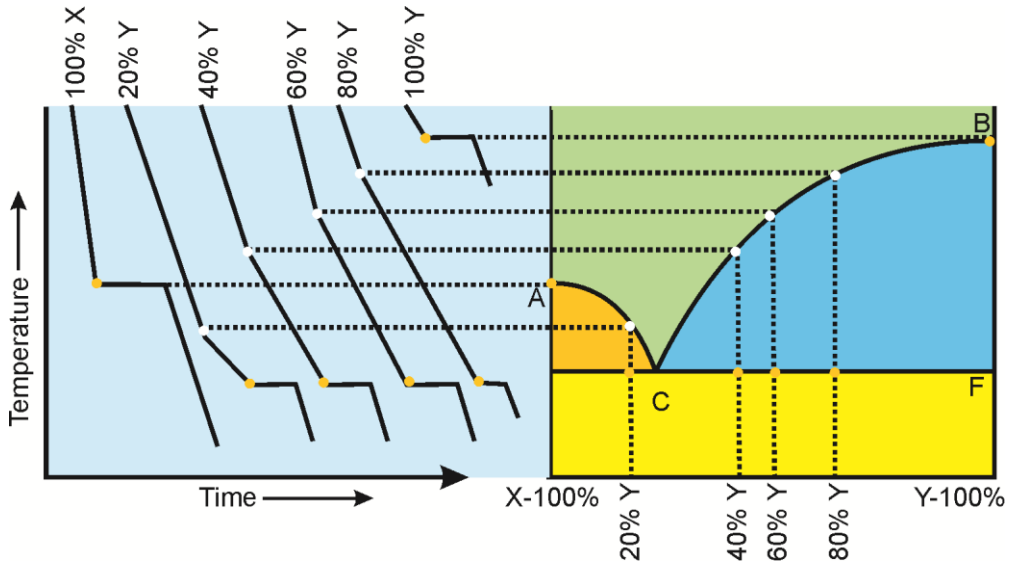


Fig. 4.7: Generating the phase diagram of simple eutectic system from cooling curves of pure components and their mixtures.

4.4.2 Phase diagram for Pb-Ag system

$F' = 3 - P$

The phase diagram of lead-silver simple eutectic system is given in Fig. (4.8). The diagram indicates different phases in equilibrium and phase transition temperatures for lead-silver system. The composition of the system varies from 100% lead (point G) to 100% silver (point H). The point A and B respectively represent the melting points of pure lead (327°C) and pure silver (961°C). Let us try to understand the same.

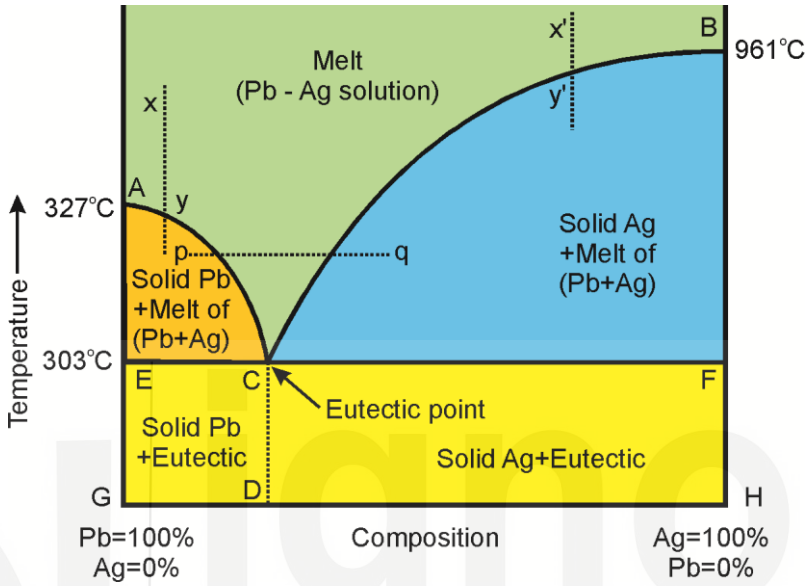


Fig. 4.8: Phase diagram of lead-silver simple eutectic system (not to scale).

The region above ACB

The curves AC and BC are the liquidus curves. In the region above ACB the liquid phase (melt) exists. For this region having single phase the degrees of freedom, $F' = 3 - 1 = 2$, i.e., it is a bivariant system. In other words, both the temperature as well as the composition of the melt can be varied independently.

The region below EFGH

Similarly, the line ECF represents solidus and in the region below this only solid phases exist as indicated in the figure.

Curve AC

The curve AC is the liquidus curve and shows the variation in the melting point of lead that decreases on addition of silver. The points on this curve also represent the composition of solutions saturated with lead in the range of temperature from the melting point of lead to the eutectic temperature, t_e (303°C). There are two phases here (pure solid lead and melt containing lead and silver). The degrees of freedom would be $F' = 3 - 2 = 1$; i.e., the system is univariant. That is, if we fix the temperature then the composition becomes fixed and vice versa.

Curve BC

Similarly, the curve BC shows the variation in the melting point of silver on addition of lead. The points on this curve give the compositions of solutions

saturated with silver in the range of temperature from the melting point of silver to the eutectic temperature, t_e (303°C). This is also univariant like the curve AC.

Point C (eutectic point)

At the intersection of the curve AC and BC i.e., at point C the solution is saturated with lead as well as silver. On cooling the melt, solid lead and solid silver both separate out simultaneously. In other words, we have three phases (two solids and a solution) in equilibrium, and the degrees of freedom, $F' = 3 - 3 = 0$; i.e., the system is invariant. At this point both the temperature and the composition are fixed; it is a unique point. This implies that any variation in temperature or composition would cause one of the phases to disappear. Say if we decrease the temperature, both solids would crystallise and the melt would disappear (we would have only solids). On the other hand, on increasing temperature both the solids would melt, and we would have only melt, no solids. This point is called **eutectic point**; the corresponding temperature is called ***eutectic temperature*** and the composition as ***eutectic composition*** respectively. At the composition corresponding to the eutectic point the melting (freezing) point of the system is minimum. The term eutectic literally means easy melting. It is important to note that the eutectic is not a compound; it is a mixture of two solid phases and has a fine grain structure that can be observed under a microscope. You must note that for any other composition, we would have only two phases, either two solids (Pb and Ag) or one solid (Pb or Ag) and the melt.

The eutectic mixture melts sharply at eutectic temperature to form a liquid of the same composition, whereas the other mixtures melt over a range of temperature. Due to the sharp melting point, the eutectic mixture was initially thought to be a compound.

Regions AEC and BCF

In the region AEC, there are two phases in equilibrium. These are solid lead and a solution of lead and silver having a composition given by the point on curve AC. Similarly, in the region BCF solid silver and a solution of lead and silver having a composition given by the points on curve BC are in equilibrium. In these regions, the degree of freedom is ($F' = 3 - 2 = 1$) one. Thus, in these regions either the temperature or the composition of the liquid need to be specified. If the temperature is specified, the composition of the liquid can be obtained from the corresponding point on the liquidus. On the other hand, if we specify the composition of the liquid the equilibrium temperature is automatically fixed.

We stated above, that the line ECF is the solidus and only solids can exist below it. Let us analyse this region.

Regions CDGE

The points on the line EC represent lead in equilibrium with melt having eutectic composition (x_e). Similarly points on the line CF represent solid silver in equilibrium with melt having eutectic composition (x_e). The region CDGE would have pure solid lead and solid (lead + silver) in eutectic composition. On the other hand, the region CDHF would have pure solid silver and solid (lead + silver) in eutectic composition. Thus, these areas represent two-phase regions in which two solids are present. The system is univariant and we need only to specify the temperature to describe the system completely at a given constant

pressure. The ratio of two solids may change but we would only have a mixture of pure lead and pure silver; therefore, there is no need to specify the composition. However, microscopic examination of the solids in the area ECDG reveal large crystals of lead along with microcrystals of lead and silver having a composition defined by eutectic point. Similarly the solid in the area CDHF consists of large crystals of silver and microcrystals of lead and silver having eutectic composition.

Having learnt about the description of different regions and curves in phase diagram of a simple eutectic system and their significance it is important to learn about two important terms called Isopleth and isotherm.

Isopleth and isotherm

Isopleth refers to a line corresponding to a constant composition on the phase diagram. An Isopleth is shown as the line XY (or X′Y′) on the phase diagram given in Fig. (4.8). On the basis of the discussion above you can describe the behaviour of the system as the system corresponding to point X in the phase diagram is slowly cooled. Similarly, the horizontal line parallel to the x-axis on the phase diagram corresponds to the systems of different composition at a given temperature. As the temperature remains constant such a line, say PQ is called an **isotherm**. Let's learn about an important industrial application of eutectic system.

Industrial application of Pb-Ag eutectic system

Pattinson's process uses the formation of eutectic mixture by lead and silver in the extraction of silver from argentiferrous lead (a lead-silver alloy containing less than 0.1% silver). The alloy is heated above its melting point and the melt so obtained is slowly cooled. When the temperature of the system reaches 600 K pure lead starts crystallising. The amount of solid lead goes on increasing with further cooling and the melt continuously becomes richer in silver (as depicted by curve AC). The solid lead is removed from the melt and at a temperature of 576 K (the eutectic temperature) eutectic mixture of lead and silver containing 2.6% silver solidifies from which silver can be extracted relatively easily.

Having learnt about simple eutectic system answer the following questions before going ahead.

SAQ 5

Two solids A and B are completely miscible in the liquid state but are immiscible in the solid state. Solid A has a higher melting point than that of B and these solids form a simple eutectic system with eutectic composition 35% A. Draw a schematic phase diagram for the system.

SAQ 6

On the basis of phase diagram of lead-silver system given in Fig. (4.8) State suitable conditions to obtain pure silver from a mixture of lead and silver containing 30 mol% of silver.

4.5 SYSTEMS INVOLVING CONGRUENT MELTING POINT

In some two component systems there could be strong interactions between the components such that they form one or more compounds. Under suitable conditions of temperature and composition the compounds separate as new solid phases. If the compound so formed is stable up to its melting point, and melts to give a liquid having same composition as the compound then it is said to be have **congruent melting point**. You should note that here we get a new compound and not the mixture of two components in a fixed ratio as in case of eutectic system.

The formation of such a compound leads to a maximum in the temperature–composition diagram and the composition that corresponds to the maximum temperature is the composition of the compound formed. In such cases the phase diagram is made up of two or more simple eutectic systems depending on the number of compounds formed. A schematic phase diagram of a two component (A and B) system involving formation of *one* congruently melting compound of composition AB_2 is given in Fig. (4.9)

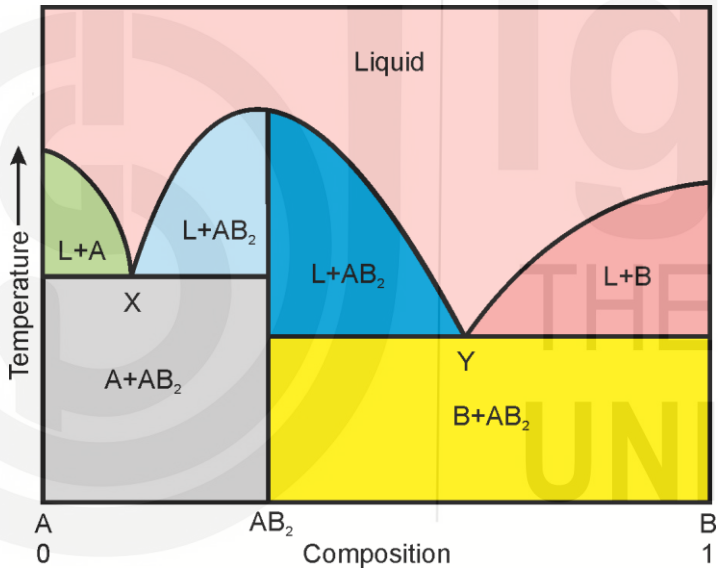


Fig. 4.9: A schematic phase diagram of a two-component system forming a congruently melting compound, AB_2.

The analysis of the phase diagram in such a case is quite simple. The phase diagram can be considered to be a combination of phase diagrams of two simple eutectic systems. You can visibly see it in the phase diagram given above. The first eutectic system is formed between the pure compound A and the compound formed say AB_2. The second eutectic, on the other hand is between AB_2 and pure B. Each one of these can be analysed as discussed above for a simple eutectic system.

Here, you may note that according to the Fig. (4.9) the phases in equilibria at the eutectic (X) are A, AB_2 and saturated solution of A and AB_2; whereas at eutectic (Y) these phases are AB_2, B and saturated solution of B and AB_2 respectively. You may note that the melting point of the compound AB_2 shows a maximum in the liquidus curve. The description of the phase diagram becomes straight forward in terms of the two eutectic systems identified. Let's

us take the phase diagram of ferric chloride-water system that shows the formation of as many as four different compounds (these are different hydrates) and five different eutectic points.

4.5.1 Phase Diagram of Ferric Chloride-Water System

Ferric chloride forms four different stable crystalline hydrates (new compounds) having congruent melting points i.e., these are stable upto their melting points. The names of four hydrates of ferric chloride formed, their composition and the corresponding melting points are summarised as under:

Name	Composition	Point	Melting point /°C
Ferric chloride dodecahydrate	$Fe_2Cl_6.12H_2O$	C	37
Ferric chloride heptahydrate	$Fe_2Cl_6.7H_2O$	E	32.5
Ferric chloride pentahydrate	$Fe_2Cl_6.5H_2O$	G	56
Ferric chloride tetrahydrate	$Fe_2Cl_6.4H_2O$	J	78.5

The formation of these compounds (hydrates) increases the number of areas and eutectic points in the phase diagram. However, it does not introduce any new feature. If we consider each newly formed compound as a new component the significance of the different areas, lines, and points can be easily understood. A schematic phase diagram of the ferric chloride-water system is given in Fig. (4.10).

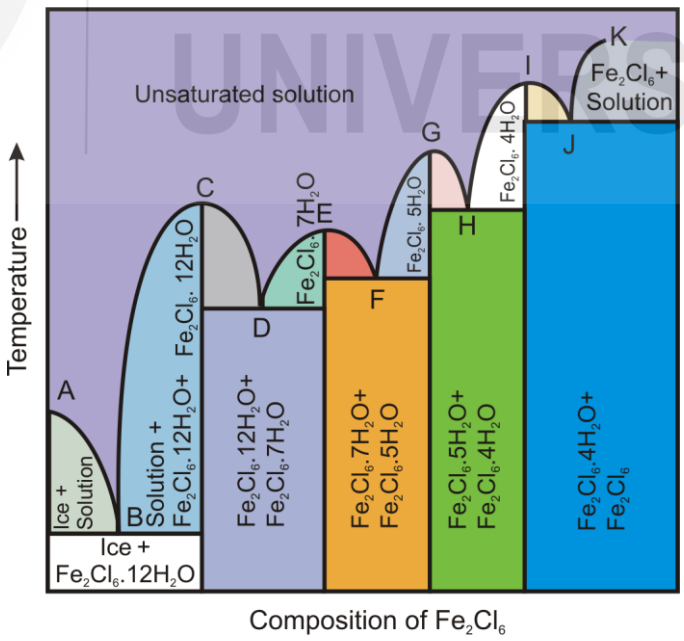
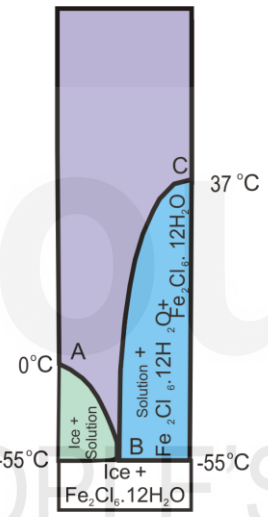


Fig. 4.10: A schematic phase diagram of ferric chloride-water system.

You can note that the phase diagram can be visualised as made up of five different eutectic systems. Different subsystems and the corresponding eutectic points of the ferric chloride –water system are as under.

Portion of liquidus curve	Eutectic sub-system	Eutectic	
		Point	Temp/°C
ABC	Ice - $Fe_2Cl_6.12H_2O$	B	-55
CDE	$Fe_2Cl_6.12H_2O$ - $Fe_2Cl_6.7H_2O$	D	27.4
EFG	$Fe_2Cl_6.7H_2O$ - $Fe_2Cl_6.5H_2O$	F	30
GHI	$Fe_2Cl_6.5H_2O$ - $Fe_2Cl_6.4H_2O$	H	55
IJK	$Fe_2Cl_6.4H_2O$ - Fe_2Cl_6	K	66

The overall phase diagram can be described by describing these five parts of the phase diagram individually. We would describe one of these as a representative example. Initially we have pure water that freezes at 0 °C**.** On adding small amount of ferric chloride the freezing point of water decreases till -55°C where the crystals of $Fe_2Cl_6.12H_2O$ start separating out. This is the first eutectic point where ice, $Fe_2Cl_6.12H_2O$ and a saturated solution of ferric chloride coexist.



On adding more and more of ferric chloride we get a region in which solid $Fe_2Cl_6.12H_2O$ and the solution are in equilibrium at relatively higher temperature. This rising part (BC) of the curve gives the solubility curve of $Fe_2Cl_6.12H_2O$. At a temperature of 37 °C there is a maxima where the liquid and solid have identical composition. This is the congruent melting point of the dodecahydrate, $Fe_2Cl_6.12H_2O$. Similarly, you can analyse the other four eutectic sub systems.

4.6 SYSTEMS INVOLVING INCONGRUENT MELTING POINT

In many two-component systems the components are completely miscible in liquid phase and form compounds in the solid state however these compounds are not stable upto their melting points. Such compounds on heating, decompose to yield a new solid phase and a melt having composition different from that of the solid phase. In other words, such compounds do not melt congruently; these break into another solid and a melt before reaching their melting points. We say that the compound has an incongruent melting point and has undergone a transition, or **peritectic** (Greek *peri* around; *tecktos*, melting) **reaction**, or incongruent fusion. The peritectic reaction is a reversible reaction and can be represented as

$$S \rightleftharpoons S' + \text{liquid} \qquad \ldots(4.22)$$

Here, S is the compound showing peritectic reaction and S' is the new solid phase obtained which may itself be a new compound or the pure constituent. As you can note that there are three phases (S, S' and liquid) in equilibrium during the peritectic reaction which make the system invariant ($F' = 0$). Therefore, the temperature as well as the compositions of all the phases are

fixed. Once the peritectic reaction is complete the temperature or composition can change. The temperature at which the peritectic reaction occurs is called the **peritectic temperature**.

A number of systems are known to show formation of compound with incongruent melting point. We would take up one such system, namely sodium-potassium alloy that form an incongruently melting compound Na_2K.

4.6.1 Phase Diagram of Sodium-Potassium System

Sodium and potassium alloy system represents a common system showing formation of an incongruently melting compound. These two elements combine in the stoichiometric ratio of 2:1 to form the compound Na_2K. The compound is unstable and at 70 °C undergoes a peritectic reaction to give solid Na and a melt. A schematic phase diagram of the sodium-potassium alloy system is given in Fig. (4.11). The point P and S respectively are the melting points of pure potassium and pure sodium. Let us analyse the phase diagram of Na-K alloy system.

Region above PQRS

PQRS is the liquidus and the area above it represents the melt or liquid phase. As there is only one phase, the degree of freedom for the condensed system would be $F' = 3 - P = 3 - 1 = 2$. As the system is bivariant both the temperature and the composition can be varied in this region marked as liquid.

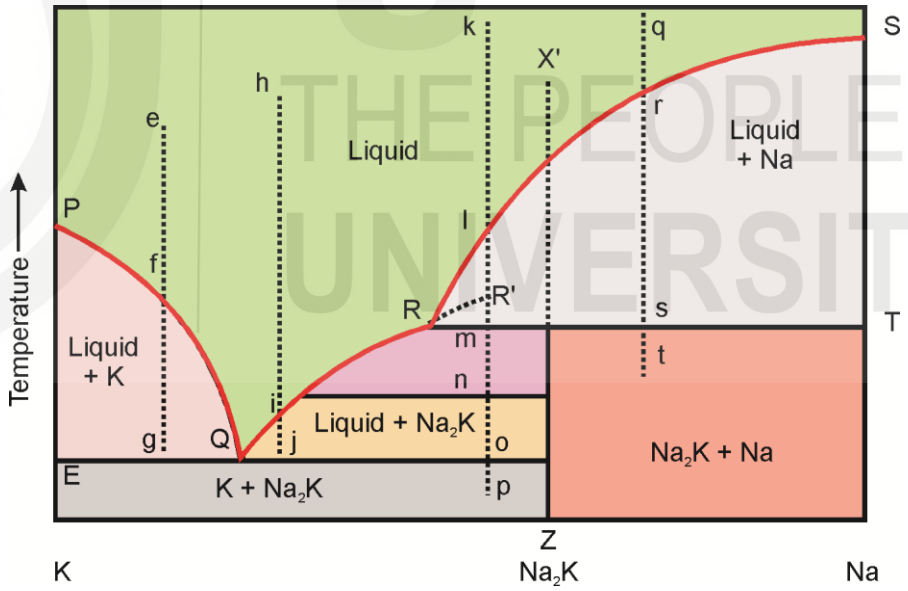


Fig. 4.11: A schematic phase diagram of sodium-pottasium alloy system.

Curves PQ and QR

The curve PQ represents the lowering of freezing point of potassium on addition of sodium. Along this curve solid potassium crystallises and the composition of the melt varies. At point Q the system has enough of sodium to allow the separation of the compound Na_2K. As there are three phases (solid K, solid Na_2K, and melt) in equilibrium at point Q, it is an eutectic point.

Further addition of sodium increases the freezing point of Na_2K along the curve QR. Here, Na_2K is in equilibrium with the liquid i.e., there are two phases

and the system is univariant. At R the compound Na_2K undergoes a peritectic reaction as given below.

$$Na_2K \rightleftharpoons Na + \text{liquid}. \quad \ldots(4.23)$$

As a consequence of the peritectic reaction the curve QR does not go to R′ which could be the melting point of Na_2K if it showed congruent melting.

Curves SR

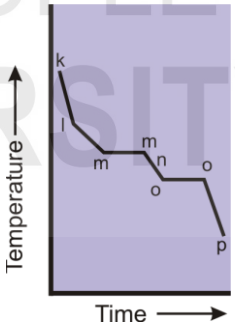
The curve, SR represents the fusion curve of Na, which shows the depression in freezing point of Na by the addition of K. The system is univariant here, Na is in equilibrium with liquid. The curve, SR does not reach a minimum between the composition of Na_2K (indicated as Z on the phase diagram) and pure Na as the rate of decrease in freezing point of Na is not steep enough. Therefore, the curve extends to point R where it meets the curve QR and peritectic reaction takes place.

Isopleths

The systems with composition 'e' and 'h' would show normal eutectic cooling curves with one break point and one halt. However the shape of the cooling curve for composition k would be somewhat complex due to peritectic reaction. In this case the crystals of sodium form at '*l*' and the cooling curve would show a break. The composition of liquid moves along *l*R. At m we get solid Na_2K due to peritectic reaction.

$$Na \rightleftharpoons Na_2K + \text{melt} \quad \ldots(4.24)$$

Here, three phases would be in equilibrium and the degrees of freedom would be zero. The temperature would remain constant and the cooling curve would show a halt (m-m). When the conversion of Na to Na_2K is complete the number of phases would reduce to two and the system becomes univariant. The temperature would start falling again and more and more of Na_2K separates out. The composition of the melt changes along the liquidus m-Q. At o, K would also start freezing out. The phases in equilibrium here are K, Na_2K and melt and the temperature would again become constant ($P = 3; F' = 0$). The cooling curve would show another halt (o-o). When the whole of the melt freezes, the cooling would begin again and the temperature drops (o-p).



If liquid of composition q is cooled, primary crystals of sodium form at r ; continued cooling crystallizes more sodium, the liquid composition moves along the curve rR. At s, the liquid of composition R forms solid Na_2K by the peritectic reaction. On further lowering the temperature all the sodium dissolves and is converted to Na_2K. Can you draw the cooling curve corresponding to these changes?

Answer the following simple questions to gauge your understanding of phase diagrams of two component systems showing compound formation.

SAQ 7

What are congruently and incongruently melting compounds?

SAQ 8

What is the difference between a eutectic point and a peritectic point?

4.7 SUMMARY

In this unit we have discussed about the application of phase rule in the understanding of different one-component and two-component systems. We started by discussing the general features of the phase diagram of a one-component system and took up analysis of the phase diagram of such systems. This was followed by a detailed account of two one-component systems viz., water and sulphur system. We highlighted the specific characteristics of these systems and explained them. For example, the negative slope of fusion curve of water, critical point, existence of metastable equilibria in water and sulphur systems etc.

In the context of the application of phase rule to two-component systems we highlighted the fact that the phase diagram for such systems would be three-dimensional solid figures that are difficult to plot and interpret. As a way out, we can reduce such systems to condensed systems by ignoring their gaseous phase and keeping the pressure constant. Under such conditions, for condensed systems the phase rule gets modified and the phase diagram is represented as a two-dimensional temperature-composition plot.

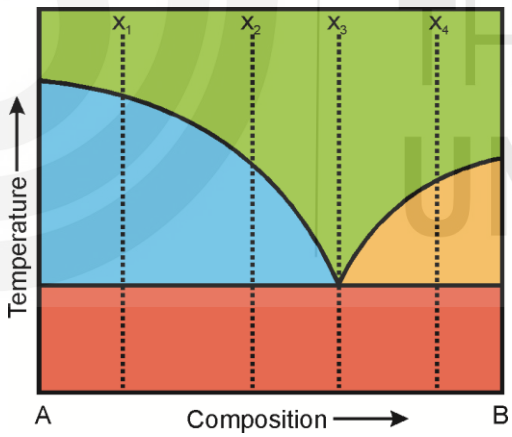
In order to understand the phase equilibria in solid-liquid systems we have taken the systems in which the components are miscible in solution or melt and are immiscible in solid state. We have taken up three different types of such systems. The first of these was ‘simple eutectic system’ wherein for a certain composition called eutectic composition the two solids crystallise from the melt simultaneously in a fixed ratio. The composition is called eutectic composition and the corresponding temperature is called eutectic temperature. An important industrial process called Pattinson's process uses the formation of eutectic mixture by lead and silver in the extraction of silver from argentiferrous lead –an alloy containing less than 0.1% silver.

After discussing the simple eutectic systems, we took up two component systems involving compound formation. The first such system discussed is the ferric chloride-water system that forms a number of stable compounds (hydrates). As these compounds are stable upto their melting point, these are called congruently melting compounds. The phase diagram of such systems can be visualised as made up of a number of simple eutectic systems. The number depends on the number of such compounds formed. The ferric chloride-water system consists of five eutectic sub-systems.

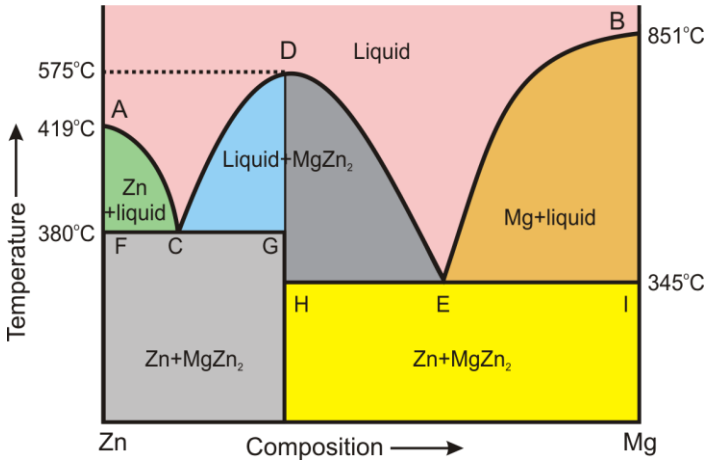
The last category of two-component systems considered is the one involving formation of compounds that are not stable till their melting points. Such compounds are called incongruently melting compounds and these decompose into a new solid and a solution having composition different from that of the compound. This reaction is called peritectic reaction and the temperature at which this happens is called peritectic temperature. We have discussed the phase diagram of sodium-potassium alloy system as an example of system involving formation of incongruently melting compound.

4.8 TERMINAL QUESTIONS

1. Can we have four phases in equilibrium for a one-component system? Justify your answer.
2. What is super critical fluid?
3. What is a condensed system? Write the phase rule equation for a condensed system.
4. What is a simple eutectic system? Give an industrial application of eutectic system.
5. Briefly explain the following terms in context of phase diagram of condensed two component systems.
   a) Isotherm
   b) Isopleth
   c) Tie line
   d) Lever rule
6. Antimony (melting point 631°C) and lead (melting point 327°C) form a simple eutectic system. The eutectic mixture having a composition 87 mass % of lead is obtained at 252°C. Draw a schematic phase diagram for the system and suitably label different regions.
7. A schematic phase diagram of a simple eutectic system is given below. Draw the cooling curves for the systems indicated by x_1, x_2, x_3 and x_4.



8. The phase diagram of Zn-Mg system is given below



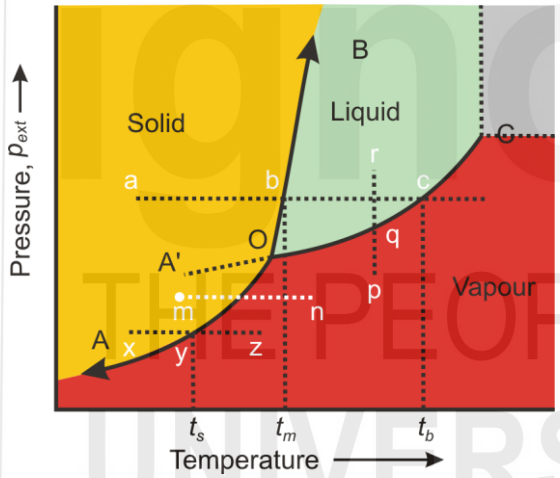
Use the diagram to complete the following table

Formula and the melting point of the compound formed	
Eutectic temperature and composition 1	
Eutectic temperature and composition 2	

4.9 ANSWERS

Self-Assessement Questions

1. The point 'm' in the diagram is located in the area indicating solid phase and has certain value of pressure and temperature. As we increase the temperature we move along the dotted white line parallel to the x-axis. At a certain temperature, where the dotted line meets the curve OA, the solid starts getting converted into vapour (i.e., it undergoes sublimation). The temperature is called sublimation temperature and here the system has two phases in equilibrium (it is univariant).



On further heating, more and more of the solid gets converted into vapour however the temperature does not change. Once all the solid has sublimed, further heating would cause the temperature of the gas to keep on increasing along the line mn.

2. A triple point in the phase diagram of a one-component system refers to a state of the system wherein three phases are in equilibrium. According to the phase rule

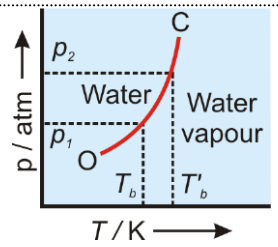
   $F = C + 2\text{-}P$

   If $C = 1$ and $P = 3$ the degrees of freedom would be

   $F = 1 + 2\text{-}3 = 0$

   The degrees of freedom would be zero; i.e., the system is invariant.

3. The boiling point of water increases with increase in pressure. The variation of vapour pressure of water as a function of temperature (i.e., the vapour pressure curve) representing water ⇌ water vapour equilibrium given below.



According to Clapeyron equation, the slope of the curve is given by

$$\frac{dp}{dT} = \frac{\Delta_{vap}H_m}{T\Delta_{vap}V_m}$$

As temperature is always positive the nature of slope of the curve would depend on the signs of $\Delta_{vap}H_m$ and $\Delta_{vap}V_m$. As both of these parameters are also positive the slope of the vapour pressure curve is positive

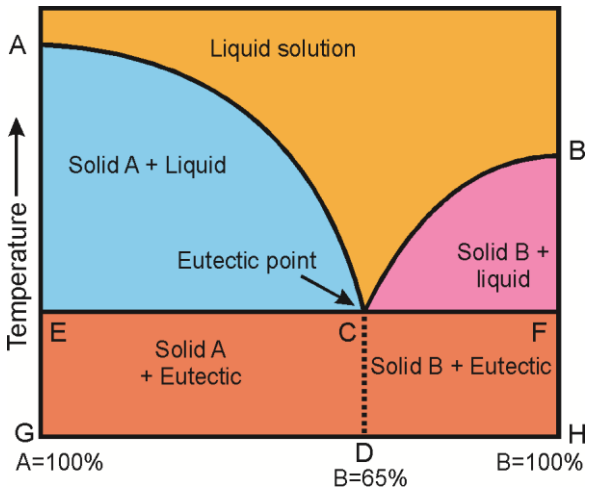
$$\frac{dp}{dT} = \frac{\Delta_{vap}H_m}{T\Delta_{vap}V_m} = \frac{+ve}{+ve \times +ve} = +ve$$

Therefore, the boiling point of water increases with pressure.

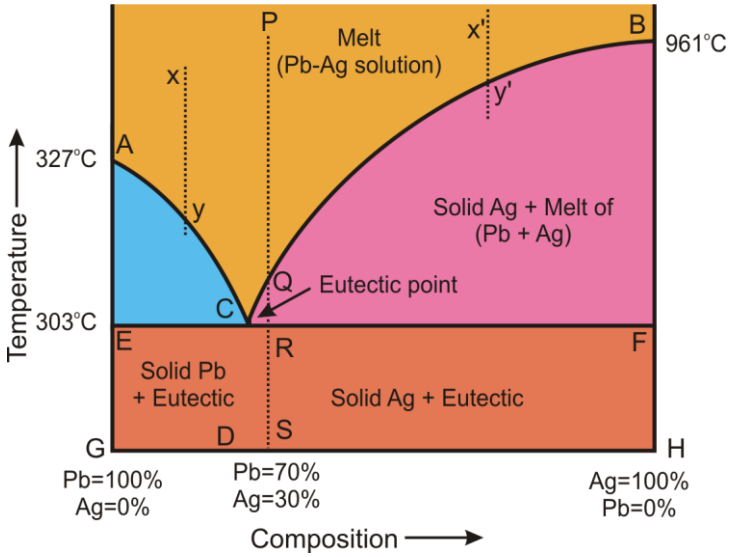
4. A metastable equilibrium is an unstable equilibrium that can be obtained only in one direction. This is contrary to the true equilibrium that can be achieved from both the forward as well as the backward directions. In case of sulphur system there are three different metastable equilibria. One of these equilibria can be obtained by rapidly heating rhombic sulphur beyond 95.5 °C without letting it get converted into monoclinic sulphur then rhombic sulphur remains in metastable state.

   Secondly, if we carefully cool the liquid sulphur below its freezing point to monoclinic sulphur we get super cooled liquid sulphur, which is also a metastable state. The third metastable equilibrium in sulphur system corresponds to the freezing of liquid sulphur into rhombic sulphur at pressures and temperatures below the triple point representing stable equilibrium between the two forms of sulphur and the liquid sulphur.

5. A schematic phase diagram of the system is given below.



6. The isopleth, PQRS corresponding to 30% silver is indicated on the phase diagram of lead-silver eutectic system.



As discussed in the text on cooling the melt of 30% silver composition (at point P) when we reach the point Q pure silver starts separating out and the composition of the melt starts changing along the curve QC. The melt gets richer and richer in lead. On reaching the point R i.e., when we reach eutectic temperature the mixture of lead and silver having eutectic composition also separates out and the pure silver that had so far separated out becomes contaminated.

Therefore, if we cool the given melt to a temperature just a bit higher than eutectic temperature then the system would have pure silver and a melt having fairly large amount of lead. At this point we don't let the melt cool any further and separate pure silver from the system.

7. In some two component systems the components react together and form compounds that can separate as a separate new solid phase. If the compound so formed is stable up to its melting point and melts to give a liquid having same composition as the compound, then it is said to be have congruent melting point. For example, formation of different hydrates in ferric chloride-water system. On the other hand if the compound is not stable upto its melting point and it decomposes to give a new solid and a liquid having different composition than that of the solid then it is said to be an incongruently melting compound. For example, the formation of incongruently melting compound Na_2K in sodium–potassium alloy system

8. In a two-component condensed system the eutectic point refers to the temperature where two solids simultaneously crystallise in a definite ratio. It is the minimum melting point in the eutectic system. On the other hand, a peritectic point is that temperature where an incongruently melting compound decomposes to give a new solid and a liquid having different composition than that of the compound. This temperature is closer to the melting point of the compound if it were stable.

Terminal Questions

1. No, we cannot have four phases in equilibrium for a one-component system. It is so because this will violate the phase rule. As we know that according to the phase rule

$F = C + 2 - P$

If $C = 1$ and $P = 4$ the degrees of freedom would be

$F = 1 + 2 - 4 = -1$

Since the degrees of freedom cannot be negative we cannot have four phases in equilibrium for a one-component system.

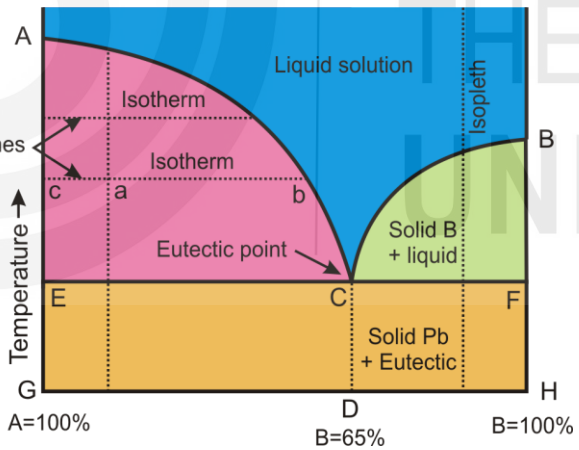
2. A substance at a temperature and pressure above its critical point is called a super critical fluid. In this phase there is no distinction between the liquid and vapour phase.

3. Heterogeneous equilibria in which the gas phase is absent are called condensed systems. Such equilibria are not affected by small changes in pressure. Solid-liquid equilibrium is an example of condensed systems. In dealing with such system the pressure is taken as constant. The phase rule equation gets modified to

$F' = C + 1 - P$

4. It is a two-component system containing two solids that are miscible in liquid phase but are immiscible in solid phase. At a certain composition called eutectic composition the mixture either melts or solidifies at a constant temperature which is lower than the melting point of any of the individual substances. The temperature is called eutectic temperature. Desilverisation of argentiferous lead by Pattinson's process is one of the important industrial applications of simple eutectic system.

5. The following figure shows the terms explained below



a) **Isopleth** refers to a line corresponding to a constant composition and runs parallel to the temperature axis in a temperature-composition phase diagram for two-component system. It can be used to know the phase changes that occur as the system having a particular composition is heated or cooled.

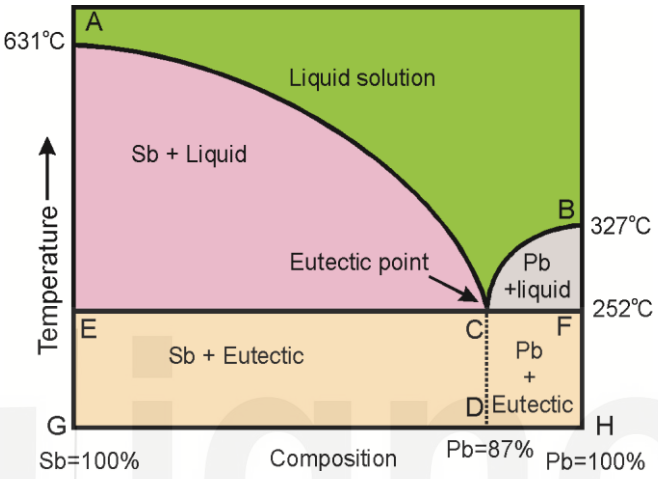
b) **Isotherm** is the horizontal line parallel to the composition axis on the temperature-composition phase diagram. It can be used to know the behaviour of the systems of different composition at a given temperature.

c) An isotherm in the region of the phase diagram and intersecting two curves depicting the two phases in equilibrium is called a **tie line**. The tie line provides information about the amounts of two phases present

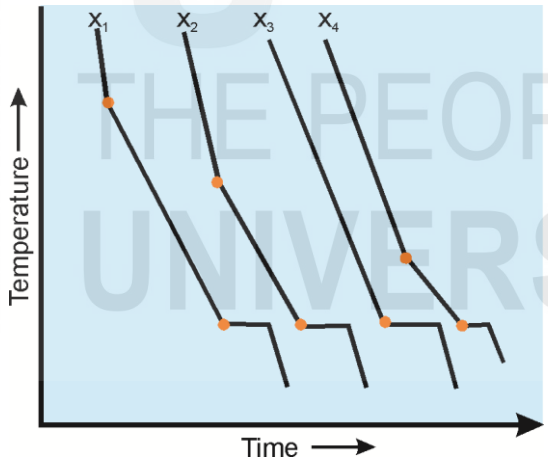
in equilibrium in the system at the point of interest and also the ratio of their amounts.

d) **Lever rule** is the principle behind the determination of the relative amounts of two phases present in the system. The rule is based on the material balance principle. For the tie line shown in the diagram the ratio of the number of moles of solution to the number of moles of solid A in the system is equal to the ratio of segments (ac/ab) of the tie line.

6. A suitably labeled schematic phase diagram for the system is given below.



7. The cooling curves corresponding to the systems indicated by x_1, x_2, x_3 and x_4 are given below.



8. The required data is as follows:

Formula and the melting point of the compound formed	$MgZn_2$; 590°C
Eutectic temperature and composition 1	380°C; Zn + $MgZn_2$
Eutectic temperature and composition 2	345°C; $MgZn_2$ + Mg