

145^o CPT

COLLIGATIVE PROPERTIES

Colligative properties are properties of solutions that depend on the ratio of the number of solute particles to the number of solvent molecules in a solution, i.e they depend upon the concentration of solute molecules or ions, but they do NOT depend upon the identity of the solute or the type of solute particles.

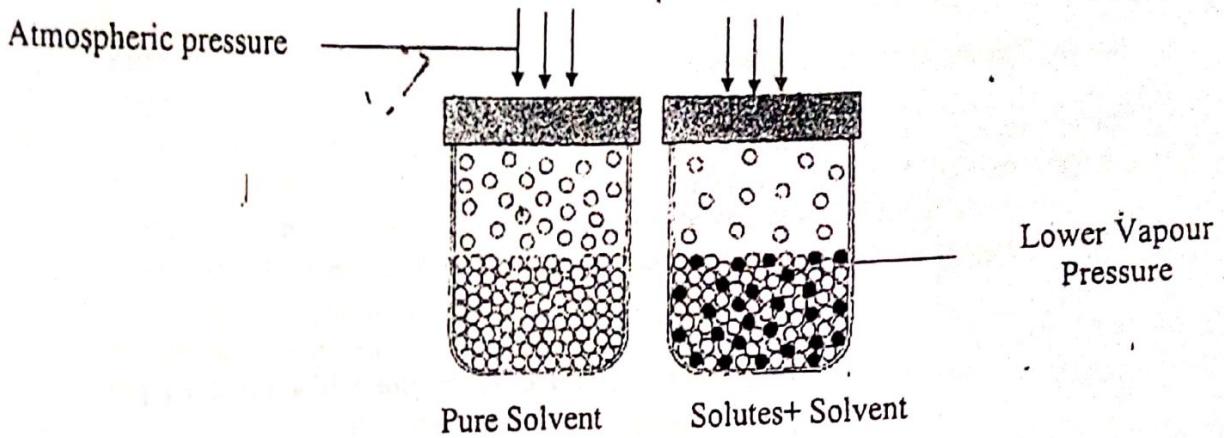
SOME COLLIGATIVE PROPERTIES

Dilute solution containing non-volatile solutes exhibit the following properties:

1. Vapour pressure lowering
2. Boiling point elevation
3. Freezing point depression
4. Osmotic pressure

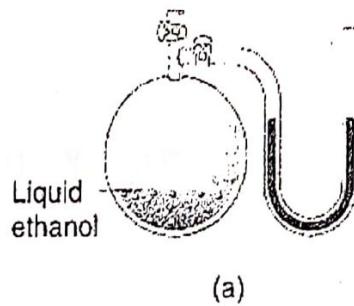
1. VAPOUR PRESSURE LOWERING

When a non-volatile solute was added to a volatile solvent it is observed that there is a decrease in vapour pressure of the solution. This decrease in vapour pressure can be quantitatively used to measure several properties of liquid solution. Thus, the vapour pressure of solution is lower than that of the pure liquid. More correctly, the vapour pressure of solution containing a non volatile (zero-Vapour Pressure) solute is lower than that of the pure solvent. So, if salt was dissolved into water, the vapour pressure of the solution (salt + water) is lower than that of pure water.



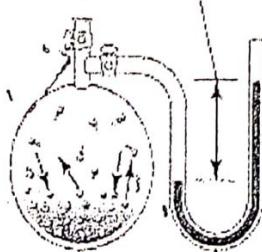
From the figure above there is a relative lowering of vapour pressure because fewer surfaces are available for solvent molecules to escape out. The vapour pressure of a solvent is lowered when a non-volatile solute is added into it. This is called "lowering of vapour pressure".

The French chemist Francoise – marie Raout's observed that the concentration of solute particles is mainly responsible for the lowering of vapour pressure and also discovered the relation between vapour pressure of solution, vapour pressure of pure solvent and mole fraction of solute and solvent. That is, the vapour pressure is directly proportional to the mole fraction of the solute.



(a)

$$P_{\text{gas}} = \text{Equilibrium vapor pressure}$$



(b)

From the figures above, the vapour pressure decrease as solute is added into pure solvent.

As a result of extensive experimentation results, Raoult (1886) gave an empirical relation connecting the relative lowering of vapour pressure and the concentration of the solute in solution. This is now referred to as Raoult's law. It states that: "The relative lowering of the vapour pressure of a dilute solution is equal to the mole fraction of the solute present in dilute solution"

Mathematical expression of Raoult's law:

For a solution with a solvent (A) and one non-volatile solute (B)

$$P_B = 0 \text{ and } P = P^o_A \times X_{\text{solvent}}$$

$$P_{\text{solution}} = X_{\text{solvent}} \times P^o_A \text{ solvent} \quad (1)$$

Where: P^o_A solvent is the vapour pressure of the pure solvent.

X_{solvent} is the mole fraction of the solvent.

Since this is a two-component system (solute and solvent), then

$$X_{\text{solvent}} + X_{\text{solute}} = 1 \quad (2)$$

Where: X_{solvent} is the mole fraction of the solvent

X_{solute} is the mole fraction of the solute

The change in vapour pressure (ΔP) can be expressed as

$$\Delta P = P^o_{\text{solvent}} - P_{\text{solution}}$$

$$\Delta P = P^o_{\text{solvent}} - X_{\text{solvent}} P^o_{\text{solvent}} \quad (3)$$

Or

$$\Delta P = (1 - X_{\text{solvent}}) P^o_{\text{solvent}}$$

By making X_{solute} the subject in equation (2),

$$\text{We have } \Delta P = X_{\text{solute}} P^o_{\text{solvent}} \quad (4)$$

Example 1:

- 1) Calculate the vapour pressure of a solution made by dissolving 50.0g glucose ($C_6H_{12}O_6$) in 500g of water. The vapour pressure of pure water is 47.1 torr at 37°C. (C=12, O=16, H=1).

Solution

Lets calculate the mole fraction of the solvent, which is water as follows

$$X_{\text{solvent}} = \frac{\text{Mole of solvent}}{\text{Mole solute} + \text{mole of solvent}}$$

$$\text{But } n_{\text{water}} = \frac{500\text{g}}{18\text{g/mol}} = 27.7\text{mol}$$

$$\text{And } n_{\text{Glucose}} = \frac{50\text{g}}{180.\text{g/mol}} = 0.277\text{mol}$$

$$X_{\text{solvent}} = \frac{27.7\text{mol}}{0.277\text{mol} + 27.7\text{mol}} = 0.99$$

The pressure of solution is then calculated via Raoult's equation

$$P_{\text{solution}} = 0.99 \times 47.1 = 46.63 \text{ torr}$$

Example 2:

The vapour pressure of an aqueous solution is found to be 24.90mmHg at 25°C. What is the mole fraction of solute in this solution? The vapour pressure of water is 25.756mmHg at 25°C.

Solution

Using Raoult's equation

$$P_{\text{solution}} = X_{\text{solvent}} P_{\text{solvent}}^0$$

$$24.90\text{mmHg} = (x) (25.756\text{mmHg})$$

$$X = 0.966765 \text{ (but this is the solvent mole fraction)}$$

To find the solute mole fraction:

$$X_{\text{solvent}} + X_{\text{solute}} = 1$$

$$\text{Therefore } X_{\text{solute}} = 1 - X_{\text{solvent}}$$

$$X_{\text{solute}} = 1 - 0.966765 = 0.033235$$

$$X_{\text{solute}} = 0.03324$$

Exercise

Calculate the vapour pressure lowering caused by the addition of 100g of sucrose (molar mass = 342) to 1000g of water if the vapour pressure of pure water at 25°C is 23.8mmHg.

2. BOILING POINT ELEVATION

When a liquid is heated, its vapour pressure rises and when it equals the atmospheric pressure, the liquid boils. The addition of a non-volatile solute lowers the vapour pressure and consequently elevates the boiling point as the solution has to be heated to a higher temperature to make its vapour pressure becomes equal to atmospheric pressure. Therefore on addition of non-volatile solute in a solvent, the vapour pressure of the solution decreases. However the boiling point of the solution is greater than that of the pure solvent, this is because vapour pressure is directly proportional to temperature. And in order to boil a solution, there is a need to raise the boiling point of the solution to a certain temperature. This rise in temperature is called elevation of boiling point, and just like the relative lowering of vapour pressure it also depends on solute particles in the solution.

Water boils at 100°C and 1atm of pressure, but a solution of salt water does not. When table salt is added to water the resulting solution has higher boiling point than the water. The ions form an attraction with the solvent particles that then prevent the water molecules from going into the gas phase. Therefore, the salt-water solution will not boil at 100°C, but above 100°C. This is true for any solute added to a solvent. The more solute dissolved, the greater the effect. An equation has been developed for this behavior:

$$\Delta T_b = i k_b M$$

The above equation is derived mathematically: if T_b^0 is the boiling point of pure solvent and T_b denotes boiling point of the solution, then elevation in boiling point (Denoted by ΔT_b) is

$$\Delta T_b = T_b - T_b^0$$

Experimentally it has been found that elevation in boiling point in dilute solution is directly proportional to molality 'M' of solute present in a solution.

$$\Delta T_b \propto M$$

$$\Delta T_b = K_b M$$

If T_b^0 is the boiling point of pure solvent and T_b is boiling point of the solution, then elevation in boiling point is given by

$$\Delta T_b = T_b - T_b^0$$

Experimentally, it has been found that elevation in boiling point in dilute solutions is directly proportional to molality 'm' of solute present in solution. The term molality 'M' denotes the number of moles of solute present in 1000g or 1kg of solvent. The standard unit of molality or molal elevation constant K_b is Kkg/mol. Let m_1 and m_2 be the given masses of solvent and solute respectively. And molar masses of solute by N_2 and that of solvent is N_1 , then molality can be evaluated from the relation

$$M = \frac{\frac{m_2}{N_2}}{\frac{m_1}{1000g}} = \frac{1000 \times m_2}{N_2 \times m_1}$$

Putting the value of molality in the boiling point elevation relation, we get,

$$\Delta T_b = \frac{K_b \times 1000 \times m_2}{N_2 \times m_1}$$

Example:

- The boiling point of a pure liquid is 353.23k, if 2.70g of a non-volatile solute was added in 90g of liquid, the boiling of the solution rises to 354.11k. what will be the molar mass of non-volatile solute? Take the value of K_b of liquid to be 2.53Kkg/mol.

Solution

$$T_b^0 = 353.23k$$

$$T_b = 354.11k$$

$$m_2 = 2.70g$$

$$K_b = 2.53\text{Kkg/mol}$$

$$m_1 = 90g$$

The elevation in boiling point

$$\begin{aligned}\Delta T_b &= T_b - T_b^0 \\ &= 354.11k - 353.23k = 0.88\end{aligned}$$

Using the above relation

$$\begin{aligned}\Delta T_b &= \frac{K_b \times 1000 \times m_2}{N_2 \times m_1} \\ 0.88 &= \frac{2.53 \times 1000 \times 2.70}{N_2 \times 90}\end{aligned}$$

Ans $N_2 = 86.25g$, hence molar mass of solute is 86.25g

2. Acetone boils at 56.38°C and a solution of 1.41g of an organic solid in 20g of an Acetone boils at 56.88°C . If K_b for acetone is 16.7, calculate the mass of one mole of the organic solid.

3) DEPRESSION OF FREEZING POINT:

When the vapour pressure of a solution is reduced, the freezing of the solution decreases. The freezing point of a solution is defined as the temperature at which vapour pressure of its substance become equal in liquid and vapour phase. If the vapour pressure of the solution equals to vapour pressure of the pure solvent, Then the solution will be frozen.

According to Raoult's law when non-volatile solute is added to a solvent, the freezing point of a solution is slightly less than that of the pure solvent. This is called depression of freezing point.

The freezing point of depression is denoted by

$$\Delta T_f = T_f^0 - T_f$$

The freezing point depression of dilute solution is directly proportional to molality of the solute just like the boiling point elevation, that is

$$\Delta T_f \propto M$$

$$\Delta T_f = K_f M$$

The proportionality constant K_f is called molal depression constant and is also known as cryoscopic which depends constant upon the nature of the solvent.

$$\text{Molality } M = \frac{1000 \times m_2}{N_2 \times m_1}$$

Putting the value of molality in above equation we get depression in freezing point as

$$\Delta T_f = K_f M$$

$$\Delta T_f = \frac{K_f \times 1000 \times m_2}{N_2 \times m_1}$$

Further investigation was made by Raoult's using non-aqueous solvents and H_2O . These results confirmed that various solutions of molar concentration produce the same depression in any particular solvent. The depression of freezing point produced when one mole of any solute is dissolved in 1000g (1kg) of a given solvent is known as the molecular depression constant or the cryoscopic constant (K). The depression of freezing point has been found to be depended upon the nature of the solvent's and on the concentration of the solvent particles.

Therefore, the lowering of the freezing point in dilutes solution has been found to be proportional to the solutes or molal concentration i.e

$$\Delta T \propto M \text{ where } M = \text{molal concentration or molality}$$

$$\Delta T = K \cdot M \text{ ----- (1)}$$

And molality is the mole of the solute present in 1kg or 1000g of the solvent

$$\Delta T = K \times \frac{m_1}{M} \text{ where } m_1 = \text{mass of solute}$$

M = molar mass of the solute in 1kg of solvent.

Example:

1. A solution of concentrated sugar containing 2.50g in 100g of water begins to freeze at -0.1350°C. Given that the cryoscopic constant of H₂O (1Kg) is 1.86, calculate the molar mass of the concentrated sugar

Solution

Using $\Delta T = K \times \frac{m_1}{M}$

$$m_1 = 2.5$$

$$K = 1.86$$

$$\Delta T = 0.1350^\circ\text{C} (-ve is ignored)$$

100g of H₂O = mass of solvent and

$$1000g \longrightarrow 1\text{kg}$$

$$100g \longrightarrow X\text{kg}$$

$$X\text{kg} = \frac{100}{1000} = 0.1\text{kg}$$

$$1000$$

$$100g = 0.1\text{kg}$$

$$0.10\text{kg of H}_2\text{O} = \frac{m_1}{M} \quad (\text{since molality is mole of solute present in 1kg of solvent})$$

From definition of molality

$$1\text{kg of H}_2\text{O} = \frac{2.5}{M} \div 0.10\text{kg}$$

$$= \frac{2.5}{M} \times \frac{1}{0.10g}$$

$$\text{Molality} = \frac{2.5}{0.10M}$$

From the formulae

$$0.135 \times 0.10 \times M = 1.86 \times 2.50$$

$$M = \frac{1.86 \times 2.50}{0.135 \times 0.10}$$

$$M = 344.44 \text{ g/mol.}$$

2. 0.440g of substance dissolved in 22.2g of benzene lowered the freezing point of benzene by 0.567°C . calculate the molecular mass of the substance.
($k_f = 5.12^{\circ}\text{C mol}^{-1}$)

4) OSMOSIS AND OSMOTIC PRESSURE

Let us consider a pure solvent and solution separated by a membrane which permit the passage to solvent molecules but to solute molecules. Only the solvent will diffuse through the membrane into solution. A membrane which is permeable to solvent and not to solute, is called a semi-permeable membrane.

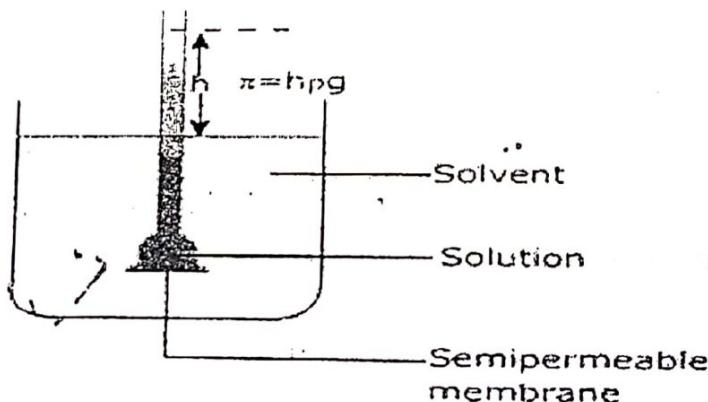


Fig (3) is the illustration of the process of osmosis. The solvent molecules can pass through the membrane from either side of the semi-permeable membrane. There is a net flow of solvent from the dilute solution to the concentrated solution. It shows up in the rise of level in the concentrated solution compartment.

If a solution is separated from its pure solvent by a semi-permeable membrane, then a net flow of solvents take place into the solution. This phenomenon is what is referred to as osmosis, by definition, osmosis is referred to as the movement of solvent molecules from region of lower concentration to higher concentration through a semi-permeable membrane.

A semi-permeable membrane is one that allows the passage of solvent molecules through it, but not the passage of solute.

Osmotic pressure, this is best defined as the pressure that is needed to prevent osmosis from taking place. "for example, a given solution standing

$$\pi \propto C \quad \dots \dots \dots (1)$$

The above equation is derived from the laws of osmosis.

- 1) Which says that at a constant temperature, the osmotic pressure of a solution is proportional to the concentration of the solute molecules.
- 2) States that; the osmotic pressure of a solution is proportional to its absolute temperature.

Mathematically:

$$\pi \propto T(K) \quad \dots \dots \dots (2)$$

The above two laws can be summarized as follows:

1. $\pi \propto C$ $\dots \dots \dots (1)$
2. $\pi \propto T(K)$ $\dots \dots \dots (2)$

Combining equation (1) and (2) we have

$$\pi \propto CT(K)$$

Where π = osmotic pressure of solution in Nm^{-2}

T = Kelvin or absolute temperature

C = concentration of solute in $mol m^{-3}$ of the solution

$$\pi \propto \frac{n_2 T(K)}{V}$$

$$\pi = R \frac{n_2 T(K)}{V} \quad \dots \dots \dots (3)$$

Where R is the molar or universal gas constant ,which is equals to $8.314 J K^{-1} mol^{-1}$

But $1J = 1Nm$

NB: R is also $= 8.314 \text{ NmK}^{-1}\text{mol}^{-1}$

$$\pi v = \frac{m}{M} RT \quad \dots \quad (4)$$

Where m is the mass of solute and M is the molar mass (g/mol) of the solute.

$$\pi = \frac{m}{v} \times \frac{RT}{M}$$

$$\pi = \frac{CRT}{M} \quad \dots \quad (5)$$

Reciprocal of M as subject, we have

$$\frac{1}{M} = \frac{\pi}{CRT}$$

Example:

- Calculate the molar mass of an unknown compound (solute), if its solutions contains 75 gdm^{-3} and they carries pending osmotic pressure is $4.85 \times 10^5 \text{ NM}^{-2}$ at 10°C .

Solution

Using the ideal equation of solution

$$\frac{1}{M} = \frac{\pi}{CRT}$$

$$M = \frac{CRT}{\pi}$$

$$\pi = 4.85 \times 10^5 \text{ NM}^{-2}, R = 8.314 \text{ Jk}^{-1}\text{mol}^{-1},$$

$$T = 283 \text{ K}, C = 75 \text{ gdm}^{-3} \neq 75 \times 10^3 \text{ gm}^{-3}, M = ?$$

$$\text{Therefore } M = \frac{75 \times 10^3 \times 8.314 \text{ NmK}^{-1}\text{mol}^{-1} \times 283 \text{ K}}{4.85 \times 10^5 \text{ Nmm}^{-2}} = 363.8 \text{ gmol}^{-1}$$

Therefore molar mass = 364 g/mol

DETERMINATION OF MOLECULAR WEIGHT OR MOLAR MASS.

Relative molecular mass: molecules also have mass since they consist of atoms called molecular mass, and it is expressed in terms of C-12.

The relative molecular mass (R.M.M) of a molecule is the number of times the average mass of one molecule is heavier than one-twelfth the mass of an atom of C-12.

Thus, relative molecular mass: the sum of R.A.M of the individual atoms present in one molecule of a given substance (compound).

Example:

1. Calculate the relative molecular mass of CaCO_3 given that Ca = 40, C = 12, O = 16.

Solution

Recall that, one molecule of CaCO_3 consists of 1Ca, 1C, and 3O atoms hence,

$$\text{R.M.M} = (1 \times \text{R.A.M of Ca}) + (1 \times \text{R.A.M of C}) + (3 \times \text{R.A.M of O})$$

$$\text{R.M.M} = [(1 \times 40) + (1 \times 12) + (3 \times 16)]$$

$$= 40 + 12 + 48 = 100\text{g}$$

Therefore R.M.M of CaCO_3 = 100g

But, the molecular weights of polymers (macromolecular compounds) can be determined by chemical or physical methods.

The chemical method includes functional group analysis (end-group assay) while the physical methods include:

Colligative properties, light scattering, ultracentrifugation and dilute-solution viscosity.

The methods used to determine the molar mass M are either relative or absolute. Relative method requires calibration with samples of known M and include viscosity and vapour pressure osmometry. The absolute methods are often classified by the types of averages they yield, for example colligative techniques yield M_n (number averages) light scattering and ultracentrifuge yield higher averages M_w (weight averages).

Assignment

Briefly explain the physical and chemical methods of determining the molecular weight/molar mass of high molecular compounds, with examples.

CHARACTERISTICS OF THE SOLID STATE

Gases and liquids can flow and take up the shape of their container. Solids, on the other hand have a definite volume and shape. They are rigid and lack the ability to flow.

In both gases and liquids, atoms, ions and molecules continually move. They translate randomly as well as rotate and vibrate. This determines the ability of gases and liquids to flow. In solids, atoms, ions and molecules are held together by relatively strong chemical forces : ionic bond, covalent bond, or by intermolecular vander waals forces. They do not translate although they vibrate to some extent in their fixed positions. The solid are characterized by incompressibility rigidity and mechanical strength. The molecules, atoms and ions in solids are closely packed, i.e they are held together by strong forces and they can not move about at random. Thus, solid have definite volume, shape, slow diffusion, low vapour pressure and posses the unique property of being rigid, such solid are known as true solid. E.g NaCl, KCl, sugar, Ag, Cu, e.t.c

On the other hand, the solid which loses shape on long standing, flows under its own weight and is easily distorted by even mild distortion force is called pseudo solid e.g glass, pith e.t.c

Some solid such as a NaCl, Sugar, sulphur e.t.c have properties not only of rigidity and imcompressibility but also of having typical geometrical forms. These solids are called crystalline solids. In such solids there is definite arrangement of particles (atoms, ions or molecules) throughout the entire three dimensional network of a crystal. This is named as long-range order

This three dimensional arrangement is called crystal lattice or space lattice. Other solid such as glass, rubber, plastics e.t.c which have rigidity and incompressibility to a certain extent but they do not have definite geometrical forms or do not have long-range order are known as amorphous solid.

TYPES OF SOLIDS

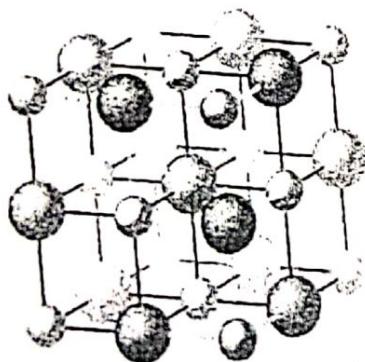
Solids are of two types

- a. Cysatalline solid
- b. Amorphous solid
- a. A crystalline solid exists as small crystals, each crystal having a characteristic geometrical shape. In a crystal, the atoms, molecules or ions are arrange in a regular, repeating three-dimensional pattern called the crystal lattice. Sugar, and salt are crystalline solids.
- b. An amorphous solid has atoms, molecules or ions arranged at random and lacks the order crystalline lattice. Examples are rubber, plastics and glass.

LATTICE STRUCTURE

- Crystals: are types of a solid material composed of atom or group of atoms that are arrange in a three-dimensional pattern that is very ordered. In a crystal, the groups of atoms are repetitive at evenly spaced intervals, all maintaining their orientation to one another. In other words, the geometric shape of a crystal is highly symmetrical:
- A crystal lattice: is the arrangement of these atoms, or groups of atoms, in a crystal. These atoms or groups of atoms are commonly referred to as points within a crystal lattice site. These point simply points "in space" oriented in such a way to build a lattice structure.

CRYSTAL LATTICE STRUCTURE



Example of a crystal lattice structure

The pattern of arrangement of each point as well as their symmetry of the crystal lattice structure sites are only viewed microscopically and are invisible to the naked eye. In order to view these structures, it has to be placed under a microscope.

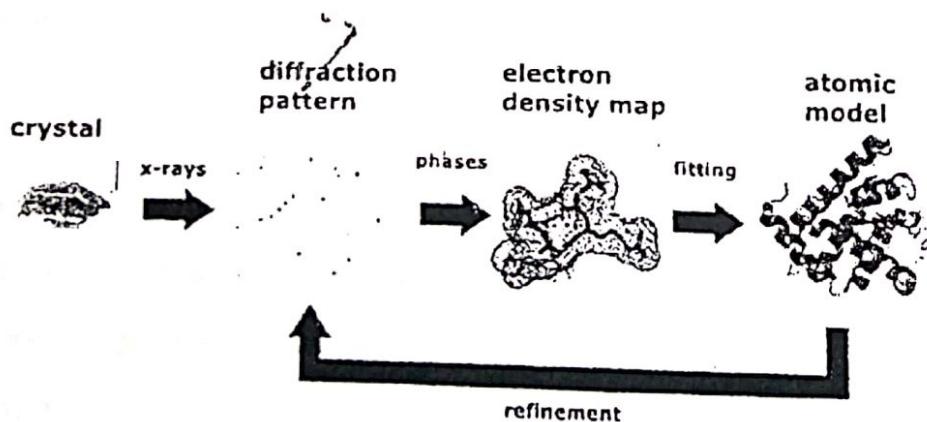
A crystal lattice is the arrangement of atoms in a crystal (the black and white points in the example above are atoms). This arrangement can be defined as the intersection of these parallel planes.

X-RAY DIFFRACTION

x-ray crystallography: is a technique used for determining the atomic and molecular structure of a crystal, in which the crystalline atoms cause a beam of incident x-rays to diffract into many specific directions. By measuring the angles and intensities of these diffracted beams, a crystallographer can produce a three-dimensional picture of the density of electrons within the crystals. From this electron density, the mean positions of the atoms in the crystal can be determined as well as their chemical bonds, their disorder, and various other information.

A crystal lattice is considered to be made up of regular layers or planes of atoms equal distance apart. Since the wavelength of x-rays is comparable to the interatomic distances, crystal can act as grating to x-rays. Thus, when a beam of x-rays is allowed to fall on a crystal, a large number of images of different intensities are formed. If the diffracted waves are in the same phase, they reinforce each other and a series of bright spots are produced on a photographic plate placed in their path. On the other hand, if the diffracted waves are out of phase, dark spots are caused on the photographic plate. The study of crystal structure with the help of x-ray diffraction is called x-ray crystallography

Lecture 53: X-ray crystallography



ISOMORPHISM

Isomorphism is an identity or close similarity in the crystalline form of substances usually containing different element but having similar composition. Such substances are called isomorphs or isomorphous to each other.

CHARACTERISTICS OF ISOMORPHOUS SUBSTANCES

- The crystal of isomorphous substances have the same shape.
- If crystal of one substance are suspended in a saturated solution of another, the former continues to grow as latter is deposited all over it. Thus, they form overgrowth on each other
- They can form a mixed crystal with each other

Examples:

- Ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and magnesium sulphate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$),
- Potassium perchlorate (KClO_4) and potassium permanganate (KMnO_4)

GIANT MOLECULE

A covalently bonded substance containing a huge number of atoms is called a giant molecule or a giant covalent lattice.

The giant covalent structures contain a lot of non-metal atoms, each joined to adjacent atoms by covalent bonds. The atoms are usually arranged into giant lattice, extremely strong structures because of the many bonds involved. There are four examples of molecules (made from non-metals) which form giant structure. They are:

Silicon, silicon dioxide and two forms of the element carbon called diamond and graphite.

Carbon and silicon are both in group 4 of the periodic table. They both need to form 4 bonds with themselves or other elements they have valency of 4.

When two or more forms of an element exist in the same physical state, they are called allotropes. Diamond and graphite are allotropes of carbon.

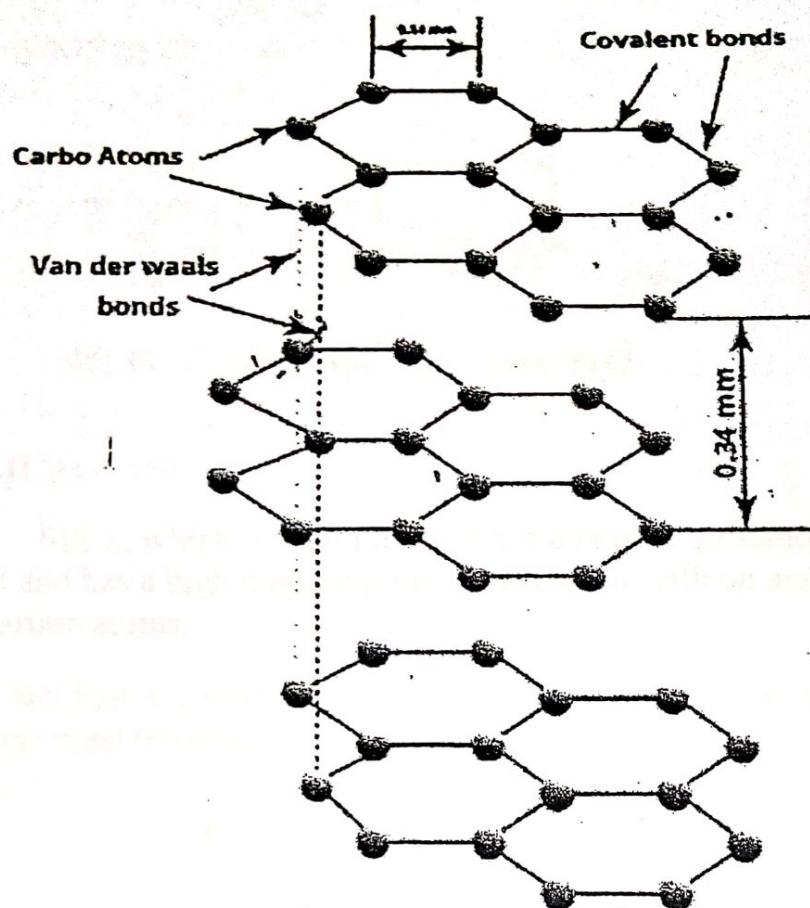
PROPERTIES OF GIANT STRUCTURE

- Very high melting points: substances with giant covalent structures have very high melting point because a lot of strong covalent bonds must be broken. Graphite for example has a melting point of more than $3,600^{\circ}\text{C}$.
- Variable conductivity: diamond does not conduct electricity. Graphite contains free electrons, so it does conduct electricity. Silicon is semi-conductor. That is, midway between non-conductive and conductive.

GRAPHITE:

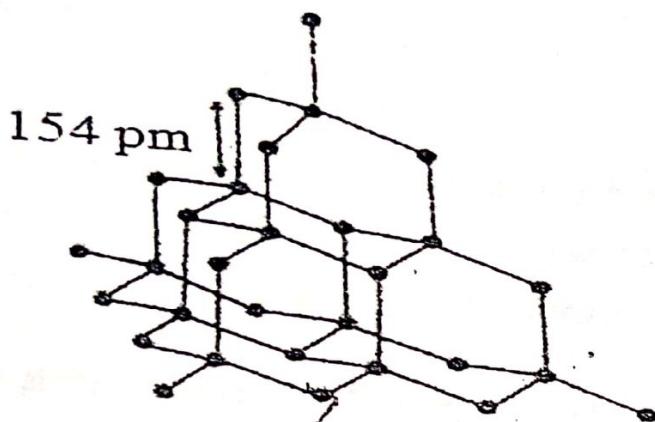
Graphite is a form of carbon in which the carbon atoms form layers. These layers can slide over each other, so graphite is much softer than diamond, it is used in pencils and as a lubricant. Each carbon atom in a layer is joined to only three other carbon atoms. Graphite conducts electricity.

Graphite Structure



DIAMOND:

Diamond is a form of carbon in which each carbon atom is joined to four other carbon atoms, forming a giant covalent structure. As a result, diamond is very hard and has a high melting point. It does not conduct electricity.

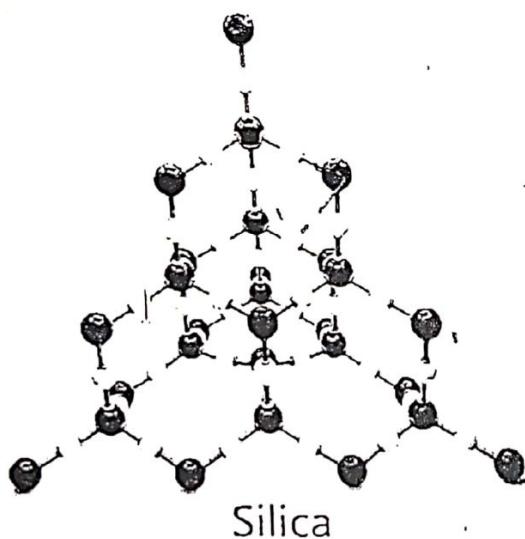


Structure of diamond

SILICA:

Silica, which is found in sand has a similar structure to diamond. It is also hard and has a high melting point, but contains silicon and oxygen atoms, instead of carbon atoms.

The fact that it is a semi-conductor makes it immensely useful in the electronics industry: most transistors are made of silica's.



PHASE EQUILIBRA

Phase: a phase is a form of matter that is homogenous in chemical composition and physical state. It refers to any part of a system which is physically separated from other part of the system by a distinct boundary.

A phase can be a solid, liquid, vapour (gas) or aqueous solution which is uniform in both chemical constitution and physical state. Two immiscible liquid (or liquid mixtures with different composition) separated by a distinct boundary are counted as two different phase as are two immiscible solids.

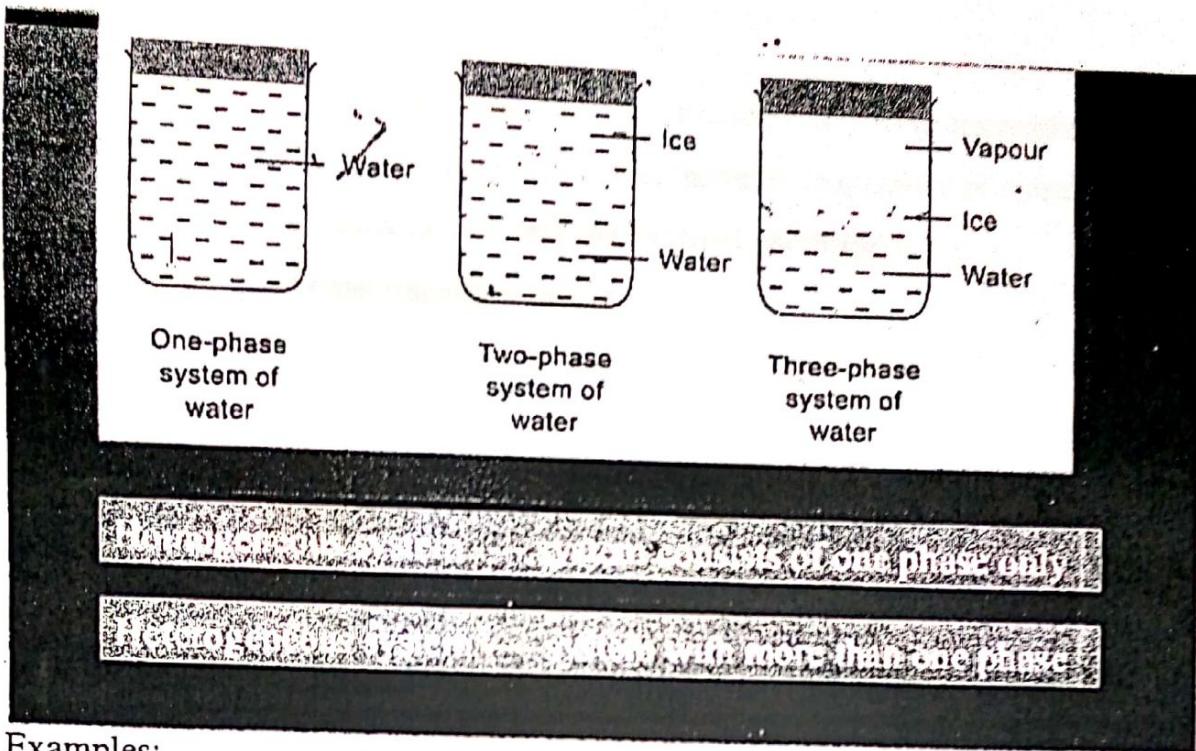
- A phase may be gas, liquid or solid
- A gas or a gaseous mixture is a single phase
- In an immiscible liquid system, each layer is counted as a separate phase
- Every solid constitutes as a single phase except when a solid solution is formed.
- A solid solution is considered as a single phase
- Each polymorphic form constitutes as a separate phase.

Therefore, The number of phase does not depend on the actual quantities of the phase present. It also does not depend on the state of subdivision of phase.

PHASE OF DIFFERENT SYSTEMS

S/No	System	Examples	Number of phase
1.	Mixture of gases	Air (mixture of N ₂ , O ₂ , CO ₂)	1 gaseous phase
2.	Mixture of two miscible liquids	Ethanol and water	1 liquid phase
3.	Mixture of two immiscible liquid	Oil and water	2 liquid phases
4.	Mixture of two solids	Salt and sand	2 solid phase
5.	Mixture of a solid and liquid	Ice and water	1 solid phase and 1 liquid phase
6.	Mixture of a solid, liquid and gas	Ice, water and vapour	1 solid, 1 liquid and 1 gaseous phase
7.	Mixture of 2 solids and a gas	CaCO ₃ , CaO and CO ₂	2 solid phases and 1 gaseous phase

A system with more than one phase is described as a heterogenous system, while a homogeneous system consists of one phase only.



Examples:

Containing the number of phases.

- Liquid water, pieces of ice and water vapour are present together. The number of phase is 3 as each form is a separate phase. Ice in the system is a single phase even if it is present as a number of pieces.
- Calcium carbonate undergoes thermal decomposition. The chemical reaction is;



Number of phase = 3

This system constitute of 2 solid phase, CaCO_3 and CaO and are gaseous phase, that of CO_2

- Ammonium chloride undergoes thermal decomposition the chemical reaction is:



Number of phase = 2

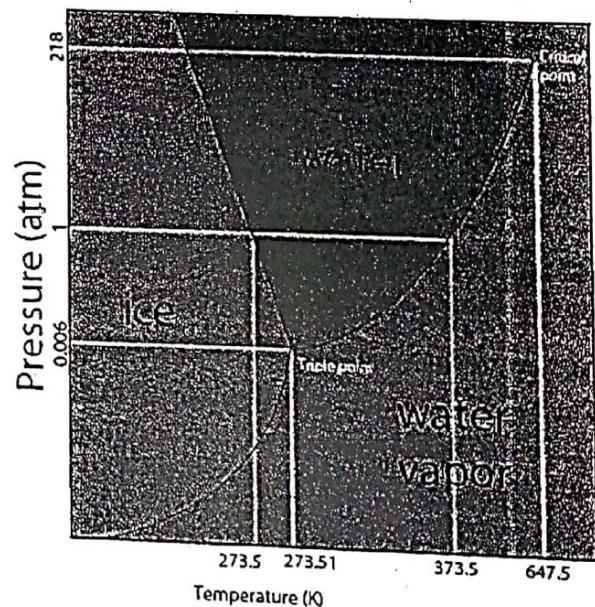
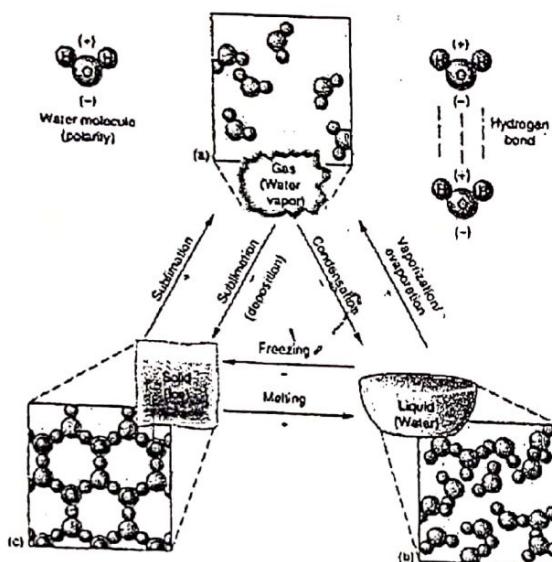
This system has two phases, one solid, NH_4Cl and one gaseous, a mixture of NH_3 and HCl

- d. A solution of NaCl in water
Number of phase = 1

PHASE EQUILIBRIUM

This is a balance between phases that is the co-existence of two or more phases in a state of dynamic equilibrium. In other words, the relative quantity or composition of each phase remains unchanged unless the external condition is altered.

Examples of a phase transition below:



<http://www.sci.uidaho.edu/scrinter/geo1001/>

A phase transition occurs when the external condition is altered.

Phase equilibrium are classified according to the number of components present in a system

COMPONENTS:

The number of components of a system at equilibrium is a smallest number of independently varying chemical constituents using which the composition of each and every phase in the system can be expressed, OR A component is a chemical species which may be used to specify the composition of a system. A system may have one or more components. It should be noted that the term 'constituents' is different from "components" which has a special definition. When no reaction is taking place in the system, the number of components is the same as the number of components is the same as the number of constituents. For example, pure water is a one component system because all the different phase can be expressed in terms of the single constituent water.

PHASES AND COMPONENTS OF DIFFERENCES

s/no	Example	Phase	Number of components	Components
1	An ice block	A solid phase only	One	water
2	A bottle of perfume	Liquid and vapour phase(a small amount of perfume vapour over liquid per)	One	perfume
3	A small amount	Solid and liquid phases(A small	Two	

Phase Rule: when a heterogeneous system in equilibrium at a definite temperature and pressure, the number of degrees of freedom is equal to by 2 the difference in the number of components and the number of phases provided the equilibrium is not influenced by external factors such as gravity, electricity or magnetic forces surface tension e.t.c

Mathematically, the rule is written as

$$F=C-P+2$$

Where:

F= number of degrees of freedom

C= number of component

P= number of phases of the system

For understanding the various applications of phase rule a clear understanding of the various terms: phase (P), components(C) and degrees of freedom (F) present in the phase rule

NOTE: phase(P) and components(C) explained above:

Degrees of Freedom:

The smallest number of independently variable factors such as temperature, pressure and concentration which must be required in order to define the system completely are called the degree of freedom. Degree of freedom of a system is also known as variance.

- When a system having no degree of freedom

$F=0$ it is called non-variant system or invariant system

- When a system having only one degree of freedom,

$F=1$ it is called invariant or monovariant

- A system having two degree of freedom

$F=2$ is a Bavarian system e.t.c.

Example

- a. The system ice water vapour has no degree of freedom (i.e $F = 0$). Because the three phases of water i.e ice, liquid water and vapour can exist together in equilibrium only at a particular temperature and pressure (corresponding to the freezing point) and no factor is necessary to be specified to define the system. Hence, a system consisting of ice, water and vapour in equilibrium has no degree of freedom i.e is a non-varient or invariant system.

Ice_(s) water_(l) vapour_(g)

Number of phase = 3

Number of component = 1

$$F = C - P + 2$$

$$F = 1 - 3 = 2$$

$$F = -2 + 2 = 0$$

Degree of freedom $F = 0$

2. Calculate the degree of freedom F of the following equation at equilibrium.



Solution

There are also three different chemical constituents, but the number of components is only two because any two constituents completely define the system in equilibrium. Any third constituent may be determined if the concentration of the other two is known.

Number of phases (P) = 3

Number of component (C) = 2

$$F = C - P + 2$$

$$F = 2 - 3 + 2 = 1$$

Therefore, only one variable, either temperature or pressure, can be changed independently. (the number of components is not always easy to determine at first glance, and it may require careful examination of the physical conditions of the system at equilibrium).

PHASE DIAGRAM FOR ONE COMPONENT SYSTEM

The least number of phases possible in any system is one. So, according to the phase rule equation, a one-component system should have a maximum of two degrees of freedom.

Where $C = 1, P = 1$

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

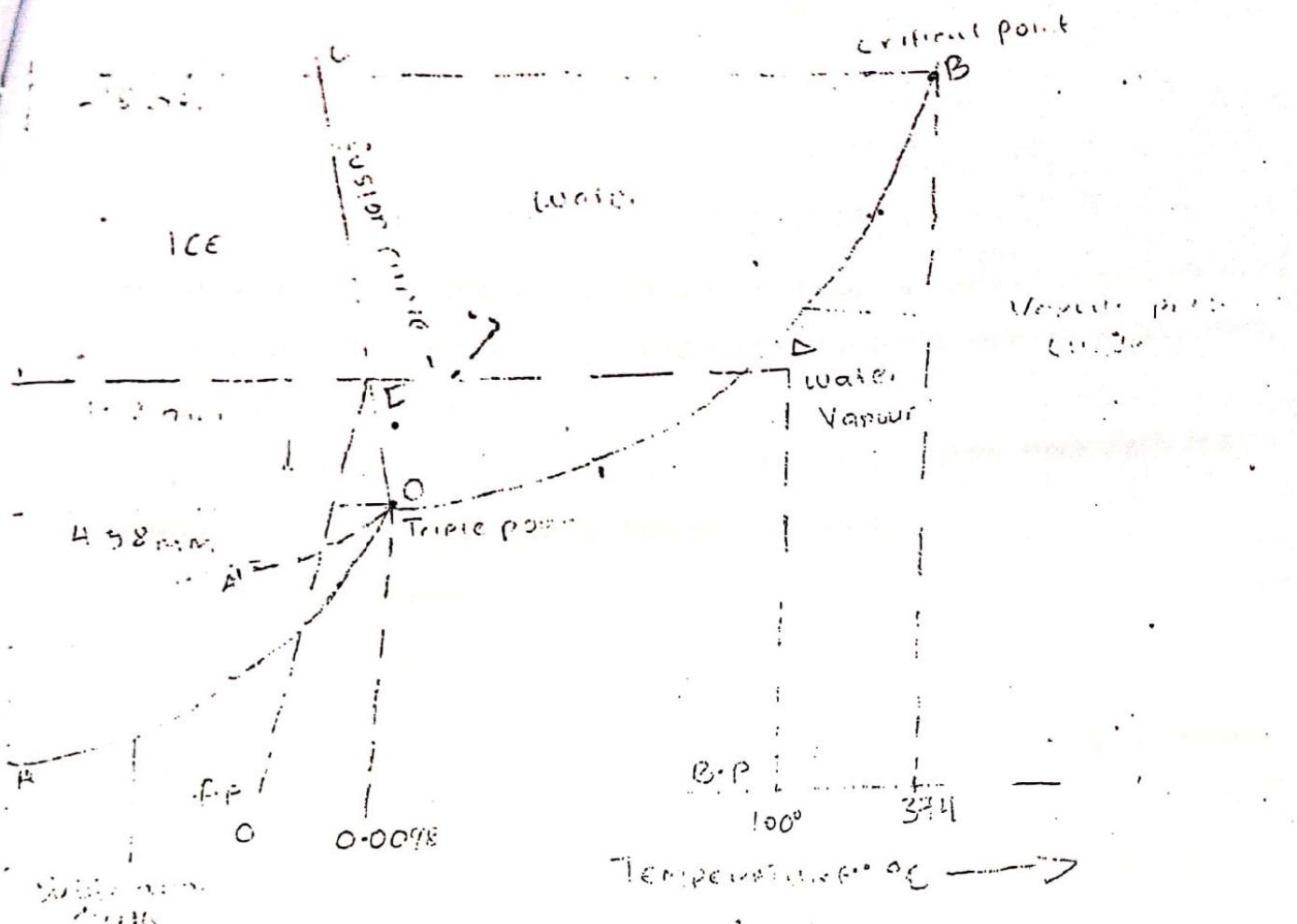
Hence a one-component system requires a maximum of two variables are temperature and pressure. Therefore the phase diagram for one component system can be obtained by plotting PVST.

A phase diagram is a graph summarizing the conditions of pressure and temperature under which a particular phase (Solid, Liquid, or Vapour) can remain stable, and also the conditions that bring about the phase changes.

In case of a one-component system, phase diagram consists of areas, curves or lines and points which provide the following information regarding the system:

- Point on a phase diagram represent a non-varient system
- Area represent a bivariant system
- Curve or line represents a univariant system.

A typical phase diagram of vapour pressure against temperature is illustrated below and the general features of a phase diagram is summarized in Table below:



GENERAL FEATURES OF A PHASE DIAGRAM

Area/line/point	Name	Dynamic equilibrium
Area	Solid Liquid Vapour	Only solid phase can exist Only liquid phase can exist Only vapour phase can exist
Line	S-L (fusion curve) L-V (vaporization curve) S-V(sublimation curve)	Solid & liquid phases in equilibrium Liquid & vapour phases in equilibrium Solid & vapour phases in equilibrium
Point	T(triple point) C(critical point)	Solid, liquid & vapour phrase in equilibrium Liquid phase is indistinguishable from vapour phase

ONE COMPONENT SYSTEM – WATER

Water is a one component system which is chemically a single compound involved in the system. The three possible phases in this system are: ice (solid phase), water (liquid phase) and vapour (gaseous phase).

Hence, water constitutes a three-phase, one-component system, since water is a three phase system, it can have the following equilibria:

Ice vapour

Ice water

Water vapour

The existence of these equilibria at a particular stage depends upon the conditions of temperature and pressure, which are the variables of the system. If the values of vapour pressures at different temperatures are plotted against the corresponding temperature, the phase diagram of the system is obtained.

The phase diagram of the water system and the explanation are as follows:

a. Curves

The phase diagram of the water system consists of three stable curves and one metastable curve which are explained as follow:

1. Curves OB: The curve OB is known as vapour pressure curve of water and tells about the vapour pressure of water at different temperatures. Along this curve, the two phase- water and vapour exist together in equilibrium.

At point D; the vapour pressure of water become equal to the atmospheric pressure (100°C), which represent the boiling point of water. The curve OB finishes at point B (temp 374°C and pressure 218atm) where the liquid water and vapour are indistinguishable and the system has only one phase. This point is called the critical point.

Applying the phase rule on this curve

$$C=1 \text{ and } P=2$$

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

Hence, the curve represents a univariant system. This explain that only one factor (either temperature or pressure), is sufficient to be fixed in order to define the system.

2. Curve OA: it is known as sublimation curve of ice and gives the vapour pressure of solid ice at different temperatures. Along sublimation curve, the two phases ice and vapour exist together in equilibrium. The lower end of the curve OA extends to absolute zero (-273 °C) where no vapour exists.

s/no	Area	Phase exists	Components
i.	Area AOC	Ice	H_2O
ii.	Area COB	Water	H_2O
iii.	Area below BOA	Vapour.	H_2O

Thus, for every area contains

$$C=1 \text{ and } P=1$$

Therefore applying phase rule on areas

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

Hence, each area is a bivariant system. So, it becomes necessary to specify both the temperature and the pressure to define a one-phase system.

TWO -COMPONENT SYSTEMS

When the two independent components are present in a heterogeneous system, the system is referred to as a two-component system. Hence, according to the phase rule, for a two-component system having one phase.

$$F = C - P + 2 = 2 - 1 + 2 = 3$$

Therefore, the two-component system having one phase will have three degree of freedom on three variables would be required to define the system. The three

variables are: pressure (P), temperature (T) and concentration (C). This will require a three-dimensional phase diagram for the study of a two-component system.

However, in order to simplify the study, a two component system is usually studied in the form of a condensed system. A condensed system can be studied by reducing a comparatively less important variable. This reduces the degree of freedom of the system by 1 and the system can easily be studied with the help of two-dimensional phase diagram.

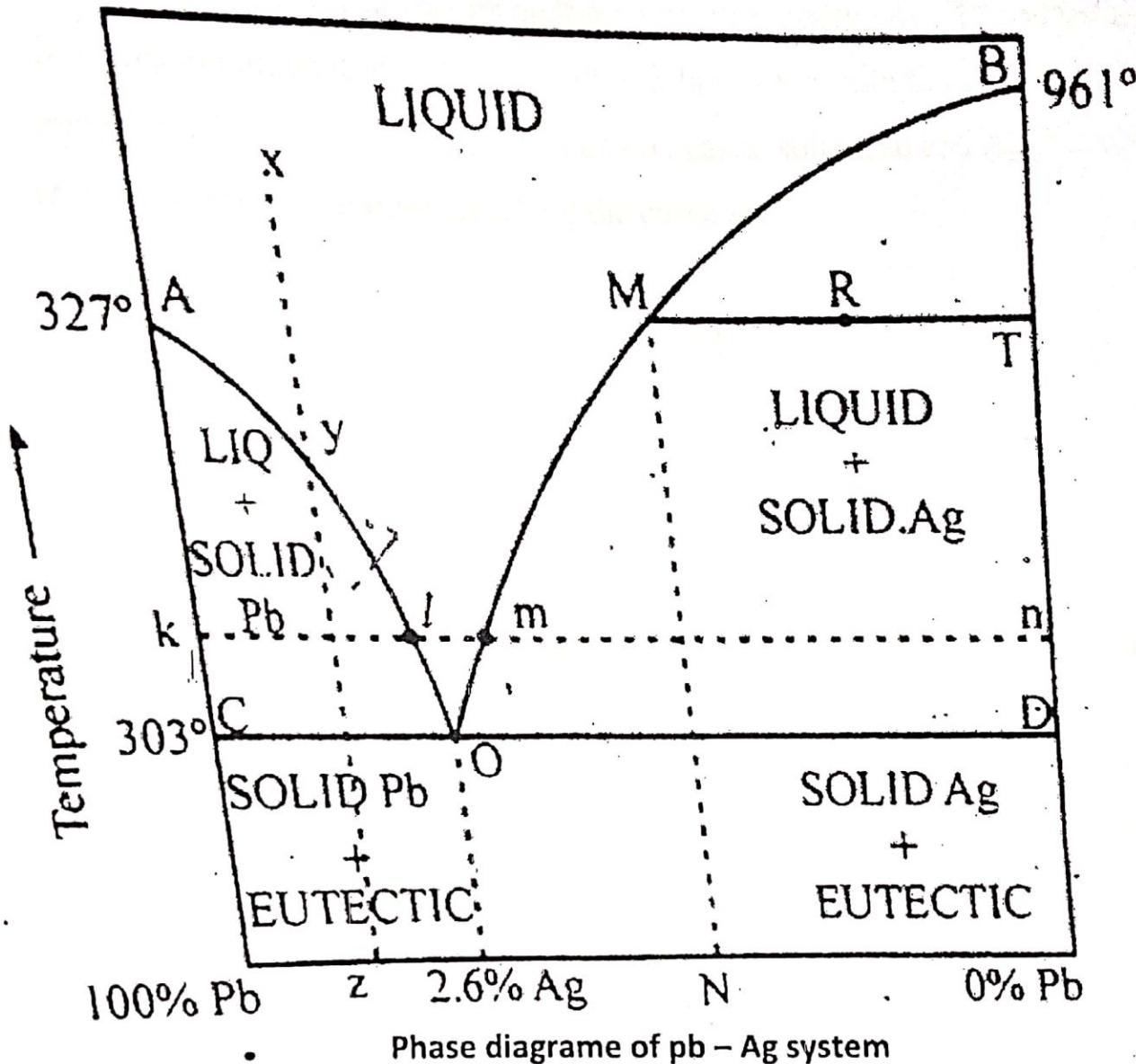
It can have a maximum of the following four phases: solid lead, solid silver, solution of molten silver & lead and vapour.

The boiling point of silver and lead are considerably high and the vapour pressure of the system is very low. Therefore, the vapour phase can be ignored and the system can be studied as a condensed system. This system thus, can be easily studied with the help of a two-dimensional T-C diagram and the reduced phase rule equation;

$$F^* = C - P + 1$$
, can be used. This system is generally studied at constant pressure.

The phase diagram of lead-silver system is shown below:

www.adbhutvigyan.com



a. CURVES

the phase diagram of the lead - silver system consists of the following curves, which are explained as follows:

- i. curve AC (freezing point curve of lead): the AC curve shows the variation of the melting point of lead on addition of silver. The pure lead melts at 327°C (Point A). Addition of silver lowers its melting point along curve AC. The added silver dissolves in molten lead to form Ag-Pb solution which with the separation of some part of solid lead. Therefore, the two phases, solid lead and Ag-Pb solution remain together in equilibrium along the curve AC.

HENCE

$$P=2, (\text{solid Pb and melt of Ag-Pb})$$

$$C=2 (\text{Pg and Ag})$$

On apply the reduced phase rule

$$F = C - P + k = 2 - 2 = 1 = 1$$

Therefore the system is univariant.

- ii. Area BCF: the area consists of two phases which are solid Ag and a solution of Pb and Ag. Hence it also univariant.
- iii. Area DCFH: This area also has the two phases which are solid Ag crystals and solid entectic crystals. Hence $C=2$ and $P=2$, the system is univariant.
- iv. Area CEGD: the area also has the solid Pb crystals and solid entectic crystals phases. The system is also univariant.

THREE- COMPONENT SYSTEM

System having 3 phase, i.e $P=3$

$$F = 3, P = 3 - 3 = 0$$

The system is univariant and three phase can exist in equilibrium only at definite values of temperature and pressure. The three phases in equilibrium

with each other may be solid- liquid-vapour, solid-solid-liquid and solid-solid-vapour.