

UNIT-I: Distribution Law and Phase Rule

Phase Rule-Terms involved in Phase Rule-Types of liquids-Derivation of Phase Rule-Phase Diagrams of One Component System (Water, CO₂ and Sulphur systems), Two Component System-Eutectic Point (Lead Silver System) - Applications of Phase Rule.

Introduction:

- Phase rule is given by an American physicist Willard Gibbs to explain the equilibrium existing in a heterogeneous system, which deals with the behavior of heterogeneous systems in the state of equilibrium. This rule was deduced on the basis of principles of thermodynamics.
- With the application of phase rule, it has been possible to predict qualitatively the effect of changing temperature, pressure and concentration on a heterogeneous system in equilibrium. Such a diagram is known as phase diagram.

Gibbs Phase Rule: Gibbs's Phase rule he stated as, "provided equilibrium between any number of phases is not influenced by gravitational, electric or magnetic forces or by surface action, but only by temperature, pressure and concentration, then the number of degrees of freedom (F) of the system is related to the number of components (C) and phases (P) by the phase rule equation".

$$F = C - P + 2$$

For any system at equilibrium at definite temperature and pressure.

Where F is the number of degrees of freedom

C is the number of components

P is the number of phases

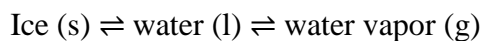
Apart from composition there are other intensive variables like temperature and pressure. So, at the end that 2 is basically the number of intensive variables which are not dependent on the composition. So, we add here 2 for that.

Terms involved in Gibbs Phase Rule:

Phase: A Phase is defined as any homogeneous, physically distinct and mechanically separable portion of a system, which is separated from other such parts of the system by definite boundary surfaces.

Examples:

(i). In the water system, at the freezing point of water, equilibrium exists where ice, water & water vapors are the three phases, each of which is physically distinct and homogeneous.



(ii). All gases mix freely to form homogeneous mixtures. Therefore, any mixture of gases, O₂ and N₂ and H₂ forms one phase only.

(iii). Two completely miscible liquids yield a uniform solution. Thus a solution of alcohol and water is a one phase system.

(iv). A mixture of two non-miscible liquids on standing forms two phases. Thus, a mixture of the oil and water constitutes a two phase system.

(v). Solution of a solute in a solvent constitutes a single phase such as salt solution in water.

(vi). Each solid substance makes a separate phase except in the case of solid solutions.

(vii). A heterogeneous mixture of the type



Solids are physically separable and hence each solid constitutes a phase.

In the above system we have two solid phases and a gaseous phase. So, it is a three phase system.

(viii). $\text{Fe(s)} + \text{H}_2\text{O (g)} \rightleftharpoons \text{FeO (s)} + \text{H}_2 \text{ (g)}$

In the above system we have two solid phases and a gaseous phase. Two solid phases of Fe and FeO and one gaseous phase consisting of H₂O (g) and H₂ (g). So, it is a three phase system.

(ix). Pure substances (solid, liquid, or gas) made of one chemical species only, is considered as one phase.

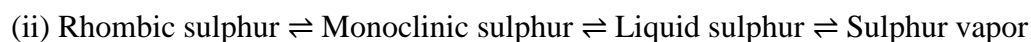
Components (C):

The term component is defined as, the number of components of a system at equilibrium is the smallest number of independently variable constituents by means of which the composition of each phase present can be expressed either directly or in the form of a chemical equation. While expressing the composition of a phase in terms of its components, zero and negative quantities are permissible. The components of a system do not represent the number of constituents or chemical individuals present in the system.

Examples:



In the water system, we have three phases, i.e. ice (solid), water (liquid) & water vapour (gaseous) in equilibrium. Each of the phases are different physical forms of the same chemical substance, i.e., H_2O . Hence the system is regarded as one component system.



Since each phase is expressed in terms of sulphur only, it is a one-component system.

The composition of all four phases can be expressed by one chemical individual sulphur (S). Hence the sulphur system is regarded as one component system.

(iii) An aqueous solution of NaCl is a two-component system. The constituents are NaCl and H_2O and both are necessary to describe the composition of the solution phase.

The unsaturated solution of NaCl in water is a one-phase and two-component system, whereas saturated solution of NaCl in water is a two-phase and two-component system.

In a chemically reactive species, the number of components is given by $C = N - E$.

Where N is the number of chemical species, E is the number of independent chemical equations relating the N species.



$$C = 3 - 1; C = 2$$

The composition of each of these three phases can be expressed in terms of at least two constituents. Hence it is a two-component system.

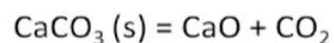
If CaCO_3 and CaO are the components

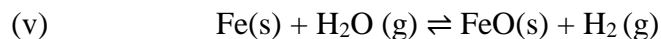


If CaCO_3 and CO_2 are the components



If CaO and CO_2 are the components





$$C = 4-1; C = 3$$

The minimum number of components required to express the composition is three, and hence it is a three-component system.



$$P_{\text{NH}_3} = P_{\text{HCl}}$$

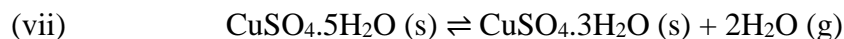
Where the partial pressure of NH_3 is equal to the partial pressure of HCl .

$$C = 3-2; C = 1$$



Where the partial pressure of NH_3 is not equal to the partial pressure of HCl

$$C = 3-1; C = 2$$



The chemical composition of all the three phases can be expressed in terms of CuSO_4 & H_2O . Hence, it is a two component system.

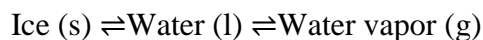
Degree of Freedom (F):

Degree of freedom is defined as the minimum number of independent variable factors such as temperature, pressure and composition (concentration) of the phases, which must be specified in order to define the system completely.

A system having 1, 2, 3 or 0 degrees of freedom is called univariant, bivariant, trivariant and non-variant respectively.

Example:

(i) Consider the water system,



$$C=1, P=3 \text{ then } F=1-3+2=0$$

When all the three phases are present in equilibrium, the degree of freedom is zero and the system is said to be invariant or non-variant. This is because the three phases coexist at the freezing point of water where the temperature and pressure are automatically fixed and there is no need to specify any variable.

(ii) Consider a system consisting of water in contact with its vapor,

Water (l) \rightleftharpoons Water vapor (g)

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

To this system, the degree of freedom is one and the system is univariant. Only one variable, either temperature or pressure is to be specified to define the position of the system because on specifying one variable the other automatically becomes fixed.

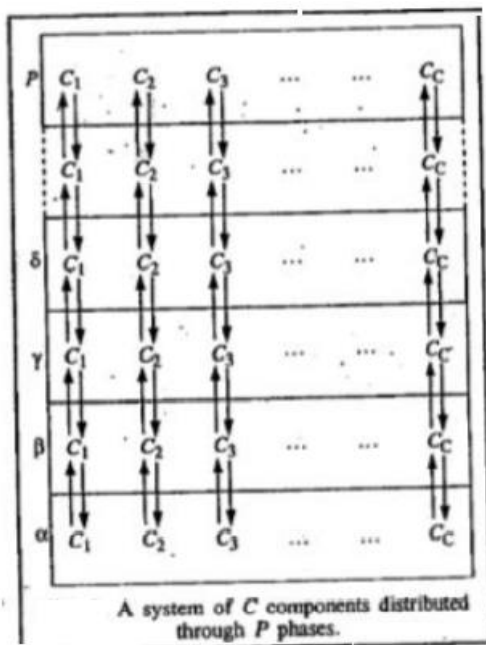
(iii) For a system containing pure gas or only one phase, both temperature and pressure have to be defined to specify the position of the system. Hence the system is bivariant and the degree of freedom is two.

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

Derivation of Phase Rule:

The Gibb's phase rule on the basis of the thermodynamics can be derived as follows:

Consider a heterogeneous system in equilibrium consisting of C components ($C_1, C_2, C_3, \dots, C_C$) distributed between P phases ($\alpha, \beta, \gamma, \delta, \dots, P$) as shown in the figure.



As has been already defined, the number of degrees of freedom of a system in equilibrium is that number of variable factors (such as temperature, pressure and composition) that must be arbitrarily fixed to define the system completely.

Assume the passage of any component from one phase to another phase does not constitute any chemical reaction.

When a system is in equilibrium, there can be only one temperature and one pressure hence, the total of these variables is two only.

In general, concentration (or composition) of each component is expressed in terms of mole fraction. As a rule, in order to define the composition of each phase, the number of composition variables required are (C-1) because the composition of the remaining component can be obtained by difference.

For instance, if we have three components and if the composition of two is known, the composition of the third can be found out. Thus, if we have 'C' components, we must know the concentrations of (C-1) components. So, for 'P' phases the total number of composition variables are P(C-1).

The total number of variables in a system = Composition variables + Variables (T, P)

$$= P(C-1) + 2$$

The total number of variables required to specify the state of the system = P(C-1) + 2.....(i)

On the basis of thermodynamic considerations, when a heterogeneous system is in equilibrium, at a constant temperature and pressure, the chemical potential, μ of a given component must be same in every phase, i.e.

$$\mu_{1,\alpha} = \mu_{1,\beta} = \mu_{1,\gamma} = \dots\dots\dots = \mu_{1,P}$$

$$\mu_{2,\alpha} = \mu_{2,\beta} = \mu_{2,\gamma} = \dots\dots\dots = \mu_{2,P}$$

$$\dots\dots\dots$$

$$\mu_{c,\alpha} = \mu_{c,\beta} = \mu_{c,\gamma} = \dots\dots\dots = \mu_{c,P}$$

(Chemical potential of a substance is the chemical energy per mole of the substance)

For each component in equilibrium in 3 phases, 2 equations (or relations) are possible. Hence, we have P-1 separate equations for each component. If there are 'C' components, we have C (P-1) such equations.

The number of relations = C (P-1).....(ii)

Degrees of freedom (F) = total variables – relations between these variables

$$= P(C-1) + 2 - C (P-1)$$

$$= PC - P + 2 - PC + C$$

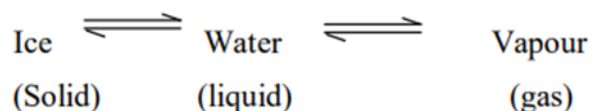
$$\mathbf{F = C - P + 2}$$

Phase diagrams of one component system:

- A diagram which shows the conditions of equilibrium between phases of a heterogeneous system is called a phase diagram. Phase diagrams are also called equilibrium diagrams.
- The phase diagram is a graphical representation obtained by plotting one degree of freedom against another.
- If the phase diagram is plotted between temperature and pressure, the diagram is called P-T diagram. P-T diagram is used for one component system.
- Important properties of a substance like its melting point, boiling point, transition temperature and triple point can be found with the help of a phase diagram. A phase diagram is usually studied under three heads:
 - ✓ Areas or regions
 - ✓ Curves or lines
 - ✓ Points
- True Equilibrium: Which is obtained from either direction.
Ex: The equilibrium between ice and water at 0°C and at 1 atm pressure is a true equilibrium.
- Metastable Equilibrium: A state of system which can be obtained only from one direction and too very careful change of conditions.
Ex: Liquid water at -4°C is said to be in a state of metastable equilibrium because this state can be achieved only by carefully cooling water below 0°C.

(A) Water system:

The water system is a one-component system. It consists of three phases: ice, water and water vapour. All these are represented by one chemical entity (H₂O); hence C = 1.



From the phase rule, when C = 1,

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

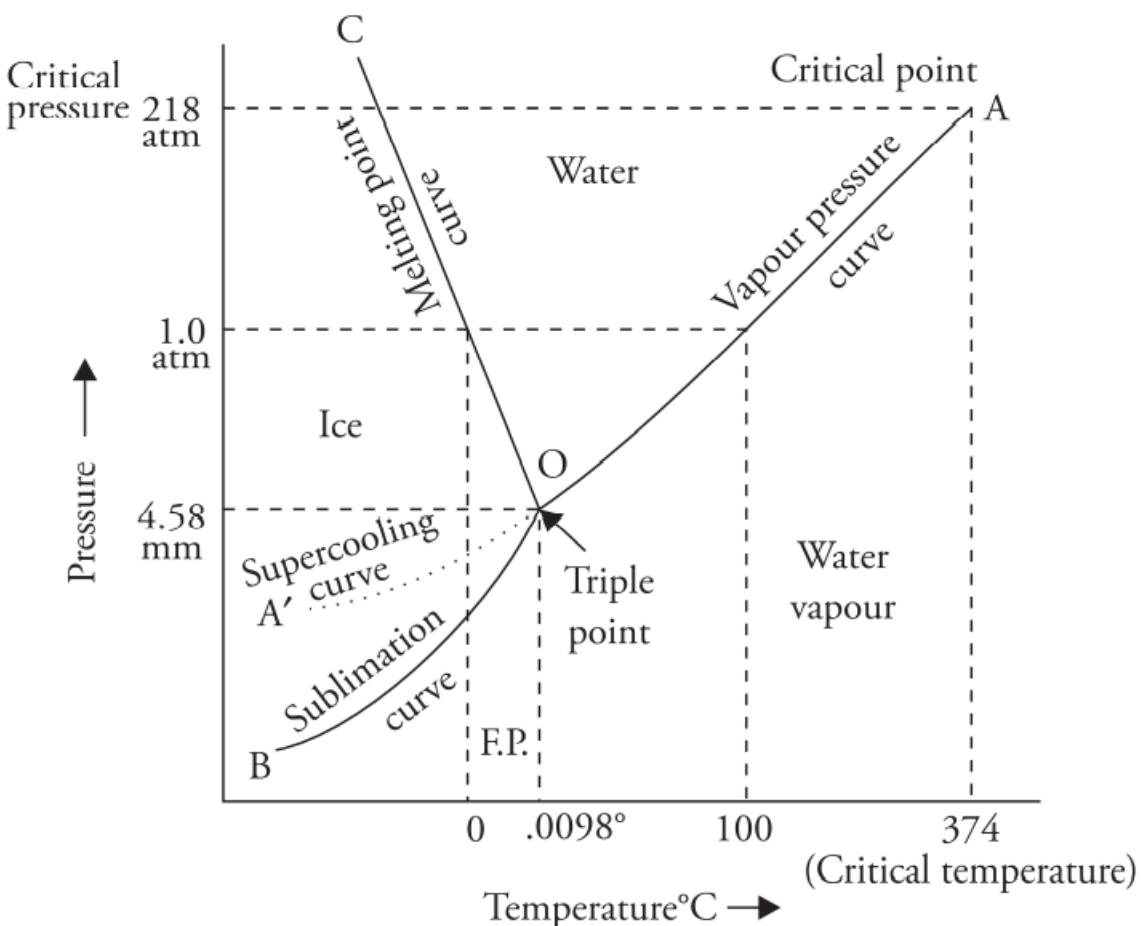
That is the degree of freedom depends on the number of phases in equilibrium. Three different cases are possible:

(i) $P = 1$; $F = 3 - 1 = 2$ (bivariant system)

(ii) $P = 2$; $F = 3 - 2 = 1$ (univariant system)

(iii) $P = 3$; $F = 3 - 3 = 0$ (invariant system)

The maximum number of degrees of freedom is two, hence, the phase diagram can be conveniently represented by a two-dimensional diagram on paper using pressure and temperature as variables.



Phase diagram of water system consists of:

1. Areas: The phase diagram consists of three areas: BOC, AOC and AOB consisting of ice, liquid water and water vapour, respectively. All these three areas consist of a single phase only.

Hence, according to the phase rule equation,

$$F = C - P + 2 = 1 - 1 + 2 = 2 \text{ (bivariant)}$$

The system in each of these areas is bivariant which means that to locate the position of any point in these areas, it is essential to specify both the variables, that is, temperature and pressure.

2. Curves: There are three curves in the phase diagram. Two phases exist in equilibrium along each of these curves. Hence, according to the phase rule equation,

$$F = C - P + 2 = 1 - 2 + 2 = 1 \text{ (univariant or monovariant)}$$

The system is univariant along each of these curves which means that to locate the position of any point along these curves, only one variable, either temperature or pressure is to be specified to define the position of the system because on specifying one variable the other automatically becomes fixed. The various curves in the phase diagram are:

- *Curve OA:* This curve is known as the vapor pressure curve of water or vaporization curve. It represents equilibrium between two phases. Along this curve, liquid water and water vapor coexist in equilibrium. The curve shows the vapor pressure of liquid water at different temperatures. The curve has its upper limit at temperature 374°C and pressure 218 atm. This is the critical point beyond which the liquid phase merges into the vapor phase and they are no longer distinguishable from each other.
- *Curve OB:* This curve is known as the sublimation curve of ice. Two phases, ice and its vapor, coexist in equilibrium along this curve. It shows the vapor pressure of solid ice at different temperatures. The lower limit of this curve is -273 °C beyond which the vapor phase does not exist.
- *Curve OC:* This curve is known as the fusion or melting curve of ice. Two phases, ice and water, coexist in equilibrium along this curve. This curve shows how the melting point of ice varies with pressure. The curve slopes towards the pressure axis which means that the melting point of ice decreases with the increase in pressure.

3. Triple point: The point O where all the three curves meet is known as the triple point. At the triple point, all the three phases, ice, water and water vapour, exist in equilibrium. Hence, at O, the value of $P = 3$. According to the phase rule equation,

$$F = C - P + 2 = 1 - 3 + 2 = 0 \text{ (invariant or non-variant)}$$

The degree of freedom at O is zero. The equilibrium is attained at a specific temperature and pressure (0.0098 °C and 4.58 mm pressure), where the temperature and pressure are automatically fixed and there is no need to specify any variable. If either pressure or temperature is varied even slightly, then at least one of the phases will disappear and all the three phases will no longer coexist.

Metastable Curve OA’: The dotted line OA’ is the continuation of the vaporization curve OA and represents the vapor pressure curve of super cooled water. This equilibrium is said to be metastable because it can be achieved only by carefully cooling water below 0°C.

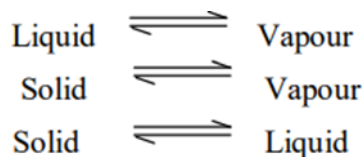
Sometimes water can be cooled below its freezing point (0°C), without the formation of ice, remaining as water. This water is called super cooled water. Super cooled liquid is the liquid which does not change its phase (liquid) below its freezing point. Super cooled water is unstable and on slight disturbance the super cooled water immediately changes to the stable form i.e., ice.

Phase diagram of water system

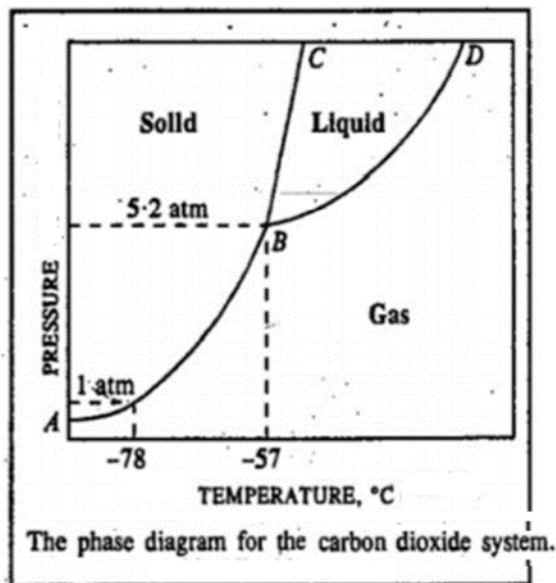
Region of the phase diagram	Phases in equilibrium	Number of phases (P)	Degree of freedom (F) (C – P + 2)
Areas			
BOC	Solid phase (solid ice)	1	2 (bivariant)
AOC	Liquid phase (liquid water)	1	2 (bivariant)
AOB	Vapour phase (water vapour)	1	2 (bivariant)
Curves			
OA (vapour pressure curve of water or vaporisation curve)	Water \rightleftharpoons water vapour	2	1(monovariant)
OB (sublimation curve of ice)	Ice \rightleftharpoons vapour	2	1(monovariant)
OC (fusion or melting curve of ice)	Ice \rightleftharpoons water	2	1(monovariant)
OA’(super cooling curve)	Liquid \rightleftharpoons vapour	2	1(monovariant)
Points			
O(0.0098 °C, 4.58 mm)	Ice \rightleftharpoons water \rightleftharpoons vapour	3	0 (non-variant)
It is a one-component system, hence C = 1			

(B) Carbon dioxide system:

The phase diagram of a carbon dioxide system has one component and three phases similar to a water system. Hence there can be three forms of equilibria similar to water systems.



- Each equilibrium involves two phases, the phase diagram for the carbon dioxide system is as shown in Figure.



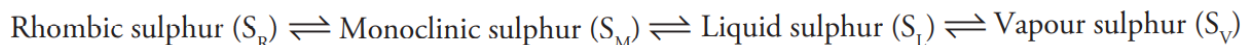
- The curve BD represents the equilibrium between liquid and vapor at different temperatures. It is called the vapor pressure curve of CO₂ as it gives the vapor pressure of CO₂ at different temperatures.
- The BC curve represents the equilibrium between solid and liquid CO₂. It is called a fusion curve.
- As we can see the BC curve is inclined away from the pressure axis which indicates that the melting point of CO₂ is increased by increase of pressure (Since the density of solid is greater than liquid in CO₂).
- The BA curve represents the equilibrium between solid and gaseous CO₂. It is called the sublimation curve.
- On the curves BA, BC, BD there exist two phases and one component hence any system placing on these curves are monovariant ($C=1, P=2, F=1-2+2=1$).
- At point B, where three phases solid, liquid and gas coexist at temperature -57°C and 5.2 atm pressure is called triple point. According to phase rule 'B' is an invariant point.

$$F = C - P + 2 = 1 - 3 + 2 = 0$$

- The areas or regions between the lines represent the phases solid, liquid and gas respectively which are bivariant ($C=1, P=1, F=1-1+2=2$).
- Solid form of carbon dioxide is commonly known as dry ice.

(C) Sulphur system:

It is a one-component, four-phase system. The four different phases of the sulphur system are:



As the composition of all the four phases can be represented by one chemical compound, sulphur, it is a one-component system.

When $C = 1$, then from the phase rule equation,

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

The degree of freedom for different cases will be:

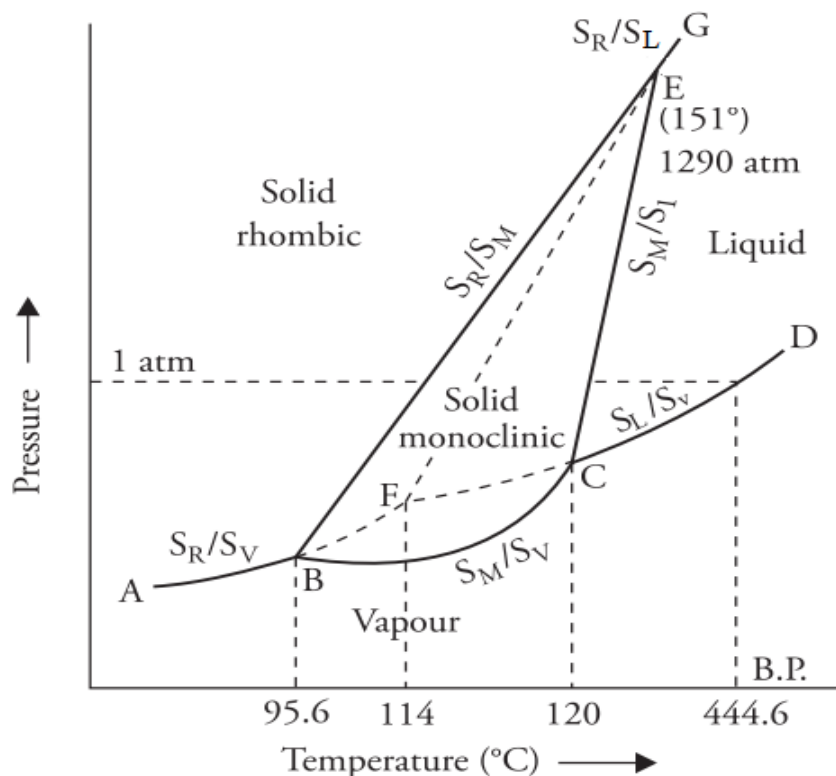
$$P = 1; F = 3 - 1 = 2 \text{ (bivariant system)}$$

$$P = 2; F = 3 - 2 = 1 \text{ (univariant system)}$$

$$P = 3; F = 3 - 3 = 0 \text{ (invariant system)}$$

$$P = 4; F = 3 - 4 = -1$$

When $P = 4$, the degree of freedom will be negative which is not possible. Therefore, all the four phases of the sulphur system can never exist in equilibrium. Only three phases can be present at a time. In the sulphur system, one solid allotropic form transforms into the other. Such a system in which two or more solid states exist in equilibrium is called a polymorphic system.



The phase diagram of sulphur system consists of:

1. Areas: The phase diagram has four areas each of which consists of a single phase.

(i) ABG (rhombic sulphur)

(ii) BECB (monoclinic sulphur)

(iii) GECD (liquid sulphur)

(iv) ABCD (vapour sulphur)

For each area, $C = 1$; $P = 1$, hence the degree of freedom will be

$$F = 1 - 1 + 2 = 2 \text{ (bivariant system)}$$

Hence to locate the position of any point in these areas, both the variables—pressure and temperature—need to be specified.

2. Curves: There are six curves in the phase diagram.

(i) *Curve AB:* It is the vapour pressure curve of rhombic sulphur. Along this curve, two phases S_R and S_V exist in equilibrium.

(ii) *Curve BC:* It is the vapour pressure curve of monoclinic sulphur. Two phases S_M and S_V exist in equilibrium along this curve.

(iii) *Curve CD:* It is the vapour pressure curve of liquid sulphur. S_L and S_V exist in equilibrium along this curve.

(iv) *Curve BE:* It is the transition curve of S_R to S_M . Along this curve, two solid phases are in equilibrium. The line BE slopes away from the pressure axis showing that the transition temperature can be raised with increase in pressure.

(v) *Curve CE:* It is the fusion curve of S_M . Monoclinic and liquid sulphur (S_M and S_L) exist in equilibrium along this curve. The melting point rises with the increase in pressure. The curve ends at point E because monoclinic sulphur does not exist beyond this point.

(vi) *Curve EG:* It is the fusion curve of S_R . Rhombic and liquid sulphur (S_R and S_L) exist in equilibrium along this curve.

Along all the six curves, two phases are in equilibrium. Hence the degree of freedom along these curves is:

$$F = C - P + 2 = 1 - 2 + 2 = 1 \text{ (univariant).}$$

The system along each of these curves is univariant, hence only one variable (either pressure or temperature) is needed to express the system completely along these curves.

3. Points: There are three stable triple points in the sulphur system: B (95.6°C, 0.006 mm), C (120°C, 0.04 mm) and E (151°C, 1290 atm). Three phases exist in equilibrium at these points.

B S_R, S_M, S_V

C S_M, S_L, S_V

E S_R, S_M, S_L

According to the phase rule equation, the degree of freedom at these triple points is

$$F = C - P + 2 = 1 - 3 + 2 = 0 \text{ (invariant or non-variant).}$$

The system corresponding to each point is non-variant. Variation of any one of the variables, temperature or pressure causes the disappearance of one of the three phases.

Metastable curves: There are three metastable curves in the phase diagram.

(i) *Dashed curve BF:* It is the vapour pressure curve of metastable S_R . If rhombic sulphur is heated rapidly, it will bypass the transition point B without changing to monoclinic sulphur and will melt at F. The metastable phases S_R and S_V are in equilibrium along this curve and the system is monovariant.

(ii) *Dashed curve CF:* It is the vapour pressure curve of super cooled liquid sulphur. If liquid sulphur is cooled rapidly, it does not change to monoclinic sulphur at point C and continues to exist as super cooled liquid. This curve represents metastable equilibrium between super cooled S_L and S_V .

(iii) *Dashed curve FE:* This is the fusion curve of metastable S_R . Along this curve, S_R and S_L are in equilibrium.

Metastable triple point F: The three metastable phases S_R, S_L and S_V are in equilibrium at this point and the system is non-variant.

Phase diagram of sulphur system

Region of the phase diagram	Phases in equilibrium	Number of phases (P)	Degree of freedom (F) (C-P+2)
Areas			
ABG	Rhombic sulphur	1	1-1+2=2(bivariant)
BECB	Monoclinic sulphur	1	1-1+2=2(bivariant)
GECD	Liquid sulphur	1	1-1+2=2(bivariant)
ABCD	Vapour sulphur	1	1-1+2=2(bivariant)
Curves			
AB (vapour pressure of rhombic sulphur)	$S_R \rightleftharpoons S_V$	2	1-2+2=1(univariant)
BC (vapour pressure of monoclinic sulphur)	$S_M \rightleftharpoons S_V$	2	1-2+2=1(univariant)
CD (vapour pressure of liquid sulphur)	$S_L \rightleftharpoons S_V$	2	1-2+2=1(univariant)
BE (transformation curve of S_M and S_R)	$S_R \rightleftharpoons S_M$	2	1-2+2=1(univariant)
CE (fusion curve of S_M)	$S_M \rightleftharpoons S_L$	2	1-2+2=1(univariant)
EG (fusion curve of S_R)	$S_R \rightleftharpoons S_L$	2	1-2+2=1(univariant)
Metastable curves			
BF (metastable v.p curve of S_R)	$S_R \rightleftharpoons S_V$	2	1-2+2=1(univariant)
CF (metastable v.p curve of S_L)	$S_L \rightleftharpoons S_V$	2	1-2+2=1(univariant)
FE (metastable v.p curve of supercooled rhombic sulphur)	$S_R \rightleftharpoons S_L$	2	1-2+2=1(univariant)
Triple points			
B	$S_R \rightleftharpoons S_M \rightleftharpoons S_V$	3	1-3+2=0 (invariant)
C	$S_M \rightleftharpoons S_L \rightleftharpoons S_V$	3	1-3+2=0 (invariant)
E	$S_R \rightleftharpoons S_M \rightleftharpoons S_L$	3	1-3+2=0 (invariant)
F(metastable)	$S_R \rightleftharpoons S_L \rightleftharpoons S_V$	3	1-3+2=0 (invariant)

Eutectic system:

- The term eutectic means ‘easy to melt’.
- A eutectic system is a binary system consisting of two substances which are miscible in all proportions in the liquid phase and which do not react chemically is known as the ‘eutectic system’.
- The two substances have the tendency to lower each other’s freezing point.
- A solid solution of two or more substances having the lowest freezing point of all the possible mixtures of the components is called the *eutectic mixture*.

- Two or more solid substances capable of forming solid solutions with each other have the property of lowering each other's freezing point and the minimum melting point attainable by the eutectic mixture is termed as the *eutectic point* (lowest melting point).

Ex:

A mixture of Ag and Pb of composition 97.4% Pb and 2.6% Ag with eutectic point (freezing point) at 303 °C.

A mixture of Bi–Cd of composition 60% Bi and 40% Cd with eutectic point 144 °C

- *Characteristics of eutectic point*
 - The system at eutectic point is invariant, the degree of freedom $F = 0$. For a two-component system, at eutectic point, $C = 2$, $P = 3$ (both the solids and their solution)

$$F = C - P + 1$$

$$F = 2 - 3 + 1 = 0$$

- It is the lowest freezing point of the system, that is, below this temperature, the liquid phase does not exist.
- If the liquid is cooled below the eutectic point, both the components will solidify without change in composition.
- Eutectics are mixtures and not compounds. When they were examined under an electron microscope, both the constituents are seen to lie as separate crystals.
- The alloys of eutectic composition have greater strength than their individual components because of their crystal characteristics.

Two component systems:

- In a two-component system ($C = 2$), the degree of freedom of a two-component system is given by $F = C - P + 2$

$$F = 2 - P + 2 = 4 - P$$

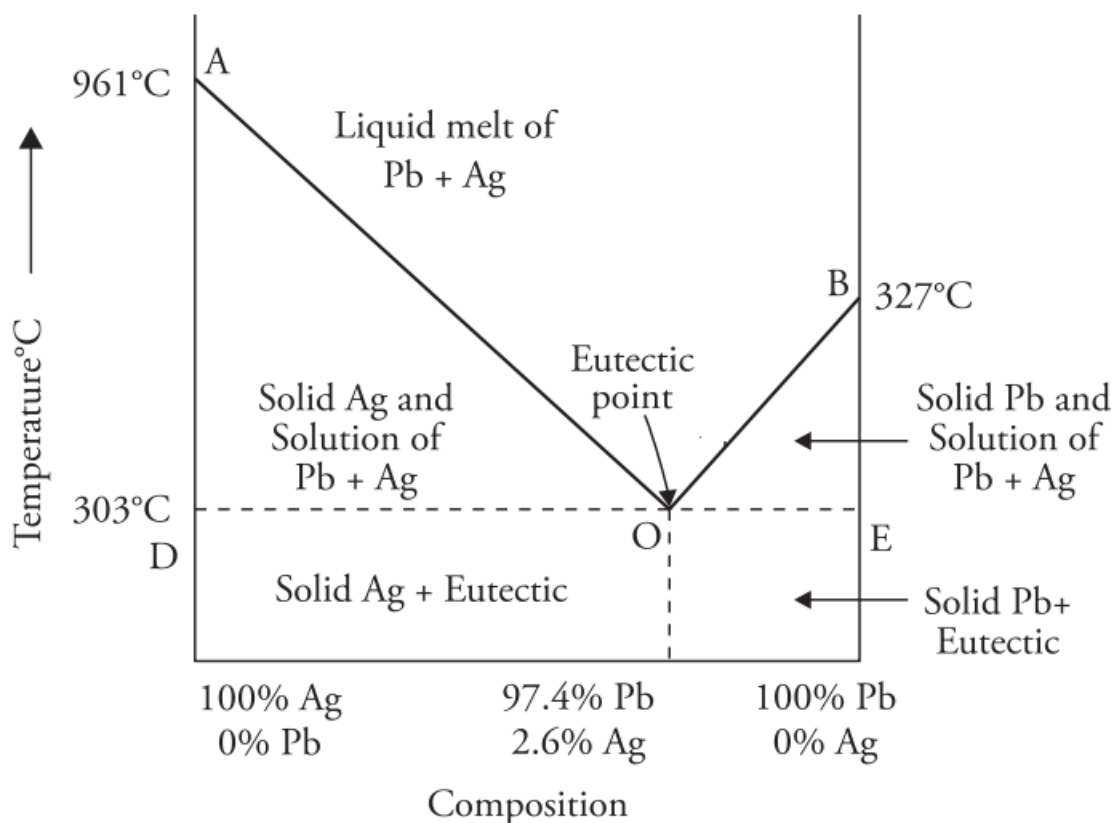
When $P = 1$, the degree of freedom has the highest value: $F = 4 - 1 = 3$.

- It means that three variables—temperature, pressure and composition—are required to explain the system completely. Such a three-dimensional diagram cannot be expressed conveniently on paper.
- A solid-liquid equilibrium of an alloy has practically no gas phase and the effect of pressure on these equilibria is negligible. Hence in most cases, pressure is kept constant at 1 atm and the phase diagram is constructed using the variables, temperature and concentration.

- Such a solid–liquid equilibrium with the gas phase absent is termed as the condensed system. This will reduce the degree of freedom by one and for such a system, the phase rule becomes $F = C - P + 1$.
- This is known as the reduced or condensed phase rule and is widely applicable to solid–liquid two-component systems.

Lead–silver system:

- Lead–silver system is an example of a simple eutectic system. Silver and lead are miscible in all proportions and do not react chemically. When molten silver and lead are mixed together in all proportions, a single homogenous solution is formed. The system consists of three phases:
 - (i) Solid silver
 - (ii) Solid lead
 - (iii) Solution of molten silver and lead



Phase diagram of lead–silver system consists of:

(i) Areas:

Area above AOB: It consists of only one phase (liquid solution). On applying the reduced phase rule equation, the degree of freedom comes out to be two. Hence, the system is bivariant and both temperature and composition are required to be specified to define the system completely.

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

Area ADOA: It contains two phases—solid Ag and solution containing Pb and Ag.

Area BOEB: It contains two phases—solid Pb + solution containing Pb and Ag.

Both these areas have two phases and are univariant.

$$C = 2 \text{ (Pb and Ag), } P = 2 \text{ (Liquid + solid phase),}$$

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

Area below DOE: It represents a solid mixture of Pb or Ag with eutectic. The number of phases is 2 (either Ag or Pb + eutectic) and the system is univariant.

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

(ii) Curves:

It is clear from the diagram that the addition of Pb to pure Ag lowers the melting point of Ag; similarly, addition of Ag to pure Pb lowers the melting point of Pb.

The curve AO represents the freezing point curve of Ag on gradual addition of Pb. The curve indicates that the melting point of Ag gradually falls on addition of Pb. Along this curve, solid Ag and solution are in equilibrium.

The curve BO represents the freezing point curve of Pb on gradual addition of Ag. The curve indicates that the melting point of Pb gradually falls on addition of Ag. Along this curve, solid Pb and solution are in equilibrium. Both AO and BO represent univariant systems.

$$C = 2, P = 2,$$

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

(iii) Points:

In the phase diagram, point A represents the melting point of pure Ag (961°C) and point B represents the melting point of pure Pb (327°C). At these points, $C = 1, P = 2$ (pure Ag in equilibrium with its liquid or pure Pb in equilibrium with its liquid); hence,

$$F = C - P + 1; F = 1 - 2 + 1 = 0$$

Eutectic point O:

The two curves AO and BO intersect at point O at a temperature of 303°C. The point O is known as the eutectic point. At this point, three phases—solid Ag, solid Pb and the melt are in equilibrium. On applying the phase rule equation, we get:

$$C = 2, P = 3,$$

$$F = C - P + 1; F = 2 - 3 + 1 = 0$$

Thus, the system at this point is invariant. Both temperature (303°C) and composition (Ag: 2.6 % and Pb: 97.4 %) are fixed at this point. If the temperature is increased above the eutectic point, the solid phase (silver or lead) will disappear and if the temperature decreases below the eutectic point, the solution phase disappears and only the solid phase (eutectic + solid lead or silver) will remain. A lead-silver system can never have a melting point below the eutectic temperature.

Phase diagram of lead -silver system

Region of the phase diagram	Phases in equilibrium	Number of phases (P)	Degree of freedom (F) (C-P+1)
AO (freezing point curve of Ag on addition of Pb)	Crystallisation of Ag begins $\text{Ag (s)} \rightleftharpoons \text{liquid}$	2	$2 - 2 + 1 = 1$ (univariant)
BO (freezing point curve of Pb on addition of Ag)	Crystallisation of Pb begins $\text{Pb (s)} \rightleftharpoons \text{liquid}$	2	$2 - 2 + 1 = 1$ (univariant)
Area above AOB	Liquid phase (solution of Pb + Ag)	1	$2 - 1 + 1 = 2$ (bivariant)
Area below DOE	Solid mixture (eutectic + solid Ag or Pb)	2	$2 - 2 + 1 = 1$ (univariant)
Area ADOA	Solid Ag in equilibrium with liquid having composition given by the curve OA	2	$2 - 2 + 1 = 1$ (univariant)
Area BOEB	Solid Pb in equilibrium with liquid having composition given by the curve OB	2	$2 - 2 + 1 = 1$ (univariant)
Point O (eutectic point)	Solid Ag, solid Pb and their solution coexist	3	$2 - 3 + 1 = 0$ (invariant)

Applications:

Application of Ag–Pb system:

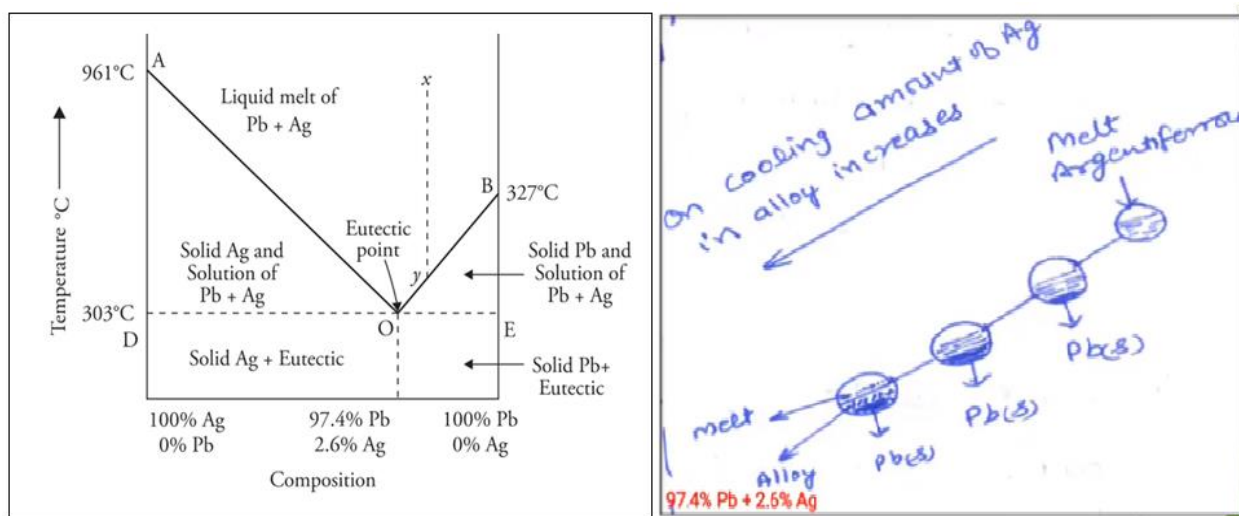
Pattinson's process for desilverisation of argentiferous lead:

The process of heating argentiferous lead containing a very small quantity of Ag (0.1% by mass) and cooling it to get pure lead and liquid rich in silver is called Pattinson's process.

Argentiferous lead is first heated to a temperature above its melting point. The system consists of only the liquid phase represented by point x in Figure. It is then allowed to cool. The temperature of the melt will fall along the perpendicular line xy without change in composition. As the point y is reached, lead will begin to crystallize and the percentage of silver will increase in the solution.

The system moves along the curve yO. The melt continues to be richer and richer in silver until the point O is reached. At point O, the percentage of silver is 2.6% by mass.

After removing the lead that separates out, the liquid is cooled further to give a mixture of eutectic composition (97.4% Pb + 2.6% Ag). This is treated for the recovery of silver profitably (cost-effective).

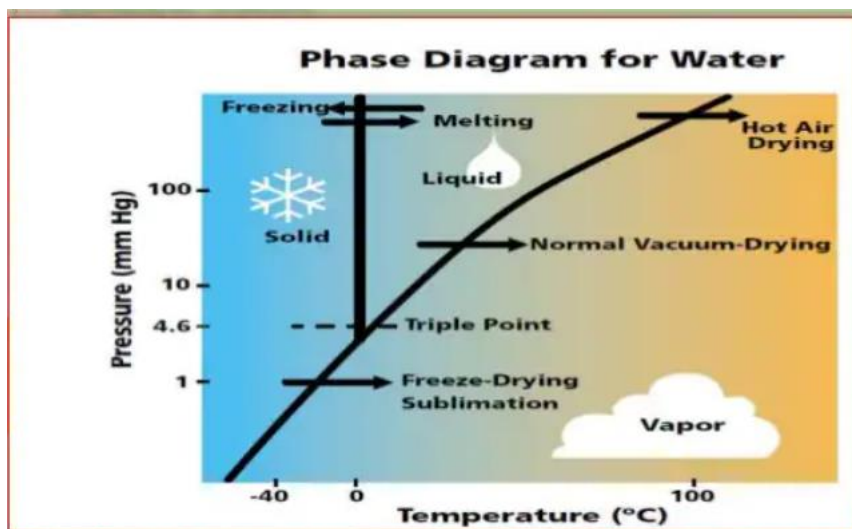


Ex:

Pb	Ag	Total	% Pb	% Ag
99.5	0.5	100	99.5	0.5
49.5	0.5	50	99	1.0
24.5	0.5	25	98	2.0
19.5	0.5	20	97.5	2.5

Freeze drying is a process in which a completely frozen sample is placed under a vacuum in order to remove water or other solvents from the sample, allowing the ice to change directly from a solid to a vapor without passing through a liquid phase.

Freeze drying is a low temperature dehydration process that involves freezing the product, lowering pressure, then removing the ice by sublimation.



Freeze drying is a relatively recent method of preserving food. It is the most important technique to dry coffee, enzymes, food ingredients, and high value foods. This process could be considered as a valuable alternative to preserve foods.

The food material can be preserved for a long time.

By removing water from material its weight decreases and thus transportation cost decreases.

Freezing mixture: It is the mixture of ice and salt. It is used to obtain low temperature.

Mixture	Eutectic temperature (C)	Composition % (salt)
NH ₄ Cl + ice	-16	21%
NH ₄ NO ₃ + ice	-18	43%
NaNO ₃ + ice	-18	33%
KI + ice	-23	52%
CaCl ₂ + ice	-55	30%
NaCl + ice	-22	23%

Out of all freezing mixtures, CaCl₂ and ice has the lowest eutectic temperature and so best freezing mixture.

Use of eutectic system: Used for creating low melting alloys which can be made into safety fuses. Safety fuse is a device containing a small piece of low melting alloy that melts under excessive heat or excessive current.

Examples:

1. Safety valve in pressure cookers is made of an alloy having a definite composition and definite eutectic temperature. As the temperature rises above this temperature, the alloy melts, preventing any accident.
2. Safety fuses are employed for plugs in water sprayers in buildings. In case of accidental fires, the plugs melt away and the water is released automatically to extinguish the fire.
3. Fuse wire used in electric circuits melts away on over-heating.

Important safety fuse making alloys:

1. Wood metal contains Bi (50%), Pb (25%), Sn (12.5%) and Cd (12.5%). It melts at 70°C and is used for making fire – alarms, automatic sprinklers, safety plugs in cookers, electric fuses and boiler fuses.
2. Rose metal contains Bi (50%), Pb (28%) and Sn (22%). It melts at 89°C and is used for making fire – alarms, electric fuse wires and in automatic sprinklers.
3. Fuse wires for 1. Small currents are made of Pb-Sn alloy, 2. High currents are made of Pb, Sn, Zn, Sb, Cu, Al etc.

Solders are readily fusible alloys which are applied to the point between metal objects to unite them closely without heating the objects to their melting point. The capability of a solder to join the metal objects closely depends on the surface alloy formation between the solder and metal objects being joined. The selection of solder for a particular joining purpose depends on the melting point at which the solder forms a surface alloy with the metal objects to be joined.

Examples of solders:

1. Soft solders containing 37–67% Pb, 31–60% Sn and 0.12–2% Sb, melts at low temperatures and are used for soldering electrical connections.
2. Brazing alloy containing 92% Sn, 5.5% Sb and 2.5% Cu is used for soldering steel joints.

