

2.1 PHASE RULE

The phase rule is invented by J. Willard Gibbs to study the heterogeneous systems in equilibrium. It helps to study the effect of changing temperature, pressure and composition on the behaviour of heterogeneous system in equilibrium by means of a phase diagram.

2.2 STATEMENT

[Oct. Dec. 17, May 18, 19]

Gibbs phase rule states that, provided the equilibrium between any number of phases is not influenced by gravity or electrical or magnetic forces or by surface tension and only by temperature, pressure and concentration, then the degrees of freedom (F) of the system is related to the number of components (C) and phases (P) by the phase rule equation,

$$F = C - P + 2$$

2.3 EXPLANATION OF THE TERMS

The terms involved in the phase rule are phase, component and degree of freedom which are explained below.

2.3.1 Phase

[Oct., Dec. 17, May 18, 19]

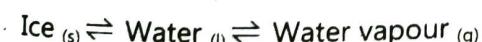
A phase is defined as a homogeneous, physically distinct and mechanically separable portion of a system, which is separated from other such parts of the system by definite boundary surfaces.

For a system in equilibrium obeying phase rule, the number of phase cannot be a negative number or zero, i.e., minimum one phase must exist to define a system.

Examples:

Each solid phase constitutes a single phase.

- At triple point (specific temperature and pressure) in a water system, number of phases is three.



- In the thermal decomposition of solid CaCO_3 as,

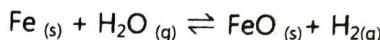


Number of phases is three, two solid phases and a gaseous phase.

- Any number of miscible liquids together constitutes a single phase.

A mixture of alcohol and water constitutes a single phase.

- Two immiscible liquids constitute two phases. A mixture of benzene and water constitutes two phases.
- Any number of gases together constitutes a single phase.
- A mixture of N_2 and H_2 forms a single phase.
- When steam is passed over iron as,



Number of phases is three, two solid phases and a gaseous phase.

- A solid compound such as sugar or salt dissolved in water constitutes a single phase.

2.3.2 Components

[Dec. 18]

A component is defined as the smallest number of independent variable constituent, taking part in the state of equilibrium, by means of which the composition of each phase can be expressed in the form of a chemical equation.

For a system in equilibrium obeying phase rule, the number of component cannot be a negative number or zero, i.e., minimum one component must be specified to define a system.

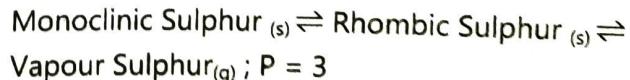
Examples:

- In a water system, irrespective of the number of phases, the composition of each phase is expressed by a single constituent, H_2O .



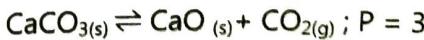
Hence, it is a one component system.

- In a sulphur system, irrespective of the number of phases, the composition of each phase is expressed by a single constituent, S .



Hence, it is a one component system.

- In the thermal decomposition of solid CaCO_3 as,



The composition of any single phase cannot be represented by a single constituent. It can be expressed by any two constituents out of three.

This can be explained as tabulated in Table 2.1 :

Table 2.1

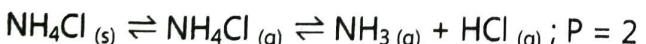
Phase	Constituent/s Considered	Composition of Each Phase
Phase 1 : CaCO ₃		CaCO ₃ = CaCO ₃
Phase 2 : CaO	Consider only one constituent, e.g. CaCO ₃	Composition of CaO cannot be expressed by only CaCO ₃
Phase 3 : CO ₂		Composition of CO ₂ cannot be expressed by only CaCO ₃

Similarly, it is applicable for other constituents, viz. CaO and CO₂. Hence, it cannot be a one component system.

Phase 1 : CaCO ₃	Consider a combination of two constituents, e.g. CaCO ₃ and CaO	CaCO ₃ = CaCO ₃ + 0CaO
Phase 2 : CaO		CaO = 0CaCO ₃ + CaO
Phase 3 : CO ₂		CO ₂ = CaCO ₃ - CaO
Phase 1 : CaCO ₃	Consider a combination of two constituents, e.g. CaO and CO ₂	CaCO ₃ = CaO + CO ₂
Phase 2 : CaO		CaO = CaO + 0CO ₂
Phase 3 : CO ₂		CO ₂ = 0CaO + CO ₂
Phase 1 : CaCO ₃	Consider a combination of two constituents, e.g. CaCO ₃ and CO ₂	CaCO ₃ = CaCO ₃ + 0CO ₂
Phase 2 : CaO		CaO = CaCO ₃ - CO ₂
Phase 3 : CO ₂		CO ₂ = 0CaCO ₃ + CO ₂

Since the composition of each phase can be expressed by minimum two constituents, it is a two component system.

4. In the dissociation of NH₄Cl in a closed vessel,



If the proportions of NH₃ and HCl are equivalent, then the composition of each phase can be expressed in terms of NH₄Cl alone. Hence, it is a one component system as composition of any one constituent needs to be known to express the composition of any of the phases.

If the proportions of NH₃ and HCl are not equivalent, then it is a two component system as concentration of both constituents needs to be known to express the composition of any of the phases.

2.3.3 Degree of Freedom

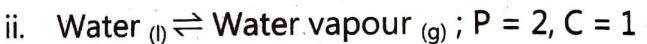
- Degree of freedom is defined as the minimum number of independently variable factors such as temperature and composition of the phases, which may arbitrarily specified in order to represent perfectly condition of a system.
- For a system in equilibrium obeying phase rule, number of degree of freedom cannot be a negative number. However, the system can be defined with minimum zero degree of freedom.

Examples:

1. In a water system (one component system), consider the following conditions-



This particular equilibrium exists at a definite temperature and pressure. Thus, to define this system, no parameter needs to be specified. Hence, it is a zero variant or invariant system. It has zero degree of freedom.



To define this system, either of the parameters temperature or pressure needs to be specified, the other parameter gets automatically fixed.

Hence, it is a univariant or monovariant system and has one degree of freedom.



The system contains only one phase, either solid liquid or gaseous.

To define this system, both the parameters temperature and pressure needs to be specified. Hence, it is a bivariant system. It has two degrees of freedom.

2. The system of saturated solution of NaCl in equilibrium with solid NaCl and water vapour at a definite temperature.



Hence, this system has one degree of freedom.

3. For a sample of pure gas obeying the equation PV = RT, if pressure and temperature are specified, the volume gets automatically fixed. Hence, this system has two degrees of freedom.

4. For a mixture of two or more gases at equilibrium, all the three parameters viz. temperature, pressure and composition need to be specified to define the system. Hence, this system has three degrees of freedom.

2.4 ONE COMPONENT WATER SYSTEM

[May 17, 18]

The water system comprises of three possible phases namely solid (ice), liquid and gaseous (vapour). Since only one constituent H_2O is sufficient to express the composition of each phase, it is a one component system, i.e., $C = 1$.

Substituting for $C = 1$ in Gibb's phase rule equation,

$$F = C - P + 2$$

$$F = 1 - P + 2$$

$$F = 3 - P$$

The minimum number of degree of freedom can be zero for a system, i.e., when $F = 0$, then $P = 3$. This implies that all the three phases can exist in equilibrium for a water system.

Minimum one phase is required to define the system at equilibrium, i.e., when $P = 1$, $F = 2$. Thus, for water system, the maximum number of degrees of freedom is two. These two degrees of freedom for one component system are pressure and temperature. The phase diagram for one component system can be represented by plotting a graph of pressure against temperature. (Fig. 2.1)

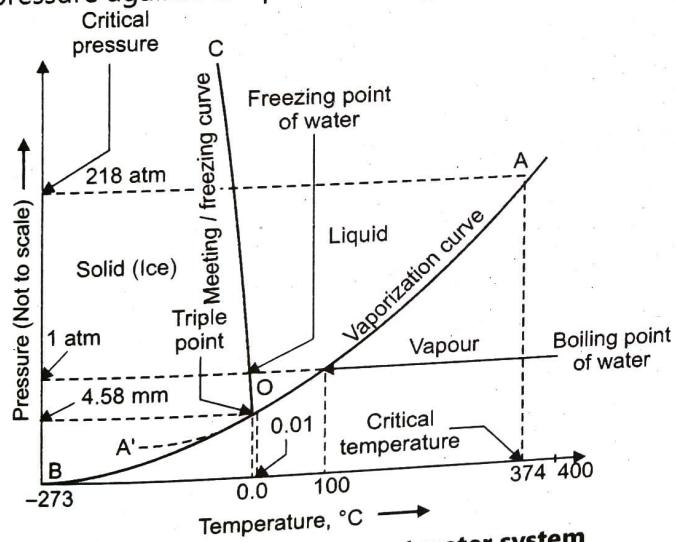


Fig. 2.1 : One component water system

The water system is explained as follows:

1. Areas: In the areas AOB , AOC and BOC , only single phase (namely vapour, liquid and solid respectively) exists and the degrees of freedom are two, i.e., both temperature and pressure need to be specified in order to define the system.

2. Boundary Lines: The boundary lines, namely melting point or freezing or fusion curve (OC), vaporization curve (OA) and sublimation curve (OB) divide the phase diagram into three areas. Along the boundary lines, two phases are in equilibrium and the degree of freedom is one, i.e., either temperature or pressure needs to be specified in order to define the system.

The curve OC shows that the melting point of ice is decreased with increase in temperature. A point on curve OC corresponding to 1 atmosphere pressure and 0°C temperature is the melting or freezing point of water.

The curve OA terminates at point A, called critical point corresponding to 218 atmosphere pressure and 374°C temperature, above which the liquid phase and the vapour phase merge into each other. A point on curve OA corresponding to 1 atmosphere pressure and 100°C temperature is the boiling point of water.

The curve OB terminates at point B, corresponding to -273°C temperature, below which the solid phase and the vapour phase merges into each other.

3. Triple Point: The curves OC, OA and OB meet at point 'O' called triple point of water. At triple point, all the three phases, i.e., solid, liquid and gas co-exist in equilibrium.

The degree of freedom is zero, i.e., neither temperature nor pressure needs to be specified in order to define the system. The triple point exists at 4.58 mm pressure and 0.0098°C temperature.

4. Metastable Curve: The curve OA' is called the metastable curve, which is the extension of curve OA. At the freezing point, water would normally freeze and form ice. But by careful removal of solid particles, which promote this crystallization, water may be cooled way below its freezing point without forming ice. Thus, by preventing water to freeze at its freezing point, it is possible to extend the vapour pressure curve even below the normal freezing point. It signifies the vapour pressure curve of supercooled water.

The above discussion is tabulated below ($C = 1$):

Table 2.2

Name of the System	Phases in Equilibrium	Degrees of Freedom $F = C - P + 2$
Areas		
(1) BOC	Solid, $P = 1$	$F = 1 - 1 + 2 = 2$
(2) COA	Liquid, $P = 1$	The systems are bivariant.
(3) AOB	Vapour, $P = 1$	
Curves		
(1) OC (Melting point curve)	Solid and Liquid, $P = 2$	$F = 1 - 2 + 2 = 1$
(2) OA (Vaporization curve)	Liquid and Vapour, $P = 2$	The systems are univariant.
(3) OB (Sublimation curve)	Solid and Vapour, $P = 2$	
Triple point O	Solid, Liquid and Vapour, $P = 3$	$F = 1 - 3 + 2 = 0$
		The system is invariant.

2.5 ONE COMPONENT SULPHUR SYSTEM

[Oct. 17, Dec. 18, May 19]

- The sulphur (S) system comprises of four possible phases namely two solid phases- rhombic (or α) sulphur (S_R) and monoclinic (or β) sulphur (S_M), liquid sulphur (S_L) and gaseous- sulphur vapour (S_V). In sulphur system, allotropy (an element existing in more than one crystalline form) and solid-solid transformation are exhibited. Since only one constituent S is sufficient to express the composition of each phase, it is a one component system. $C = 1$.

Substituting for $C = 1$ in Gibb's phase rule equation,

$$F = C - P + 2$$

$$F = 1 - P + 2$$

$$F = 3 - P$$

- The minimum number of degree of freedom can be zero for a system, i.e., when $F = 0$, then $P = 3$. This implies that all the four phases of sulphur cannot exist in equilibrium together. The maximum number of phases that can be in equilibrium at a time for a sulphur system is 3.
- Minimum one phase is required to define the system at equilibrium, i.e., when $P = 1$, $F = 2$. Thus, for sulphur system, the maximum number of degrees of freedom is two. These two degrees of freedom for one component system are pressure and temperature. The phase diagram for one component system can be represented by plotting a graph of pressure against temperature. (Fig. 2.2).

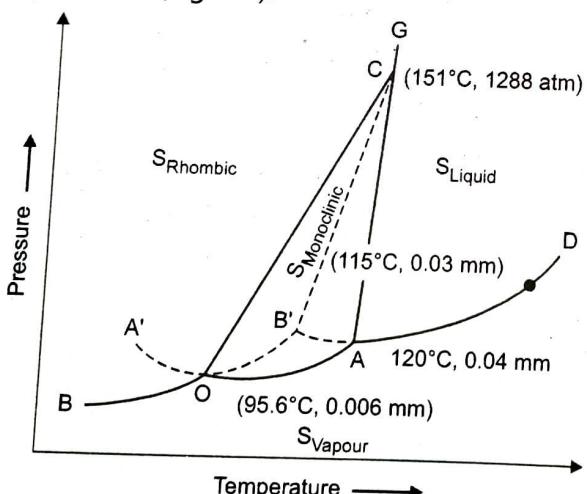


Fig. 2.2 : One component sulphur system

The sulphur system is explained as follows:

- Areas:** The areas below BOAD, on the right side of GCAD, on the left side of GCOB and enclosed by COA comprise of only one phase namely S_V , S_L , S_R and S_M respectively. Hence, the degrees of freedom are two, i.e., both parameters, temperature and pressure needs to be specified in order to define the system.

- Curves:** The curves BO, OA, AD, OC, AC comprise two phases in equilibrium and the degrees of freedom is one, i.e., either temperature or pressure needs to be specified in order to define the system.
 - The curve BO is the sublimation curve of S_R . It terminates at point O corresponding to 95.6°C temperature, which is the lowest limit, below which vapour pressure cannot be measured. The point O corresponds to 0.006 mm pressure. The curve OB' is the metastable sublimation curve of S_R .
 - The curve OA is the sublimation curve of S_M . It terminates at point A corresponding to 120°C temperature and 0.04 mm pressure, which is the melting point of S_M . The curve OA' is the metastable sublimation curve of S_M .
 - The curve AD is the vapour pressure curve of S_V . It terminates at point D, which is the critical temperature beyond which only S_V exists. The curve AB' is the metastable vapourization curve of S_L .
 - The curve OC is the transition curve. The positive slope of the curve specifies that the transition pressure between S_R and S_M is elevated by the application of pressure. It also indicates that S_R is heavier than S_M . The curve terminates at point C beyond which S_R disappears.
 - The curve AC is the melting point curve or fusion curve of S_M . The positive slope of the curve specifies that the melting point of S_M is elevated by the increase of pressure. It also indicates that S_M is heavier than S_L .
 - The curve CG is the melting point or freezing point curve of S_R . The curve CB' is the metastable vapourization curve of S_R .

3. Triple Points:

- Triple point O represents the equilibrium between S_R , S_M and S_V , corresponding to 95.6°C temperature and 0.006 mm pressure.

- Triple point A represents the equilibrium between S_M , S_L and S_v , corresponding to 120°C temperature and 0.04 mm pressure.
- Triple point C represents the equilibrium between S_M , S_L and S_R , corresponding to 151°C temperature and 1288 atmospheres pressure.
- Metastable triple point B' represents the equilibrium between S_R , S_L and S_v , corresponding to 115°C temperature and 0.03 mm pressure.

At triple points, since three phases are in equilibrium, degree of freedom is zero.

The above discussion is tabulated below ($C = 1$):

Table 2.3

Name of the System	Phases in Equilibrium	Degrees of Freedom $F = C - P + 2$
Areas		
(1) Below BOAD	S_v	
(2) Towards the right of GCAD	S_L	$F = 1 - 1 + 2 = 2$
(3) Towards the left of GCOB	S_R	The systems are bivariant.
(4) AOC	S_M	
Curves		
(1) BO (Sublimation curve of S_R)	S_R and S_v	
(2) OA (Sublimation curve of S_M)	S_M and S_v	
(3) AD (Vaporization curve of S_L)	S_L and S_v	$F = 1 - 2 + 2 = 1$ The systems are univariant.
(4) AC (Melting point curve of S_M)	S_M and S_L	
(5) CG (Melting or freezing point curve of S_R)	S_R and S_L	
(6) OC (Transition curve of S_R)	S_R and S_M	
Triple Points		
(1) Point O – Transition temperature	S_R , S_M and S_v	
(2) Point A – Melting point of S_M	S_M , S_L and S_v	$F = 1 - 3 + 2 = 0$ The systems are invariant.
(3) Point C – Melting point of S_R	S_M , S_L and S_R	
(4) Point B' – Melting point of S_R under metastable conditions	S_R , S_L and S_v	

2.6 REDUCED PHASE RULE EQUATION

[Oct., Dec. 17, May 17, 18]

For a two component system, when $C = 2$, substituting in Gibb's phase rule equation,

$$F = C - P + 2$$

$$F = 2 - P + 2$$

$$F = 4 - P$$

Minimum one phase is required to define the system at equilibrium, i.e., when $P = 1$, $F = 3$. Thus, for two component system, the maximum number of degrees of freedom is three. The phase diagram for two component system can be represented by plotting a three dimensional graph/ diagram of temperature, pressure and composition. In practice, one of the three variables is kept constant and a graph of two variables is considered. Hence, in such cases, the number of degree of freedom gets reduced by 1. Thus, phase rule becomes,

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

$$F = C - P + 1$$

This equation is called as reduced phase rule equation.

When pressure is kept constant, the system is called condensed system. Hence, in such a case, reduced phase rule is also called as condensed phase rule.

2.7 TWO COMPONENTS ALLOY SYSTEM

[May 19]

Two components alloy system follows condensed phase rule. An alloy is a mixture of two metals or of a metal and non-metal, forming a homogeneous mass having unique characteristics. The possible four phases exhibited by an alloy system are two solid phases of two metals or one metal and one non-metal, liquid phase of solution of two solids and gaseous phase of vapours of two solids. However, for an alloy system, gaseous phase is practically absent and effect of pressure is negligible. Thus, an alloy system can be studied by keeping pressure constant. Therefore, reduced or condensed phase rule is applicable for an alloy system.

2.8 PHASE DIAGRAM OF SILVER- LEAD ALLOY SYSTEM

[Dec. 17, May 19]

It is a two component system. It consists of four possible phases, (i) Solid silver (Ag), (ii) Solid lead (Pb), (iii) Liquid of (silver + lead), (iv) Vapour of molten lead and silver which

contributes gas phase. Since gaseous phase is practically absent and effect of pressure is negligible, reduced or condensed phase rule is applicable.

Substituting for $C = 2$ in reduced phase rule equation,

$$F = C - P + 1$$

$$F = 2 - P + 1$$

$$F = 3 - P$$

The minimum number of degree of freedom can be zero for a system, i.e., when $F = 0$, then $P = 3$. This implies that all the three phases can exist in equilibrium for a silver-lead alloy system.

Minimum one phase is required to define the system at equilibrium, i.e., when $P = 1$, $F = 2$. Thus, for silver-lead system, the maximum number of degrees of freedom is two. These two degrees of freedom are temperature and % composition. The phase diagram for two component system can be represented by plotting a graph of temperature against % composition. (Fig. 2.3).

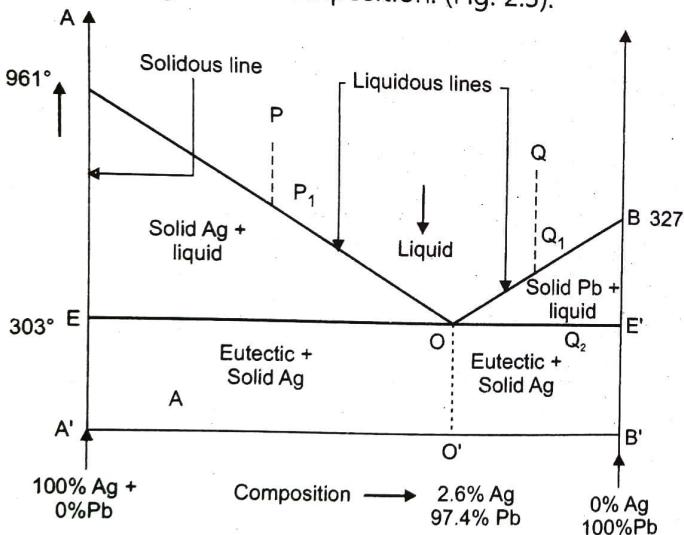


Fig. 2.3: Two component Silver-Lead system

The silver-lead system is explained as follows:

1. Curves:

(i) Curve AO : It is the freezing point curve of silver. The curve starts from point A, at 961°C temperature, which is the melting point of silver. It indicates that on addition of lead to silver, the melting point of silver decreases gradually along AO till point O is reached. At point O, no more lead can go in solution (Point O is the lowest limit where lead can be added to solution) and if it is added, it separates out as solid lead.

(ii) Curve BO : It is the freezing point curve of lead. The curve starts from point B, at 327°C temperature, which is the melting point of lead. It indicates that on addition of silver to lead, the melting point of lead decreases gradually along BO till point O is reached. At point O, no more silver can go in solution (Point O is the lowest limit where silver can be added to solution) and if it is added, it separates out as solid silver.

Along curve AO, solid silver and liquid are in equilibrium while along curve BO, solid lead and liquid are in equilibrium. Thus along both the curves, two phases are in equilibrium and the degree of freedom is one, i.e., either composition or temperature needs to be specified in order to define the system.

- 2. Eutectic Point:** The curves OA and OB meet at point O called eutectic point of the system. At eutectic point, all the three phases, i.e., solid Ag, solid Pb and liquid co-exist in equilibrium.

The degree of freedom is zero, i.e., neither composition nor temperature needs to be specified in order to define the system. At eutectic point, the composition is 2.6% Ag and 97.4% Pb, called eutectic composition whereas temperature is 303°C , called eutectic temperature. Eutectic composition of an alloy is the solid solution of fixed proportions of the constituents involved which has the lowest freezing point. Eutectic phase can exist in the system.

- 3. Area AOB:** It consists of a single phase of liquid of silver and lead and the degrees of freedom are two, i.e., both parameters, composition and temperature needs to be specified in order to define the system.

Consider a sample of liquid melt of Ag and Pb corresponding to point Q, having the composition less than 2.6% Ag is taken. On cooling the melt, the temperature gradually decreases without any change in composition till point Q_1 is reached on curve BO. Further cooling allows the composition to vary along Q_1O and lead starts separating out till the eutectic composition is obtained. Similarly, if a melt having composition more than 2.6% Ag (at point P) is taken and cooled till P_1 , silver gets separated till the eutectic point composition is attained.

The phase diagram also shows following regions:

- Region enclosed by AOE shows a stable composition of solid crystalline silver and the liquid melt of silver and lead.
- Region enclosed by BOE' shows a stable composition of solid crystalline lead and the liquid melt of silver and lead.
- Region enclosed by EOO'A' shows a stable composition of silver crystals and solid eutectic crystals.
- Region enclosed by E'OO'B' shows a stable composition of lead crystals and solid eutectic crystals.

SUMMARY

- Phase rule explains the behaviour of heterogeneous system in equilibrium.
- Gibb's phase rule equation is $F = C - P + 2$
- Terms involved in Phase rule are,
 - (i) Phase (P)
 - (ii) Component (C)
 - (iii) Degree of freedom (F)
- Water system can be explained by a single constituent, H_2O . Hence, it is a single component system. It contains three phases, solid, liquid and gas. Since minimum degree of freedom can be zero, all the three phases can co-exist in equilibrium at a time.
- Sulphur system can be explained by a single constituent, S. Hence, it is a single component system. It contains four phases, two solid, liquid and gas. Since minimum degree of freedom can be zero, only three phases can co-exist in equilibrium at a time.
- In one component systems, at triple point, degree of freedom is zero. Degree of freedom exists at a particular pressure and temperature.
- A system studied by keeping one degree of freedom constant follows reduced phase rule. The Reduced phase rule equation is $F = C - P + 1$

- Silver-Lead alloy system is studied by using reduced phase rule since vapour pressure is practically absent.
- In two component system, at eutectic point, degree of freedom is zero. Eutectic point exists at particular temperature and composition.

EXERCISE

- State Gibb's phase rule.
- Define
 - Phase
 - Component
 - Degree of freedom
- Give number of phases and component involved in the following systems:
 - $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$
 - A mixture of water and alcohol
 - A mixture of water and oil
 - $Ice(s) \rightleftharpoons Water(l) \rightleftharpoons Water\ vapour(g)$
 - $Fe(s) + H_2O(g) \rightleftharpoons FeO(s) + H_2(g)$
 - A mixture of H_2 and N_2
- Draw a phase diagram for sulphur system.
- Explain the application of Gibb's phase rule to water system.
- Describe the triple point of water with suitable phase diagram.
- Elucidate the sulphur system using Gibb's phase rule.
- Explain the triple points shown by sulphur system using phase diagram.
- Explain the application of reduced phase rule to silver-lead system.

UNIVERSITY QUESTIONS

May 2017

- Draw phase diagram of one component water system and explain curves/ lines, triple point and areas of the phase diagram.
- Describe reduced phase rule equation.

[5]

[5]

December 2017

1. State Phase rule equation. Explain the term component of phase rule with examples. [6]
2. What is meant by Eutectic point? Explain Silver-lead two component alloy system with phase diagram. [6]

May 2018

1. State Phase rule equation. Explain the term Phase involved in it with examples. [6]
2. Explain areas, curves, triple point and metastable curve of water system with the help of phase diagram. [6]

December 2018

1. Explain the term Components and degree of freedom involved in it with examples.
2. Explain one component Sulphur system with diagram.

May 2019

1. What is Phase Rule? Explain the term Phase Degree of Freedom with examples.
2. Explain in detail Phase Diagram of Sulphur system.
3. Describe Phase Diagram of two component alloy system.

