4. phase rule

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1) The document discusses Gibbs phase rule, which relates the number of degrees of freedom in a system to the number of components and phases present. …
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- ✓ When a system is in equilibrium, there can be only one temperature and one. Pressure hence, the total of these variables is two only.
- ✓ However, the number of concentration (or composition) variables can be more. In order to define the composition of each phase, it is necessary to specify only (C - 1) composition variables because the composition of the remaining component can be obtained by difference.
- ✓ Since there are P phases, the total number of composition or concentration variables will be P (C -1). On adding the temperature and pressure variables, the total number of variables of the system are P (C — 1) + 2.
- ✓ 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.
- ✓ Thus, if there is one component in three phases $(say\ \alpha, \beta, \&\ \gamma)$ and one of these $(say\ \alpha)$ is referred to as standard phases, then, this fact must be expressed in the form of the following two equations.

$$\mu_\alpha = \mu_\beta$$

$$\mu_\alpha = \mu_\gamma$$

- ✓ Thus, for each component in equilibrium in 3 phases, 2 equations are possible. Hence for each component in 'P' phase, (P - 1) equations can be written. If there are 'C' component the number of equations or variables possible from the conditions of equilibrium are C (P - 1).
- ✓ Since chemical potential is a function of temperature, pressure and concentration, each equation must represent one variable.
- ✓ Hence, the number of possible variables of degree of freedom can be given

$$F = \{P (C - 1) + 2\} - C (P - 1)\} \qquad \therefore\ F = C - P + 2$$

❖ **Terms involved in Gibbs Phase Rule:**

The following terms are involved in phase rule,

1) Phase
2) Components
3) Degrees of Freedom (variance)

1) Phase:

a. Definition:

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

b. Examples:

i. In Waiter system, at freezing point of water, equilibrium exists where ice, water & water vapors are the three phases, each of which is physically distinct and homogeneous, & water definite boundaries between ice, water & water vapors. as,

$$Ice_{(s)} \rightleftharpoons Water_{(L)} \rightleftharpoons Water\ Vapour_{(G)}$$

ii. All gases mix freely to form homogeneous mixtures. Therefore any mixture of gases. say O_2 and N_2 and H_2 forms one phase only.

iii. Two completely miscible liquids yield an 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 Thus, a mixture of the oil and water constitutes a two phase system.

v. An aqueous solution of solid substances like salt (NaCl) through-out. Therefore, it is a one phase system.

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

E.g. Allotropic forms of Sulphur or Carbon, though all exist together but are all separate phases.

vii. Equilibrium given below,

$$\underset{(Solid)}{CaCO_3} \rightleftharpoons \underset{(Solid)}{CaO} + \underset{(Gas)}{CO_2}$$ [Contain two phases solid & gaseous]

$$\underset{(Solid)}{Fe} + \underset{(Gaseous)}{H_2O} \rightleftharpoons \underset{(Solid)}{FeO} + \underset{(Gas)}{H_2}\uparrow$$

Phase: $Ice_{(S)} \rightleftharpoons Water_{(L)} \rightleftharpoons Water\ Vapour_{(G)}$

Component: H_2O H_2O H_2O

ii. In sulphur system, there are four phases, i.e. rhombic sulphur, monocline sulphur, liquid sulphur & sulphur vapors. The composition of all four phases can be expressed by one chemical individual sulphur (S). Hence sulphur system is regarded as one component system.

iii. When calcium carbonate is heated in a closed vessel, the following reaction

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component system, this is because the composition of both can be expressed in terms of NH_4Cl alone.

But if NH_3 or HCl is in excess, the system becomes a two components system.

vi. Saturated solution of NaCl in water contains solid salt, salt solution & water vapors. The chemical composition of all the three phases can be expressed in term of NaCl & H_2O. Hence, it is two component system.

vii. Dissociation reaction,

$$\underset{(Solid)}{CuSO_4 . 5H_2O} \rightleftharpoons \underset{(Solid)}{CuSO_4 . 3H_2O} + \underset{(Gas)}{2H_2O}$$

(Two Component System: $CuSO_4$ and H_2O)

3) Degree of Freedom (Variance):

a. Definition:

Term degree of freedom is defined as, "the minimum number of independently variable factors such as temperature, pressure and composition of the phases which must be arbitrarily specified in order to represent perfectly the condition of a system.

b. Examples:

i. In case of Water System:

- If all the three phases are in equilibrium, then no condition need to be specified because the three phases can be in equilibrium only at particular temperature and pressure,

$$Ice_{(s)} \rightleftharpoons Water_{(L)} \rightleftharpoons Water\ Vapour_{(G)}$$

The system is no degree of freedom or invariant or zero variant or non-variant.

- If condition or pressure in altered, three phases will not remain in equilibrium and one of the phase disappears.

$$Water_{(L)} \rightleftharpoons Water\ Vapour_{(G)}$$

We must state either the temperature or pressure to define it completely. Hence the degree of freedom is one system univariant.

- For a system consisting of water in vapor phase only we must state the values of both, the temperature and pressure in order to describe the system completely. Hence, the system has two degree of freedom or system is bivariant.

ii. For mixture of gases, degree of freedom is two because a system containing a of two or more gases e.g. $N_2 + H_2$ is completely defined when its temperature and pressure are specified. If pressure and temperature are specified, the composition, i.e. third variable could be automatically definite. Some, it is necessary to specify two variable to define a system completely. Hence, the system is a bivariant.

iii. A system containing saturated solution of sodium chloride in equilibrium with a solid sodium chloride and water vapor is

$$\underset{(Solid)}{NaCl} \rightleftharpoons \underset{(Solutoin)}{NaCl-Water} \rightleftharpoons \underset{(Gas)}{Water\ Vapour}$$

Completely defined if the temperature is specified. Hence, the system has one degree of freedom. The other two variables, i.e. composition of NaCl solution, a pressure have definite value at a fixed temperature.

❖ **One Component System (Water):**

- In one component system, the equilibrium conditions may be represented with the help of diagrams taking pressure and temperature as the two axes. This diagram is called as **Pressure-Temperature (P-T) diagram.**
- In this diagram any line or curve represents an univariant system, because equilibrium conditions at any point on line could be completely defined by just fixing either temperature or pressure.
- All areas represents bivariant systems, because to define the completely at any point in the area, both temperature and pressure should be fixed.
- In the diagram where all the three phases are in contact with each other at a specific point called as triple point represents zero variant system because system is completely defined by itself.

➢ **Water system:**

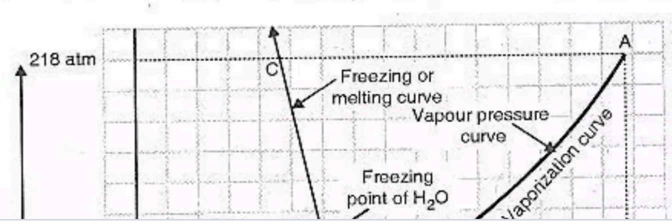
- The water system under normal condition is of three phases and one component system. The system involved three phases are solid - ice, liquid -water, and gas - water vapors. All these phases can be represented by one chemical entity 1120, hence it is one component system.

$$\underset{H_2O}{Ice_{(s)}} \rightleftharpoons \underset{H_2O}{Water_{(L)}} \rightleftharpoons \underset{H_2O}{Water\ Vapour_{(G)}}$$

- Let us apply the phase rule to one component, i.e. water system. Substitute the

- From the above value of degree of freedom (F), we can say that, the degree freedom (F) depends on the number of phases present at the equilibrium.
- Therefore, the following three different cases are possible, (Explained with the help of phase diagram,
- Hence when,

P = 1	Then F = 2	System is Bivariant
P = 2	Then F = 1	System is Monovariant
P = 3	Then F = 0	System is Zero Variant



vi. Hence, each two phases system has one degree of freedom, i.e. system ..

of stable existence. Thus,

i. Area AOC represents conditions for liquid phase, i.e. water.
ii. Area AOB represents conditions for gaseous phase, i.e. water vapour.
iii. Area BOC represents conditions for solid phase, i.e. ice.

b. In all the three areas, there being one phase' and 'one component'.
Therefore,

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

c. Hence, each system has two degree of freedom, i.e. system is bivariant or divarient.

3) The Triple Point 'O':

a. All the three curves, OA, OB and OC meet at the point 0- called as where all the tree phases solid, liquid and vapour are simultaneously in equilibrium.

b. This triple point occurs at 0.0675'C and 4.58 mm Hg pressure. Since, are three phases and one component, therefore

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

c. The system at triple point is zero variant or nonvariant. Thus, neither pressure nor temperature can be altered.

d. Even slightly changed three phases would not exist if one of the phase disappears.

➢ **Reduced or Condensed Phase Rule:**

- When a single phase is present in a two component system, then the degree of freedom (F) is represented by following equations.

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

- From the values of F (F = 3) we can say that, three variables must be specified in order to describe the condition of phase, i.e. in addition to

4. phase rule

1. **INFOMATICA ACADEMY CONTACT:** 9821131002/9029004242 Degree Sem - I Phase Rule146 Phase Rule ⊠ Syllabus: ⊠ Gibb's phase Rule, Explanation, One Component System (Water), Reduced Phase Rule, Two components System (Pb-Ag), Limitations of phase Rule. ⊠ Introduction: ⊠ Phase rule is an important generalization given by Willard Gibbs (1874) inch deals with the behavior of heterogeneous systems in the state of equilibrium. ⊠ In general, with the application of phase rule, it has been possible to predict qualitatively (by means of a diagram) the effect of changing temperature, pressure and concentration on a heterogeneous system in equilibrium. Such a diagram is known as 'phase diagram. ⊠ This heterogeneous system containing two or more different phases which exist in equilibrium with each other is studied with the help of generalization called phase rule. This rule was deduced on the basis of principles of thermodynamic by an American physicist Willard Gibbs to explain the equilibrium existing in heterogeneous system. ⊠ 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. This rule does not have an exception, if applied properly by maintaining the variables at a fixed level. ⊠ Explanation: ⊠ Let us consider a heterogeneous system in equilibrium consisting of "C" components distributed in 'P' phases. 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. ⊠ Obviously, the number of such variables is given by the total number of variables of the system minus the number of variables which are defined automatically by virtue of the system being in equilibrium.

2. **INFOMATICA ACADEMY CONTACT:** 9821131002/9029004242 Degree Sem - I Phase Rule147 ⊠ When a system is in equilibrium, there can be only one temperature and one: Pressure hence, the total of these variables is two only. ⊠ However, the number of concentration (or composition) variables can be more. In order to define the composition of each phase, it is necessary to specify only (C - 1) composition variables because the composition of the remaining component can be obtained by difference. ⊠ Since there are P phases, the total number of composition or concentration variables will be P (C -1). On adding the temperature and pressure variables, the total number of variables of the system are P (C — 1) + 2. ⊠ 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. ⊠ Thus, if there is one component in three phases ⊠ ⊠, ,&say ⊠ ⊠ ⊠ and one of these ⊠ ⊠say ⊠ is referred to as standard phases, then, this fact must be expressed in the form of the following two equations. ⊠ ⊠⊠ ⊠⊠ ⊠ ⊠⊠ ⊠⊠ ⊠ Thus, for each component in equilibrium in 3 phases, 2 equations are possible. Hence for each component in 'P' phase, (P - 1) equations can be written. If there are 'C' component the number of equations or variables possible from the conditions of equilibrium are C (P - 1). ⊠ Since chemical potential is a function of temperature, pressure and concentration, each equation must represent one variable. ⊠ Hence, the number of possible variables of degree of freedom can be given F = {P (C - 1) + 2} - C (P - 1)} ⊠ F = C – P + 2 ⊠ Terms involved in Gibbs Phase Rule: The following terms are involved in phase rule, 1) Phase 2) Components 3) Degrees of Freedom (variance) 1) Phase: a. Definition: A Phase is defined as any homogeneous, physically distinct and mechanically separable portion of a system, which is separated from other such parts the system by definite boundary surfaces.

3. **INFOMATICA ACADEMY CONTACT:** 9821131002/9029004242 Degree Sem - I Phase Rule148 b. Examples: i. In Waiter system, at freezing point of water, equilibrium exists where ice, water & water vapors are the three phases, each of which is physically distinct and homogeneous, & water definite boundaries between ice, water & water vapors. as, ⊠ ⊠ ⊠ ⊠ ⊠ ⊠s L G Ice Water Water Vapour ii. All gases mix freely to form homogeneous mixtures. Therefore any mixture of gases. say 2O and 2N and 2H forms one phase only. iii. Two completely miscible liquids yield an 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 Thus, a mixture of the oil and water constitutes a two phase system. v. An aqueous solution of solid substances like salt (NaCl) through-out. Therefore, it is a one phase system. vi. Each solid substance makes a separate phase except in the case of solid solutions. E.g. Allotropic forms of Sulphur or Carbon, though all exist together but are all separate phases. vii. Equilibrium given below, ⊠ ⊠ ⊠ ⊠ ⊠ ⊠ 3 2CaCO CaO CO Solid Solid Gas ⊠ [Contain two phases solid & gaseous] ⊠ ⊠ ⊠ ⊠ ⊠ ⊠ ⊠ ⊠ 2 2Fe H O FeO H Solid Gaseous Solid Gas ⊠ ⊠ ⊠ (Two phases exist in equilibrium) 2) Components: a. Definition: The term component is defined as, —the smallest number of independently variable constituents taking part in the state of equilibrium by means of which the composition of each phase can be expressed directly or in the form of chemical equation. b. Examples: i. In 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. 2H O Hence system is regarded one component system.

4. **INFOMATICA ACADEMY CONTACT:** 9821131002/9029004242 Degree Sem - I Phase Rule149 Phase: ⊠ ⊠ ⊠ ⊠ ⊠ ⊠S L G Ice Water Water Vapour Component: 2 2 2H O H O H O ii. In sulphur system, there are four phases, i.e. rhombic sulphur, monocline sulphur, liquid sulphur & sulphur vapors. The composition of all four phases can be expressed by one chemical individual sulphur (S). Hence sulphur system is regarded as one component system. iii. When calcium carbonate is heated in a closed vessel, the following reaction takes place. ⊠ ⊠ ⊠ ⊠ ⊠ ⊠3 2S S G CaCO CaO CO ⊠ ⊠ From the above reaction, it comes to know that, there are three phases ⊠ ⊠3 S CaCO , ⊠ ⊠S CaO and ⊠ ⊠2 G CO . Thus, the decomposition of 3CaCO , gives ⊠ ⊠S CaO and ⊠ ⊠2 G CO i.e. system is two component system. Although this system has three different constituents, it is considered as two component system because the composition of each of the above phase can be expressed in terms of any two of the three constituents present. This can be understood from following illustration. If only 3CaCO & CaO considered as components, then composition of each can be given as, Phase : ⊠ ⊠ 3 3 0CaCO CaCO CaO zero ⊠ ⊠ Phase : ⊠ ⊠ 30CaO CaCO CaO zero ⊠ ⊠ Phase: 2 3CO CaCO CaO⊠ ⊠ Thus, it is a two components system. iv. In the equilibrium. for reaction between non-metal and steam, ⊠ ⊠ ⊠ ⊠ ⊠ ⊠ ⊠ ⊠2 2S G S G Fe H O FeO H⊠ ⊠ The composition of each phase can be expressed in terms of the components. Fe 2H Oand 2H . Hence, it is a three component system. v. In the dissociation of 4NH Cl & in a closed vessel, which can be represented as, ⊠ ⊠ ⊠ ⊠ ⊠ ⊠ ⊠ 4 4 3NH Cl NH Cl NH HCl Solid Gas Gas Gas ⊠ In this case if proportions of 2NH & HCl are equivalent, then the system is one

5. **INFOMATICA ACADEMY CONTACT:** 9821131002/9029004242 Degree Sem - I Phase Rule150 component system, this is because the composition of both can be expressed in terms of 4NH Cl alone. But if 3NH or HCl is in excess, the system becomes a two components system. vi. Saturated solution of NaCl in water contains solid salt, salt solution & water vapors. The chemical composition of all the three phases can be expressed in term of NaCl & 2H O. Hence, it is two component system. vii. Dissociation reaction, ⊠ ⊠ ⊠ ⊠ ⊠ ⊠ 4 2 4 2 2. 5 . 3 2CuSO H O CuSO H O H O Solid Solid Gas ⊠ (Two Component System: 4 2andCuSO H O) 3) Degree of Freedom (Variance): a. Definition: Term degree of freedom is defined as, —the minimum number of independently variable factors such as temperature, pressure and composition of the phases which must be arbitrarily specified in order to represent perfectly the condition of a system. b. Examples: i. In case of Water System: ⊠ If all the three phases are in equilibrium, then no condition need to be specified because the three phases can be in equilibrium only at particular temperature and pressure, ⊠ ⊠ ⊠ ⊠ ⊠ ⊠s L G Ice Water Water Vapour The system is no degree of

freedom or invariant or zero variant or non- variant. ⊠ If condition or pressure in altered, three phases will not remain in equilibrium and one of the phase disappears. ⊠ ⊠ ⊠L G Water Water Vapour We must state either the temperature or pressure to define it completely. Hence the degree of freedom is one system univariant. ⊠ For a system consisting of water in vapor phase only we must state the values of both, the temperature and pressure in order to describe the system completely. Hence, the system has two degree of freedom or system is bivariant. ii. For mixture of gases, degree of freedom is two because a system containing a of two or more gases e.g. 2 2N H⊠ is completely defined when its temperature

6. **INFOMATICA ACADEMY CONTACT:** 9821131002/9029004242 Degree Sem - I Phase Rule151 and pressure are specified. If pressure and temperature are specified, the composition, i.e. third variable could be automatically definite. Some, it is necessary to specify two variable to define a system completely. Hence, the system is a bivariant. iii. A system containing saturated solution of sodium chloride in equilibrium with a solid sodium chloride and water vapor is ⊠ ⊠ ⊠ ⊠ ⊠ ⊠ NaCl NaCl Water Water Vapour Solid Solutoin Gas ⊠ Completely defined if the temperature is specified. Hence, the system has one degree of freedom. The other two variables, i.e. composition of NaCl solution, a pressure have definite value at a fixed temperature. ⊠ One Component System (Water): ⊠ In one component system, the equilibrium conditions may be represented with the help of diagrams taking pressure and temperature as the two axes. This diagram is called as Pressure-Temperature (P-T) diagram. ⊠ In this diagram any line or curve represents an univariant system, because equilibrium conditions at any point on line could be completely defined by just fixing either temperature or pressure. ⊠ All areas represents bivariant systems, because to define the completely at any point in the area, both temperature and pressure should be fixed. ⊠ In the diagram where all the three phases are in contact with each other at a specific point called as triple point represents zero variant system because system is completely defined by itself. ⊠ Water system: ⊠ The water system under normal condition is of three phases and one component system. The system involved three phases are solid - ice, liquid -water, and gas - water vapors. All these phases can be represented by one chemical entity 1120, hence it is one component system. ⊠ ⊠ ⊠ ⊠ ⊠ ⊠ 2 2 2 s L G Ice Water Water Vapour H O H O H O ⊠ Let us apply the phase rule to one component, i.e. water system. Substitute the value of component (C)=1, in the phase rule equation, then the equation is F = C – P + 2 F = 1 – P + 2 F = 3 – P

7. **INFOMATICA ACADEMY CONTACT:** 9821131002/9029004242 Degree Sem - I Phase Rule152 ⊠ From the above value of degree of freedom (F), we can say that, the degree freedom (F) depends on the number of phases present at the equilibrium. ⊠ Therefore, the following three different cases are possible, (Explained with the help of phase diagram, ⊠ Hence when, P = 1 Then F = 2 System is Bivariant P = 2 Then F = 1 System is Monovariant P = 3 Then F = 0 System is Zero Variant ⊠ From the above equation it is clear that, for any one component system, the urn number of degree of freedom is two and most convenient variables pressure & temperature. In the above phase diagram of water system following salient Coat ores are observed. 1) The curves OA, OB & OC 2) The areas AOC, AOB & BOC 3) The triple point 'O' 4) The metastable curve (OA')

8. **INFOMATICA ACADEMY CONTACT:** 9821131002/9029004242 Degree Sem - I Phase Rule153 1) The curves OA, OB & OC: These three curves meet at the point '0' (called as tripple point) and divide the diagram in to three areas. Therefore, these three curves are known as boundary lines. a. Curve OA (Vapor Pressure Curve): i. The curve OA terminates at A, the critical point 218 atm. and 374° temperature ii. It represents the vapor pressure of liquid water at different temperature. iii. The two phases, water and vapor coexist in equilibrium along this curve. Here, are two phases (P = 2) and one component (C = 1), therefore F = 1- 2 + 2 = 1 iv. Hence system is monovariant t or univariant or having one degree of freedom. When the vapor pressure is equal to one atmosphere, the temperature C as shown in figure is the boiling point of water i.e. 100°C. b. Curve OB (Sublimation Curve): i. The curve OB terminates at B, the absolute zero, i.e. - 273 temperature. It shows the vapour pressure of solid ice at different temperature. ii. The two phases, solid-ice and water-vapour coexist in equilibrium along this curve. Therefore, degree of freedom for this system is also one and system is monovariant. c. Curve OC (Fusion Curve): i. The curve OC terminates at C, the critical pressure. The two phases, solid-ice and liquid-water coexist in equilibrium. ii. This curve indicates that the melting point of ice decreases with increase of pressure. iii. The one atmosphere (1.0 atm.) line meets the fusion (freezing/melting) curve at 0°C which is the normal melting point of ice. Again, along the curve OC, _ there are two phases in equilibrium and system is of one component. iv. Therefore, the system is monovariant. v. From the above discussion, we can say that, along the curves OA, OB and OC there are two phases in equilibrium and one component. Therefore, F = C – P + 2 F = 1 – 2 + 2 F = 1

9. **INFOMATICA ACADEMY CONTACT:** 9821131002/9029004242 Degree Sem - I Phase Rule154 vi. Hence, each two phases system has one degree of freedom, i.e. system of is univariant or monovariant. 2) The areas AOC, AOB & BOC: a. The regions or areas between the curves show the condition temperature and pressure under which a single phase, i.e. ice, water vapour is capable of stable existence. Thus, i. Area AOC represents conditions for liquid phase, i.e. water. ii. Area AOB represents conditions for gaseous phase, i.e. water vapour. iii. Area BOC represents conditions for solid phase, i.e. ice. b. In all the three areas, there being one phase' and 'one component'. Therefore, F = C – P + 2 F = 1 – 2 + 2 F = 1 c. Hence, each system has two degree of freedom, i.e. system is bivariant or divarient. 3) The Triple Point 'O': a. All the three curves, OA, OB and OC meet at the point 0- called as where all the tree phases solid, liquid and vapour are simultaneously in equilibrium. b. This triple point occurs at 0.0675'C and 4.58 mm Hg pressure. Since, are three phases and one component, therefore F = C – P + 2 F = 1 – 3 + 2 F = 0 c. The system at triple point is zero variant or nonvariant. Thus, neither pressure nor temperature can be altered. d. Even slightly changed three phases would not exist if one of the phase disappears. ⊠ Reduced or Condensed Phase Rule: ⊠ When a single phase is present in a two component system, then the degree of freedom (F) is represented by following equations. F = C – P + 2 F = 2 – 1 + 2 F = 3 ⊠ From the values of F (F = 3) we can say that, three variables must be specified in order to describe the condition of phase, i.e. in addition to

10. **INFOMATICA ACADEMY CONTACT:** 9821131002/9029004242 Degree Sem - I Phase Rule155 temperature and pressure the concentration of one of the component has to be given. ⊠ Two Component System (Pb-Ag): General characteristic of two-component system 1) The maximum no. of phases in a two-component system will be four. P = C – F + 2 = 2 – 0 + 2 = 4 (Maximum no. of phases exists when degree of freedom = 0 Negative degree of freedom cannot exist). 2) The maximum no. of degrees of freedom in a two-component system will be three (i.e. when the system exists as a single phase). F = C – P + 2 = 2 – 1 + 2 = 3 3) The system will have three variables namely, temperature, pressure & concentration. 4) The composition of all the individual phases of the system can be expressed by means of not less than two components. 5) For constructing a phase diagram of a two components system, a three dimensional space model is required using the three variables (viz., temperature, pressure & concentration) as its coordinates. ⊠ Phase Rule for two Components Alloy System: ⊠ In two components system when P = 2 degree of freedom (F) has the highest value, i.e. 3 F = C – P + 2 = 2 – 1 + 2 = 3 ⊠ Consequently three variables – temperature, pressure & concentration of one of the two components must be specified in order to describe the system completely. ⊠ Since the maximum no. of degrees of freedom in two components system is three, the phase behavior of a binary system may be represented by a three-dimensional diagram of pressure, temperature & concentration or space models which cannot be conveniently shown on paper. ⊠ A solid-liquid equilibrium of an alloy has practically no gas phase & the effect of pressure is small on this type of equilibrium. Therefore, experiments are, usually conducted under atmospheric pressure. ⊠ Thus, keeping the pressure constant or a system in which rap not considered, is known as condensed system. ⊠ Since pressure is kept constant (at 1 atmosphere). ⊠ It will reduce the degrees of freedom of the system by one, and for such a system, the phase rule becomes F = C - P + 1

11. **INFOMATICA ACADEMY CONTACT:** 9821131002/9029004242 Degree Sem - I Phase Rule156 ⊠ This is known as the reduced phase rule having two variables, namely, - temperature and concentration (or composition) of the constituents. ⊠ Lead Silver System: ⊠ This system has two component and four phases. The phases are: 1) Solid silver 2) Solid lead 3) Solution of molten silver and lead and 4) Vapour But the boiling points of silver and lead being considerably high, the vapour phase is practically absent. ⊠ Since the pressure has nearly no effect on equilibrium so the system can be conveniently represented by a temperature-concentration diagram at a constant and one variable pressure which is neglected, the condensed form of the phase rule: F = C – P +1 = 2 – P + 1 = 3 –P will be applicable. ⊠ When system containing two phases and two components like solid and liquid, then solid-liquid equilibrium has practically no gas phase and the effect of pressure is very small that is negligible. Then, it is necessary to take into account the remaining variables, viz. temperature and concentration. Such a solid-liquid system with the gas phase is absent is called a condensed system. ⊠ The experimental measurements of temperature and concentration in condensed systems are usually carried out under atmospheric pressure. ⊠ Since, the degree of freedom in such case is reduced by one, therefore, it can be also termed as reduced phase rule and represented by the equation F = C – P + 1 ⊠ The reduced phase rule is more convenient to apply to solid –li quid two components condensed system. Example: Pb - Sb, Ag - Pb or Zn – Cd system. ⊠ The complete Temperature – Concentration (T-C Phase) phase diagram of the system Silver – Lead (Ag - Pb) is shown in fig.

12. **INFOMATICA ACADEMY CONTACT:** 9821131002/9029004242 Degree Sem - I Phase Rule157 ⊠ In the phase diagram shown above of Pb-Ag system, following salient features are observed. 1) The curve AO (Freezing curve of Ag) 2) The curve BO (Freezing curve of Pb) 3) The eutectic point 'O' 4) The Area AOB 1) Curve AO (Freezing curve of Ag): a. It shows the effect on freezing point of Ag on addition of lead in small quantities. b. The curve starts from A (9610c) the melting point of Ag, where pure Ag coexists as solid and liquid (vapour being neglected) c. This curve indicates that the melting point of Ag falls gradually on adding Pb, along AO, till the lowest point O (3030c) is reached, where the solution gets saturated with respect of lead. At O, no more lead can go in solution and consequently, the melting point does not fall any further, and if any lead is added, it separates as the solid phase. d. Along this curve, solid Ag and solution (vapour being negligible) coexist and hence, according to reduced phase rule equation: F = 3 – P = 3 – 2 = 1 i.e. the system is univariant. The point O (3030c) corresponds to a fixed composition of 2.6% Ag and 97.4% Pb and is known as eutectic composition. On cooling the whole mass crystallizes out as such.

13. **INFOMATICA ACADEMY CONTACT:** 9821131002/9029004242 Degree Sem - I Phase Rule158 2) Curve BO (Freezing curve of Pb): a. It represents the effect on freezing point of Pb on gradual addition of small amounts of Ag to it. Point B is the melting point of pure lead (3270c) b. Along BO, the melting point gradually falls on the addition of Ag, till lowest point O is reached. c. At this point the solution gets saturated with respect to Ag and the melting point of lead does not fall any more. d. On cooling the whole mass (having eutectic composition) crystallizes out. The system is univariant like AO. 3) Point O (Eutectic point) : a. The two curves AO and BO meet at O, where three phases-solid Ag, solid Pb and their solution coexist and according to condensed phase rule, the system will be invariant (F =3 – P = 3 – 3 = 0) b. The point O (3030c) represents a fixed composition of Ag = 2.6%: Pb =97.4% and is called eutectic composition temperature. c. At the eutectic composition point, the temperature remains constant, until the whole of the melt solidifies in block to become solid of eutectic composition. d. However, further cooling results in the simultaneous crystallization of a mixture of Ag and Pb in relative amounts corresponding to eutectic point O. e. Below the temperature line of the eutectic temperature, we have two regions in the diagram viz. i. Region marked as eutectic +solid Ag, in which crystalline silver and solid eutectic are stables, and. ii. Region marked eutectic + Pb, in which crystalline lead and solid eutectic are stable. 4) Area AOB: a. It represents solution of Pb-Ag. If a sample of lead containing less than 2.6% Ag is taken, at an arbitrary point on curve. On allowing the mass to cool, the temperature gradually falls without any change in composition till this point is reached on the curve BO (point may be 'P')

b. On lowering the temperature, lead begins to separate out and the composition varies along PO till point O is reached. c. On further cooling the whole mass solidifies in block to the eutectic composition (2.6% Ag: 97.4% Pb)

14. **INFOMATICA ACADEMY CONTACT:** 9821131002/9029004242 Degree Sem - I Phase Rule159 Application of Pattinson's Process: The above principle is utilized in the Pattinson's process of desilverization of lead. If a sample of argentiferious lead, containing less than 2.6% Ag, is allowed to cool gradually, lead will separate out & the solution will become progressively richer in Ag, till the % 2.6 of Ag is reached, and on further cooling, the whole mass will solidify as such. On the other hand, if lead-silver alloy containing Ag greater than 2.6% is allowed to cool, then pure silver separates along the curve AO, till the eutectic composition at O is reached. Application of Phase Rule: 1) It applied to physical as well as chemical phase reaction. 2) It provides a convenient basis for classification of equilibrium states of systems with the help of phases, components & degree of freedom. 3) It applies to microscopic systems. 4) It indicates that different systems having the same degree of freedom behave in a similar fashion. 5) It helps in predicting the behavior of a system under different condition of the governing variables. 6) It helps in deciding whether the given no. of substances together would exist in equilibrium under a given set of conditions or whether some of them will have to be inter converted or eliminated. 7) Phase rule does not take any cognizance of the nature of the amounts of substances present in the system. Demerits of Phase Rule: 1) It applies to physical as well as chemical phase reaction. 2) It provides a prevenient basis for classification of equilibrium states of with the help or phases, components and degree of freedom. 3) It applies to microscopic systems. 4) It indicates that different systems having the same degrees of freedom have in a similar fashion. 5) It helps in predicting the behavior of a system under different conditions of the governing variables. 6) It helps in deciding whether the given number of substances together would exist in equilibrium under a given set of conditions or whether some of them will have to be inter converted or eliminated. Phase rule does not take any cognizance of the nature

15. **INFOMATICA ACADEMY CONTACT:** 9821131002/9029004242 Degree Sem - I Phase Rule160 of the amounts of substances present in the system. Theory Questions: 1) State Gibbs phase rule with equation. 2) Explain the term condensed' or 'reduced' phase rule. 3) What it Triple Point? 4) Explain the term 'Degree of Freedom' with examples. 5) What do you understand by the term Phase'' and "Component"? 6) State Gibb's phase rule & explain the various terms involved in it with examples. 7) What is phase rule & explain the application of phase rule to "One Component" or "Water System"? 8) State limitations of phase rule. 9) Explain shape memory effect & give its application. University Questions: Dec 2007 1) Give the demerits / limitations of phase rule. (2 Marks) 2) State & explain phase rule. Discuss the application of phase rule to one component water system. (7 Marks) May 2008 3) What is triple point in phase diagram? Explain it Component system phase diagram. (2 Marks) 4) Explain any of the following terms: (6 Marks) a. Phase b. Components c. Degrees of freedom 5) State and explain condensed phase rule. (3 Marks) Dec 2008 6) State and explain condensed phase rule. (3 Marks) 7) Explain Heat resisting steels with suitable examples. (3 Marks) 8) Define Gibb's phase rule equation? Explain the application to one component system. (5 Marks) 9) What are stainless steels? Explain the specific effects of following on the properties of steels: a. Molybdenum c. Tungsten b. Silicon d. Cobalt (5 Marks)

16. **INFOMATICA ACADEMY CONTACT:** 9821131002/9029004242 Degree Sem - I Phase Rule161 May 2009 10) What is triple point? Explain it with reference to one component water system. (3 Marks) 11) What is condensed phase rule equation? Explain its application with the help of phase diagram to two Component Lead - Silver (Pb-Ay) system (6 Marks) 12) State phase rule equation. Mention any three application. (3 Marks) Dec 2009 13) What is triple? With reference to water-system explain it. (3 Marks) 14) State the limitations Phase Rule. (3 Marks) May 2010 15) Explain the terms: a. Degree of freedom b. Component. 16) What is phase rule? Discuss in brief Lead-silver equilibrium with diagram. (5 Marks) 17) One component system-water. (5 Marks) Dec 2010 18) What are the advantages / applications / merits of phase rule? (3Marks) May 2011 19) State the limitations of the phase rule. (3 Marks) 20) State condensed Phase Rule? Explain the Lead-Silver System with phase diagram. (5 Marks) 21) Write a short note on Component System. (8 Marks) Dec 2011 22) Explain the application of phase rule to one component system. (5 Marks) May 2012 23) Using phase rule, find the number of degrees of freedom (F) in the following systems at equilibrium. (5 Marks) a. In the water system, when Ice (s) water (I) water vapour (g) b. A gaseous mixture of Nitrogen and Hydrogen. 24) Explain application of Gibbs Phase Rule to one component system- water system. (5 Marks)