UCB008- Phase Rule -Tutorial –Solution

1. State phase rule.

   It is defined as, In heterogeneous systems, if equilibrium between phases are not influenced by gravity, magnetic & electrical forces, but are influenced only by pressure, temperature and concentration, then the number of degree of freedom (F) of the system is related to number of components (C) and number of phases(P) by the following phase rule equation F=C-P+2.

2. Define phase, component and degree of freedom with examples.

   Phase: *A phase is defined as any homogeneous and physically distinct part of a system which is bounded by a surface and is mechanically separable from other parts of the system.*

   Water consists of three phases

   $$\text{Ice (S)} \leftrightarrow \text{Water (l)} \leftrightarrow \text{Water vapor (g)}$$

   - *a gaseous mixture, miscible in all proportions, will constitute only one phase.*
   - *two immiscible liquids (benzene and water) will form two liquid phases.*
   - *two miscible liquids (i.e. alcohol and water) will form one separate phase.*
   - *a solution of a substance in a solvent consists of one phase only e.g.: Sugar solution in water.*
   - *A heterogeneous mixture like $CaCO_3$ (S) ↔ CaO(S) + CO_2 (g) Consists of three phases (i.e. two solids and one gaseous)*

   Component: *The number of components of a system at equilibrium is defined as the smallest number of independently variable constituents by means of which the composition of each phase can be expressed either directly or in terms of chemical equilibrium.*

   It can be expressed by the following equation

   $$C = N - E;$$

   Whereas *C is Component, N is Number of distinct chemical species, E = Number of independent equations relating the concentrations of N species.*

   Conditions:

   (i) Each independent chemical equilibrium involving the constituents counts as one equation.

   (ii) A solution be electrically neutral also counts as one equation if ions are considered as constituents.

   Example

   Water: ice ↔ liquid ↔ vapor) each phase can be expressed by a single chemical species H_2O and therefore is a one component system

Sulphur: *(rhombic ↔ monoclinic ↔ liquid ↔ vapor) can be expressed as S and therefore is a one component system*

Aqueous solution of sugar: *Two different chemical species (sugar and water) hence **two component system***

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

Here N = 3 E = 1 (equilibrium between the species), So, C= N-E = 3-1=2

$$NH_4Cl(s) \leftrightarrow NH_3(g) + HCl(g) \text{ in closed system}$$

here N = 3 E = 2, (one equilibrium equation and other partial pressure equation $p_{NH_3} = p_{HCl}$), hence C= N-E = 3-2=1

$NH_4Cl(s) \leftrightarrow NH_3(g) + HCl(g)$ in closed system but if NH_3 was already present

here N = 3 E = 2, (only equilibrium equation preserves) hence C= N-E = 3-1=2

The Degree of Freedom

The degree of freedom of a system is defined as the minimum number of independent variables such as temperature, pressure and concentration (or composition) which must be specified in order to define the state of the system completely.

It can be calculated using phase rule equation F=C-P+2

Example:

Pure gas: phase =1, component =1 hence F = C-P+2 = 1-1+2 = 2 i.e., either P and V or P and T

3. Give the number of phases, components and degree of freedom for the following:
   (i) Mixture of N_2 and H_2 contained in a vessel
   P =1; C=2, So, F= 1-2+2 = 3
   (ii) Ice, water and vapor in equilibrium i.e., ice ↔ water↔ vapor;
   Three different phases with a single component, F=1-3+2 = 0 (Univariant system)
   (iii) An unsaturated sugar solution
   Single phase with two component, F=1-2+2 = 1
   (iv) Dissociation of NH_4Cl in a closed vessel
   C=1 & phase 2 (explained earlier) So, F = 1-2+2 = 1
   (v) Dissociation of NH_4Cl in a closed vessel closed vessel containing NH3 also.
   C=2 & phase 2 (explained earlier) So, F = 2-2+2 = 2

4. Explain why KCl-NaCl-H2O system should be regarded as a 3-component system whereas KCl- NaBr-H2O system should be regarded as 4-component system.

Solution : We know that the number of components is given by $C = N - E$ where N is the number of species (constituents) and E is the number of *independent* equations relating their concentrations. For the $KCl - NaCl - H_2O$ system, $N=3$ (*viz.*, KCl, NaCl, H_2O). Since there is no independent equation relating their concentration, hence $E=0$.

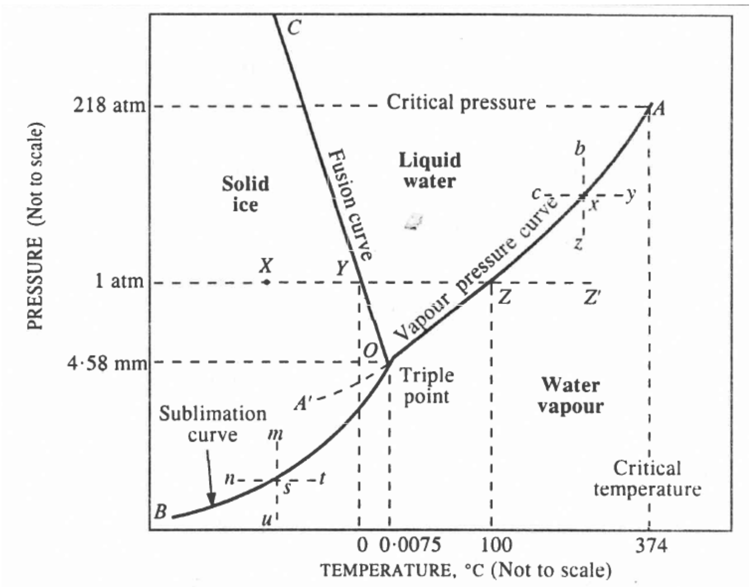
$\therefore$ $C = 3 - 0 = 3$

For the $KCl-NaBr-H_2O$ system, $N = 5$ (*viz.*, KCl, NaBr, NaCl, KBr, H_2O)

$E = 1$, *viz.*, $KCl + NaBr \rightleftharpoons KBr + NaCl$

$\therefore$ $C = N - E = 5 - 1 = 4$

5. Draw well labeled phase diagram of water system.



6. What is the effect of increase of pressure on the melting point of ice?

The curve OC in above figure represents melting point curve of ice i.e., Ice $\leftrightarrow$ Water which shows the effect of pressure on the melting point of ice.

The curve is slightly inclined towards pressure axis that implies melting point of ice decreases with increase of pressure.

7. What is an invariant system? Give an example.

Invariant means the degrees of freedom (F) = 0

Triple point

At this point *Ice (S) $\leftrightarrow$ Water (l) $\leftrightarrow$ Water vapor (g)*

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

8. Differentiate between true and metastable equilibrium.

True equilibrium *exists when the same state in the system can be achieved from either direction. Thermodynamically, true equilibrium is attained when the free energy content is minimum for given values of variables*

Ice $\leftrightarrow$ Liquid water at 1 atmosphere and 0^0C

Metastable equilibrium *can be realized carefully from one direction only and is distributed by slight variation such as shock, stirring, etc.*

Liquid water ↔ water vapor system at –5⁰C

9. What is the difference between triple point and critical point?

Triple point*: The triple point of a substance is the unique temperature and pressure at which the three phases (gas, liquid and solid) of that substance coexist in thermodynamic equilibrium i.e., C=1; P=3; F = 1-3+2 =0*

Critical point*: A point on a phase diagram at which both the liquid and gas phases of a substance have the same density, and are therefore indistinguishable.*

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

10. What is the condensed phase rule?

Used to define two component system

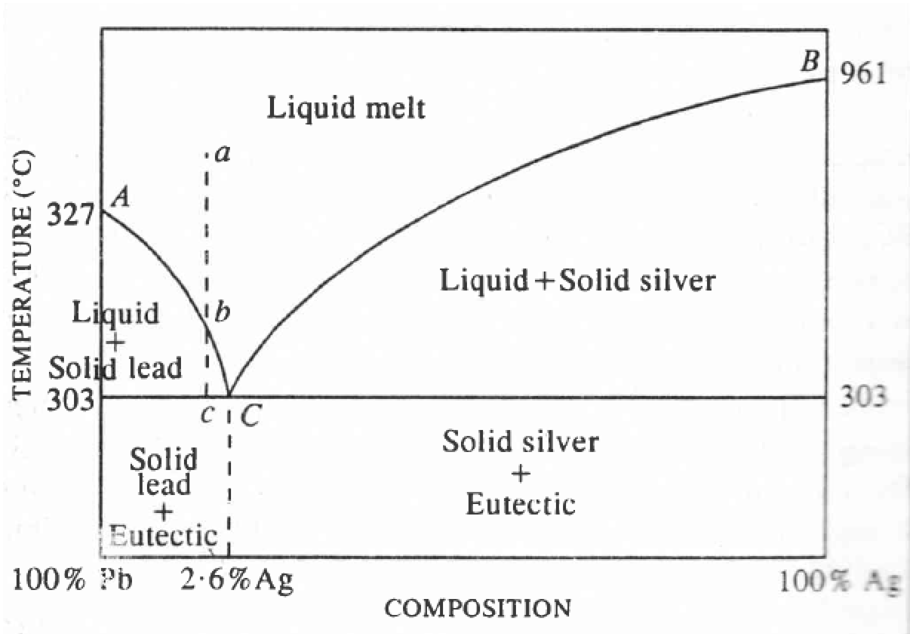
The system in which only the solid and liquid phases are considered and the gas phase is ignored is called a condensed system. Since the pressure is kept constant, the phase rule becomes.

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

Condensed systems have no gas phase. When their properties are insensitive to the (small) changes in pressure which occur, one fewer variable needs to be specified, which results in the phase rule at constant pressure.

This is actually called Phase rule at constant pressure

11. Draw well labeled phase diagram of Pb-Ag system.



12. What is meant by term eutectic? State the condition in which two substances can form a simple eutectic.

A binary system having two substances, which are completely miscible in the liquid state, but immiscible in the solid state, is known as eutectic (easy melt) system.

They do not react chemically. The different mixtures of two substances, a mixture with specific proportions having the lowest melting point is known as the eutectic mixture.

13. Difference between triple point and eutectic point?

The triple point of a substance is the temperature and pressure at which the three phases (gas, liquid, and solid) of that substance coexist in thermodynamic equilibrium.

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

Applicable to single component system

The temperature at which a particular eutectic mixture freezes or melts is called the eutectic point.

Phase =3 (two solids and their miscible liquids)

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

Applicable to binary system and reduced phase rule.

14. Explain the application of phase rule in Pattinson's process of desilverisation of Pb.

Pattinson's Process is a method for removing silver from lead.

The process is dependent on the fact that lead which has least silver in it solidifies first on liquefaction. In practice several crystallizations were required and the silver content of the silver-rich melt could not be raised above 2%. It has been replaced by the Parkes process.

15. What metal will separate out when a liquid alloy of copper and aluminium containing 25 % copper is cooled, if the eutectic mixture includes 32.5 % Cu? How many grams of that metal can be separated from 200 g of alloy?

As the % of copper increases from alloy to eutectic the other metal Al will be separated out.

% In alloy Cu- 25 & Al – (100-25) = 75 So, in 200 g alloy Cu will be 50g and Al 150 g

% in Eutectic Cu -32.5 & Al (100-32.5) = 67.5

In eutectic 32.5g Cu can coexist with 67.5g of Al;

*So, 50 g of Cu will coexist with (67.5/32.5) *50 g = 103.84 g of Al*

Hence, the amount will be separated 150 -103.84 = 46.15 g

16. An alloy of tin and lead contains 78% tin. Find the mass of the eutectic in 1 kg of solid alloy, if the eutectic contains 64% tin.

% in alloy Sn = 78 and Pb = 22; so, in 1 kg solid alloy Pb = 780 g and Pb = 220 g

% in eutectic Sn = 64 and Pb = 36

The contribution of Pb is increasing from alloy to eutectic therefor Sn will be separated out from the solution.

36g Pb can co-exist with 64g of Sn

Or, 220g Pb can co-exist with (64/36) * 220 = 391.11 g

So, the total mass of eutectic = 220 + 440 = 611 g

17. An alloy of Cd and Bi contains 25% Cd. Find the mass of eutectic in 1 kg of alloy, if the eutectic contains 40% Cd.

% in alloy Cd = 25 and Bi = 75; so, in 1 kg solid alloy Cd = 250 g and Bi = 750g

% in eutectic Cd = 40 and Bi = 60

The contribution of Cd is increasing from alloy to eutectic therefor Bi will be separated out from the solution.

40g Cd can co-exist with 60g of Bi

Or, 250g Pb can co-exist with (60/40) * 250 = 375 g

So, the total mass of eutectic = 250 + 375 = 625 g

18. 1000 kg of a sample of argentiferrous lead containing 0.1 % silver is melted and then allowed to cool. If the eutectic contains 2.6% Ag, what mass of (i) eutectic will be formed and (ii) mass of lead will separate out?

% In Alloy Ag = 0.1 and Pb = 99.9; so, 1000kg of alloy will have 1 kg of Ag and 999 kg of Pb

The contribution of Ag is increasing from alloy to eutectic so Pb will be separate out.

According to the contribution of eutectic 2.6 kg of Ag co-exist with 97.4 kg of Pb; hence 1 kg of Ag will co-exist with (97.4/2.6) = 37.46 kg

Hence the mass of eutectic = 1 + 37.46 kg = 38.46 kg

Mass of Pb will separated out 999-37.46 = 961.54 kg