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# PHASE RULE

## AIMS AND OBJECTIVES

**After study this unit you should able to,**

- Explain Phase, Phase rule
- Draw and explain Phase diagram.
- Elucidate one component system ,two component systems two component alloy system (or)multi component equilibria,Reduced phase rule (or) condensed system

## INTRODUCTION

For a system at equilibrium the phase rule relates:

**P** = number of phases that can coexist, to
**C** = number of components making up the phases, and
**F** = degrees of freedom.
Where these three variables are related in the equation
**P + F = C + 2**

The degrees of freedom represent the environmental conditions which can be independantlyvaried without changing the number of phases in the system. Conditions include:

Temperatur
e,Pressure,
Chemical Composition, Oxygen Fugacity ,etc .

## DEFINITIONS

**System:** An assemblage of materials that is isolated in some manner from rest of theuniverse.

- ***isolated system:***one that does not exchange matter or energy with its surroundings.
- ***closed system:*** one that exchanges only energy with its surroundings.
- ***open system:*** one that exchanges both matter and energy with its surroundings.
- ***adiabatic system:*** a system with changes in energy caused only by a change in volumeas pressure changes.

**Equilibrium:** The lowest energy state of a system in which there is no tendency for aspontaneous change.

**Metastable Equilibrium:** state of a system which is not in its lowest energy state at the imposed conditions, but cannot spontaneously change due to high activation energy forchange.

All chemical reactions are broadly classified into 2 types:

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1) Irreversible Reactions : $Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2\uparrow$

2) Reversible reactions:

(a) Homogeneous reversible reactions

Eg: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

(b) Heterogeneous reversible reactions

Eg: $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

The reversible reactions are represented by 2 arrows in the opposite directions. The homogeneous reversible reactions can be studied by the law of mass action and the heterogeneous reversible reactions using the phase rule, given by Willard Gibbs (1874) whichis defined as,

**PHASE RULE:**

If the equilibrium between any numbers of phases is not influenced by gravitational/electrical/ magnetic forces but is influenced by pressure, temperature and concentration, then the number of degrees of freedom (F) is related to the number of components (C) and the number of phases (P) as: $F = C - P + 2$

**Explanation of terms with examples**

**PHASE (P):**

PHASE is defined as, ‒any homogeneous physically distinct and mechanically separable portions of a system which is separated from other parts of the system by definite boundaries‖.

**a) Gaseous phase (g):**

All gases are completely miscible and have no boundaries between them. Hence all gases constitute a single phase.

Eg: Air, a mixture of $O_2$, $H_2$, $N_2$, $CO_2$ and water vapor, etc., constitutes a single phase.

(b) **Liquid Phase (l):**

The number of liquid phases depends on the number of liquids present and theirmiscibility‟s.

(i) If two liquids are immiscible, they will form two separate liquid phases. (e.g.)Benzene – Water system.

(ii) If two liquids are completely miscible, they will form only one liquid phase.(e.g.) Alcohol - Water system.

(c) **Solid Phase (s):**

Every solid constitutes a separate single phase. (e.g.) *Decomposition of* $CaCO_3$

$$\mathbf{CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)}$$

It involves 3 phases namely solid $CaCO_3$, solid CaO and gaseous $CO_2$

**Other examples:**

1) A water system has 3 phases namely one solid, one liquid and one gaseous

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phase.

$$\textbf{Ice(s)} \rightleftharpoons \textbf{Water(l)} \rightleftharpoons \textbf{Vapour(g)}$$

2) A solution of a substance in a solvent constitutes only one phase. *(e.g.)* Sugar solution inwater.

3) An emulsion of oil in water forms two phases

4) **$MgCO_3$ (s) $\rightleftharpoons$ MgO (s) + $CO_2$ (g)**
It involves 3 phases, solid $MgCO_3$, solid MgO and gaseous $CO_2$.

5) Rhombic sulphur (s) ––––> Monoclinic sulphur (s). It forms 2 phases.

6) Consider the following heterogeneous system.

**$CuSO_4$(s) + $5H_2O$ (l) $\rightleftharpoons$ $CuSO_4 \cdot 5H_2O$ (s)**
It involves 3 phases namely, 2 solids and 1 liquid phase.

**COMPONENT (C):**

Component is defined as, –the minimum number of independent variable constituents, by means of which the composition of each phase can be expressed in the form of a chemical equation‖.

**Examples:**

(a) Consider a water system consisting of three phases.

$$\textbf{Ice(s)} \rightleftharpoons \textbf{Water(l)} \rightleftharpoons \textbf{Vapour(g)}$$

The chemical composition of all the three phases is H2O. Hence the number ofcomponent is one.

(b) Sulphur exists in 4 phases namely rhombic, monoclinic, liquid and vapour, but thechemical composition is only sulphur. Hence it is a one component system.

(c) Thermal decomposition of $CaCO_3$

**$CaCO_3$s) $\rightleftharpoons$ CaO (s) + $CO_2$(g)**

The system has 3 phases namely, solid $CaCO_3$, solid CaO and gaseous $CO_2$and2 components, as the composition of each of the above phases can be expressed as equations considering any two of the three components present. When $CaCO_3$and CaO are consideredas components, the chemical equations are:

| **Phase** | **Components** |
|---|---|
| $CaCO_3$ | $CaCO_3$ + 0CaO |
| CaO | 0$CaCO_3$ + CaO |
| $CO_2$ | $CaCO_3$ – CaO |

(d) **$PCl_5$(s) $\rightleftharpoons$ $PCl_3$(l) + $Cl_2$(g)**

This system has 3 phases and 2 components namely, $PCl_3$ and $Cl_2$.

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(e) An aqueous solution of NaCl is a two component system. The constituents are NaCl and $H_2O$.

**(f) $CuSO_4.5H_2O(s) \rightleftharpoons CuSO_4.3H_2O(s) + 2H_2O(g)$**

It is also a two component system as components are $CuSO_4.3H_2O$ and $H_2O$.

(g) In the dissociation of $NH_4Cl$ , the following equilibrium occurs.

$$NH_4Cl\ (s) \rightleftharpoons NH_3\ (g) + HCl\ (g)$$

The system consists of 2 phases namely solid $NH_4Cl$ and the gaseous mixture containing $NH_3$ + HCl. When $NH_3$ and HCl are present in equivalent quantities the composition of both the phases can be represented by $NH_4Cl$ and hence the system will be a one component system.

## DEGREE OF FREEDOM (F):

Degree of freedom is defined as, ―the minimum number of independent variable factors like temperature, pressure and concentration, which must be fixed in order to define the system completely‖.

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

**Examples:**

(a) Consider the following equilibrium

$$Ice(s) \rightleftharpoons Water(l) \rightleftharpoons Vapour(g)$$

These 3 phases will be in equilibrium only at a particular temperature and pressure. Hence, this system does not have any degree of freedom, so it is non-variant (or) zero-variant (or) in-variant system.

(b) Consider the following equilibrium

$$Liquid\ Water(l) \rightleftharpoons Water\text{-}\ vapour(g)$$

Here liquid water is in equilibrium with water vapour. Hence any one of the degrees of freedom such as temperature (or) pressure has to be fixed to define the system. Therefore the degree of freedom is one.

(c) For a gaseous mixture of $N_2$ and $H_2$, both the pressure and temperature must be fixed to define the system. Hence, the system is bivariant.

## PHASE DIAGRAM

Phase diagram is a graph obtained by plotting one degree of freedom against theother.

**Types of Phase Diagrams**

**(i) P-T Diagram**

If the phase diagram is plotted between temperature and pressure, the diagram iscalled P -T diagram. P -T diagram is used for one component system.

**(ii) T-C Diagram**

If the phase diagram is plotted between temperature and composition, the diagram is

called T-C diagram.T- C diagram is used for two component system

**Uses of Phase Diagram:**

It helps in

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(i) Predicting whether an eutectic alloy (or) a solid solution is formed on cooling ahomogeneous liquid containing mixture of two metals.

Understanding the properties of materials in the heterogeneous equilibrium system.

Studying of low melting eutectic alloys, used in soldering.

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**PAPER: C8T (Physical Chemistry )**

TOPIC : Phase rule (Part -I)