Phase Rule

Introduction : Two or more different phases present in equilibrium with one another, constitute **a heterogenous** system. Such heterogenous system can be conveniently studied with the help of a generalisation called **Gibbs Phase** rule. It is applicable to all heterogenous systems and is also free from exceptions which are common features of all other generalisations of physical chemistry. This rule was deduced on the basis of thermodynamic principles by J. Willard Gibbs . This rule predicts qualitatively the effect of temperature, pressure and concentration on a heterogenous equilibrium.

Phase Rule

Phase Rule :

Gibbs phase rule may be stated as follows :

"In a heterogeneous system in equilibrium, the number of degrees of freedom plus the number of phases is equal to the number of components plus two".

Mathematically, $F + P = C + 2$

or $F = C - P + 2$

where

F = number of degrees of freedom

C = number of components

P = number of phases

2 = additional variables of temperature and pressure besides the concentration variables.

Phase Rule

Phase: “ The physically distinct, homogenous and mechanically separable part of a system are called phases”.

Examples

(i) A gaseous mixture constitutes a single phase since gases are completely miscible. Air is a mixture of N_2, O_2, CO_2, water vapour etc. Which constitute a single phase.

(ii) Two or more liquids which are miscible with one another constitute a single phase as there is no bounding surfaces separating the different liquids. e.g., water and alcohol, benzene & chloroform constitute one phase system.

(iii) A system consisting of a liquid in equilibrium with its vapour constitute a two phase system

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Component :

The number of component of a system at equilibrium is defined as the minimum number of independently variable constituents which are required to express the composition of each phase in the system.

In a chemically reactive system, the number of components is given by

$$C = N - E$$

where C = components.

N = Number of chemical species

E = Number of independent equations relating the concentrations of the N species.

Each independent chemical equilibrium involving the constituents counts as one equation.The condition that a solution be electrically neutral also counts as one equation if ions are considered as constituents.

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Examples

(i) Sulphur system: Consists of four phases namely monoclinic sulphur, rhombic sulphur, liquid sulphur and sulphur vapour. The composition of each phase of the system can be expressed in terms of sulphur only, so, it is a one component system.

(ii) Water system: It is a one component system because the composition of each of the three phases present can be expressed as H_20.

(iii) Na_2SO_4 + water system: Certain salts are capable of existing as hydrates with different number of water molecules of crystallization. These hydrates correspond to different solids and hence to different phases. The system is a two component , because the composition of each phase of the hydrates is completely described in terms of the anhydrous salt and water alone. e.g., Na_2S0_4 + water

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Degrees of Freedom :

The degree of freedom or variance of a system is defined as the minimum number of variable factors such as temperature, pressure and concentration which should be arbitrarily fixed in order to define the system completely.

Examples

(i) For a given sample of any gas PV = nRT. Any two of the three variables P, V, T define the system completely. Hence the system is bivariant or it has two degrees of freedom.

(ii) A gaseous mixture say N_2 and O_2 gases (mixed 50% each), is completely defined when three variables temperature, pressure and concentration are specified. Thus, the degrees of freedom is three or the system is trivariant.

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Conclusion·

(i) The greater the number of components in a system, the greater is the degree of freedom for a given number of phases.

(ii) The greater the number of phases, the smaller is the number of degrees of freedom.

(iii) The number of phases is maximum when the number of degrees of freedom = Zero, for a given number of components. Thus, for

one component system, $P_{max.} = 3$.

two component system, $P_{max}. = 4$

three component system, $P_{max.} = 5$