

7 CHAPTER

PHASE RULE

7.1 INTRODUCTION AND DEFINITIONS

In heterogeneous system, the conditions that must be specified to describe the state of equilibrium has been put forward in the form of a generalization, known as **phase rule**. The phase rule was put forward by J. Williard Gibbs in 1876 correlating the various conditions of equilibrium, such as the number of phases, the number of components and the degrees of freedom. The phase rule is a versatile tool in the study of heterogeneous equilibria. Before stating the rule, let us define and explain the terms involved, i.e., phase, component and degree of freedom.

7.1.1 Phase

A phase is defined as a homogeneous and physically distinct part of a system which is separated from other parts of the system by a definite boundary.

A gaseous system consisting of a single or a mixture of gases constitute a single phase as the gases are completely miscible with one another and there is no boundary between them.

Completely miscible liquids constitute one phase. In immiscible liquids, the number of phases is equal to the number of liquid layers in the system. Thus, water-ethanol mixture constitutes single phase while water-carbon tetrachloride mixture yields two phases separated by a definite boundary.

A system consisting of a liquid and its vapour in equilibrium has two phases, liquid phase and vapour phase separated by a definite boundary. Similarly, solid-liquid-vapour equilibrium, e.g., ice-water-water vapour constitute a system containing three phases.

In general, each solid constitutes a single phase unless when a solid solution is formed or the solids are isomorphous. Thus the number of phases in a solid system is equal to the number of solids present in the system. Moreover, each polymorphic form and allotropic modification constitutes a separate phase.

7.1.2 Components

The smallest number of independent chemical constituents by means of which the composition of each and every phase of a system can be expressed is the number of components

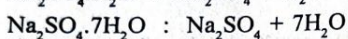
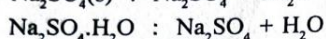
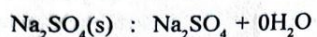
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of the system. The independent chemical constituent is the one whose concentration can be varied independent of other constituents of the system.

Thus, in water system there are three phases—ice, water and water vapour, any two of them or all three phases can be at equilibrium. But the composition of each phase may be expressed by a single component, water (H_2O). Hence, this is an example of one component system. Similarly in sulphur system there are four phases—monoclinic sulphur, rhombic sulphur, liquid sulphur and sulphur vapour. Each phase is composed of only sulphur and so it is also a one component system.

Salt-water or hydrate systems like sodium sulphate-water, copper sulphate-water, ferric chloride-water, etc., are examples of two component systems as the composition of each phase can be described in terms of the two independent chemical constituents, i.e., salt and water.

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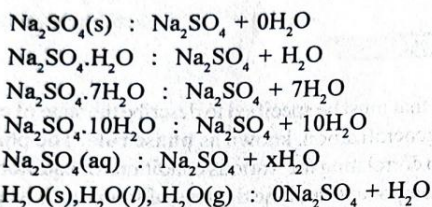
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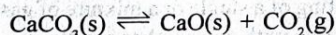
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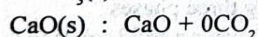
Although the composition of a few phases can be described by one component only, others require two components. Since two components are the smallest number by which the composition of all the phases can be defined, the number of components in a salt-water system is two.

Let us now consider the equilibrium between $CaCO_3(s)$, $CaO(s)$ and $CO_2(g)$ represented by the equation

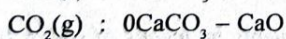
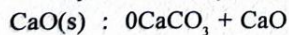
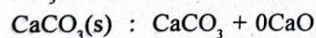


The number of phases are three but the number of components is two since any two species out of the three can express the composition of all the three phases as these are related by an equation. It is immaterial which two of the three are selected for this purpose. Thus,

(i) If CaO and CO_2 are the two components, then

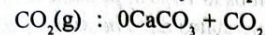
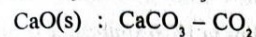
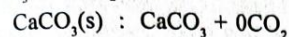


(ii) If $CaCO_3$ and CaO are chosen as the two components, then



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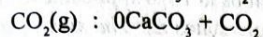
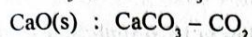
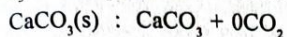
(iii) $CaCO_3$ and CO_2 are chosen as two components, then



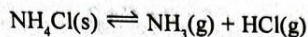
Thus, it is seen that any restriction between the constituents decreases the number of components. Let us now consider the following equilibrium:



(iii) CaCO_3 and CO_2 are chosen as two components, then



Thus, it is seen that any restriction between the constituents decreases the number of components. Let us now consider the following equilibrium:



The number of constituents in the system is three but the equilibrium existing among them places a restriction so that the number of components is two. If the dissociation is carried out in vacuum, then $p_{\text{NH}_3} = p_{\text{HCl}}$ as under this condition both NH_3 and HCl are present in equal amount. This adds on another restriction so that the number of components of the system is one. In solution of electrolytes, electrical neutrality is also a restriction.

In general, the number of components (C) in a system is equal to the total number of constituents (C') minus the number of independent equations (r) minus equations due to restricting condition (z).

$$C = C' - r - z$$

7.1.3 Degree of Freedom or Variance

The *degree of freedom or variance* of a system is the minimum number of independent variables such as temperature, pressure and concentration, that must be ascertained so that a given system at equilibrium can be completely defined. Alternatively, the degree of freedom of a system may be defined as the number of factors, such as temperature, pressure and concentration, which can be varied independently without altering the number of phases.

Let us consider a gaseous system. To describe completely the state of the system only two of the three variables need to be specified as the third one is automatically known because these three variables are linked through the equation of state. Hence, the system is bivariate, i.e., degrees of freedom is two.

If, on the other hand, a liquid is in equilibrium with its vapour, only one variable needs to be specified. Thus, if temperature is fixed, its vapour pressure is automatically fixed. So, it is necessary to specify either the temperature or the pressure to define the state of the system completely. Hence, the system is univariant and degree of freedom is one.

When three phases, say, ice, water and water vapour are at equilibrium at the triple point both the temperature and the pressure are fixed. For ice-water-water vapour system the temperature at the triple point is 0.0075°C and the pressure is 4.58 torr. The change in either the temperature or the pressure will disturb the equilibrium and will change the three phase system into two phase system. The system is said to be invariant or non-variant and the degree of freedom is zero.

7.2 PHASE RULE AND ITS DERIVATION

The phase rule is a generalization put forward by J. W. Gibbs in 1876 applicable to all types of reactive and nonreactive heterogeneous systems. The rule states as: *The sum of degrees of freedom (F) and the number of phases (P) exceeds the number of components (C) by 2.* Mathematically,

$$F + P = C + 2 \quad (1)$$

Let us consider a heterogeneous system of P phases at equilibrium containing C components. If C is the number of components required to describe the composition of one phase, then the total number of components in the system will be CP . For the system to be in equilibrium, the composition of each phase must be the same. Hence, the number of independent components is C .