भारतीय ज्ञान धरोहर

विमर्श और परंपरा

सम्पादक
डॉ. दिनेश चन्द्र शर्मा

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Ph.D., D.Lit. (Sub.)

निदेशक, कॉम्पिटिशन प्लस ग्रुप ऑफ इन्स्टीट्यूशन,

अजमेर

छवि पब्लिकेशन्स

अजमेर-305001

प्रकाशक :
छवि पब्लिकेशन्स
अजमेर-305001
मो. 9660111549

संस्करण :
प्रथम 2023

ISBN : **978 - 81 - 89435 - 69 - 1**

मूल्य - 400/-

रचना - भारतीय ज्ञान धरोहर : विमर्श और परम्परा

सम्पादक - डॉ. दिनेश चन्द्र शर्मा

मुद्रक - श्रीनिवास प्रिन्टोग्राफिक्स, अजमेर

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Applications of Phase Rule in Metallurgy

Dr. S. Sharma
HOD (Deptt. of Science and Technology)
Hukumchand Noble Institute of Science and Technology, Ajmer

Introduction

Phase rule is important way to study of the heterogeneous equilibrium, it is given by Willard Gibbs (1874). With the help of phase rule, it is important to predict the effect of changing the temperature, pressure and concentration on heterogeneous system in equilibrium. It may be stated as "provided the equilibrium between any number of phases is not influenced by gravity or electrical or magnetic forces or by surface action and only by temperature, pressure and concentration then the number of degree of freedom (F) of the system is related to the number of components (C) and of phases (P) Mathematically phase rule is expressed as

F+P=C+2

Where F =Degree of freedom

P= Number of phases

C =Number of components

According to equation (1) phase rule is defined "The sum of degree of freedom and number of phases is equal to the number of components and two variables temperature and pressure". The terms 'phase', 'components' and 'degree of freedom' involved in phase rule have a great significance and a clear understanding of these terms are essential before we proceed with the subject.

Phase

An homogeneous, physically distinct and mechanically separable portion of system, which is separated from other part of the system by definite sharp boundary, is known as" phase"

A phase is defined as a portion of the heterogeneous system

which is physically distinct, mechanically separable and uniform in composition. For examples:

(1) Mixture of two or more gases i.e. homogeneous. So that mixture has only one phase, since gases are completely miscible. Example, air.

(ii) Two liquid which are completely miscible with each other, will form a one-phase system. For example mixture of water and ethanol, milk and water etc.

(iii) Two liquids which are immiscible with each other, will form two phase systems, for example CC*I* and water, oil and water, benzene and water etc.

(iv) If the two liquids are partially miscible they shows two phases, e.g. H_2O and Ether.

(v) A solution of a substance in solvent consist of one phase only. For example; NaCl solution in water.

(vi) Each solid makes a separate phase unless a solid solution formed. A mixture of allotropes forms different phases. For example mixture of rhombic and monoclinic sulphur shows two phases.

(vii) A solid mixture consist of many phases as solids are present.

Degree of Freedom (F)

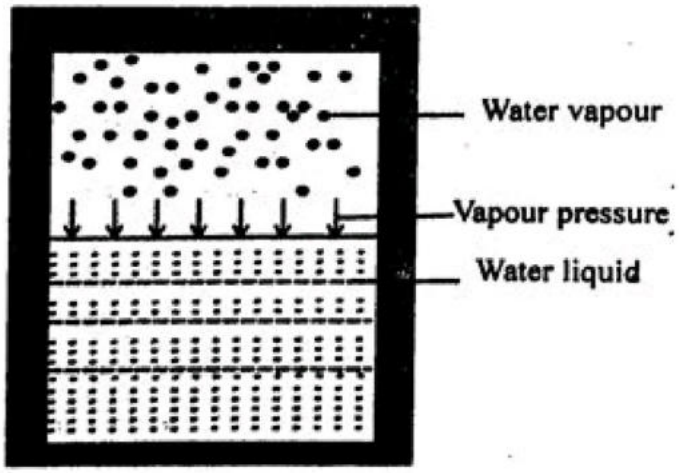
such as temperature, pressure and concentration (or composition) which must be specified inner. The degree of freedom of a system is define as the "minimum number of independent variant define the system completely.

Thus the state of pure gas can be specified by two variables P and T or P and V. since the thin variable can be calculated from the equation of state. This means that a pure gas has two degrees freedom. The system possessing one, two and three degree of freedom are said to be univarian bivariant and trivariant respectively.

APPLICATIONS OF PHASE RULE AND PHASE DIAGRAM

All the systems are classified on the basis of number of component present. Thus we have one, two, three etc. component systems. The phase rule is perfectly applicable to these systems. The phase diagram is an important medium to clearly indicate the equilibrium conditions between different phase in medium, it also

shows the region of pressure and temperature at which its various phases are thermodynamically stable. The line separating the regions are called phase boundaries, it gives the value of pressure and temperature at which two phases coexist in equilibrium.



Degree of Freedom

Degrees of freedom can be defined as the number of variable factors, such as temperature, pressure and concentration, which must be fixed in order that the condition of the system at equilibrium may be completely defined. A system having zero, one, two or three degrees of freedom are called invariant, univariant, bivariant, and trivariant respectively.

For e.g. in case of water system

$$\text{ice (s)} \rightleftharpoons \text{water (1)} \rightleftharpoons \text{vapour (g)}$$

When all the 3 phases are present

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

Degrees of freedom is zero or invariant ie. no conditions is needed to be specified since such an equilibrium can be present only at a definite temperature and pressure.

If ice (s) ===water (1)

then $F = 1 - 2 + 2 = 1$

i.e. univariant either temperature or pressure is needed to define the system completely. If the system has only one phase suppose, ice (solid). then $F = C - P + 2 = 1 - 1 + 2 = 2$

i.e. system is bivariant. It means that temperature and pressure both are needed to describe the system.

Advantages of Phase Rule

(1) If a system undergo a phase reaction, it can be applied to "physical and chemical equilibrium".

(2) It is applicable to macrosystem and require no information about microstructure.

(3) Different systems having same degree of freedom, behaves in same fashion.

(4) It is related to the number of phases, components and factors like temperature, pressure and concentration. It is not related to the quantity, nature of chemical reaction or nature of chemical species.

(5) It is convenient to predict the behaviour of the system under different sets of variables

Limitations

(1) It can be applied only to a system in equilibrium.

(2) It is applicable only to heterogeneous system.

(3) It is applicable only to a single equilibrium state. It gives no information about the other equilibrium in the same system

(4) The solid and liquid phases should not be in finely devided form because vapour pressure may be differ from normal values

One Component System

A system in which it is possible to expressed the composition of all the phases in terms of only one substance.

The complexity of one-component system depends on the number of solid phases that can in the system.

For a one component system, such as pure water, according to phase rule-

$F = C - P + 2$

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

When only onephase is present, the maximum number of degree of freedom is two. So system is bivariant.

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

So this system can defined by specifying two variables pressure and temperature. The composition remain invariable because these is only one component.

If a one component system has two phase in contact with each other, the degree of freedom will be 1.

F = C - P + 2

= 1 -2+2

F=1

The system is then said to monovariant. It can be completely defined by specifying only one variable, viz. either temperature or pressure. If the pressure is fixed, temperature of the system is fixed automatically and vice versa.

When the three phases are present in equilibrium, the degree of freedom will be zero. The system is then said to non variant.

F = C - P + 2 =|-3+2=0

The special condition can be obtained only at definite pressure and temperature. The point in phase diagram at which three phases are in equilibrium known as Triple point.

Determination of degree of freedom:

(1) Area: Areas AOC, BOC and AOB are the field of liquid water, water vapour and solid ice places exists a respectively i.e. Every area there is single phase existing. By applying phase rule the degree of freedom for areas

F=C-P+2

F=1-1+2

F=2 (bivariant)

That means system in individual area is 'bivariant' so it is essential to mention both the temperature and pressure.

(2) Curves: there are three curves in water system. Each curve shows equilibrium between two phases or two areas. (Melting point / freezing point curve)

Curve OC (Melting curve):

This curve shows equilibrium between solid ice and liquid water

Ice (s) ====Water (1)

It is called melting or fusion curve of ice, along this curve two phases are exist. Any post he curve can be located by getting the value of pressure or temperature. Thus it has onc degree of freedom.

Two Component System

In two component system, when C = 2 degree of freedom (F) has the highest values since maximum number of degree of freedom in a two component system is three, so the phase behaviour of a binary system may be represented by a three dimensional diagram

of pressure, temperature and composition, which is not possible to graphic representation on a paper.

A solid liquid equilibrium of an alloy has practically no gas phase and the effect of pressure is small on this type of equilibrium. A system in which only the solid and liquid phases are considered and the gas phase is ignored is called condensed system. Since the pressure is kept constant, it will reduce the degree of freedom of the system by one According to Phase Rule.

$F = C - P + 2$

For two component system, the phase rule becomes

$F = C - P + 1$

This is known as reduced or condensed phase rule having two variables namely temperature and concentration (composition) of the constitute hence solid liquid equilibrium are represented on Temperature- Composition diagram

Condensed System :

For slid-liquid equilibria, temperature effect of pressure is negligilible since the vapour pressure of solids are small. Thus the result obtained are substantially same as if the system were in thruc equilibrium with its vapour

Such system, where the effect of pressure is neglected are called condesned system. The reduced phase rule is applied for such systems.

Eutectic System

A binary system consiting of two substances, which are miscible in all proportions in the liquid phase, but which do not react chemically, is known as the "eutectic (easy to system", eg.. a mixture of lead and silver comprises of such a system).

Eutectic mixture is a solid solution of two or more substances having the lowest freezing point of all the possible mixture of the components. This is taken advantage of an "alloys of low melting point", which are generally eutecting mixtures

Eutectic point: Two or more solid substances capable of forming solid solutions with cach other have the property of lowering cach other's freezing point and the minimum freezing point attainable corresponding to the eutecting mixture, is termed as the eutectic point (means lowest melting point).