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 $\qquad F = C - P + 2$

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.

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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_2O.

(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_2SO_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, $P_{max.} = 5$

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Advantages of Phase' Rule :

(i) It provides a simple method of classifying equilibrium states of systems.

(ii) The phase rule confirms that the different systems having the same number of degrees of freedom behave in same manner.

(iii) It is applicable only to macroscopic systems and not concerned with molecular structure.

(iv) It predicts the behaviour of systems with changes in the variables that govern the system in equilibrium.

(v) It predicts under given conditions whether a number of substances taken together would remain in equilibrium as such or would involve interconversion or elimination of some of them.

(vi) It takes no account of nature of the reactants or products in phase reactions.

Phase Rule

(vii) It finds extensive use in the study of many heterogenous
systems. In particular it has been found

extremely useful in the extraction of metals.

Limitations:

(i)   The phase rule is applicable to heterogeneous systems in
equilibrium, so, it is therefore of no use for such systems
which are slow in attaining the equilibrium state.

(ii)   It is applicable to a single equilibrium state, so it never
gives information about the other possible equilibrium in
the system.

(iii)   In Gibbs phase rule, various variables are temperature,
pressure and composition. It does not take in account
the electric and magnetic influences. For consideration of
such variables, the factor 2 of the Phase rule has to be
adjusted accordingly.

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(vi) All the phases in the system must be present under the same temperature, pressure and gravitational force .

(v) No solid or liquid phases should be finely divided, otherwise deviation occurs.

Phase diagrams :

The number of phases that exist in equilibrium depends upon the conditions of temperature and pressure or temperature and composition, pressure being constant. These conditions are determined experimentally and interdependence of values of the variables can be shown graphically using appropriates coordinates. These diagrams are termed phase diagram. **A phase diagram is the sum total of the description of the behaviour of the phases under equilibrium.** It is very easy to describe the phase behaviour of a system by such diagrams and to investigate the conditions in which various phases will constitute the system .

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Application of Gibbs Phase Rule to One Component System:

From the mathematical expression,

F = C – P + 2

When C = 1, P = 1

F = 1-1+2

= 2

Hence, all one component systems can be completely described graphically by stating only two variables, pressure and temperature on appropriate axis.

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<u>The Water System :</u>

It is a one component system. Water exists in three possible phases viz. ice (solid) , water (liquid), and vapour (gas). These three single phases may form four possible equilibria.

(i) Solid $\rightleftharpoons$ Liquid
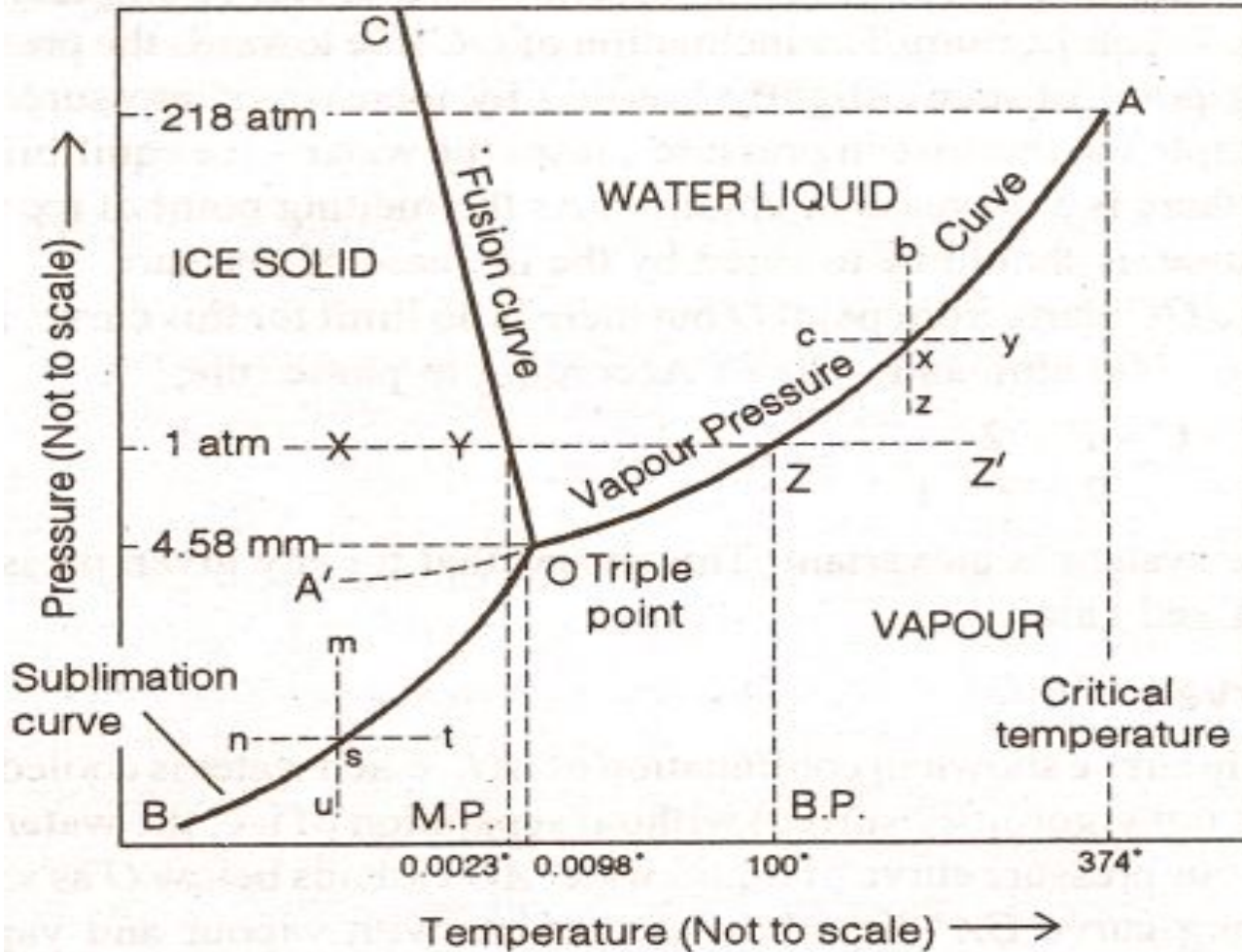
(ii) Liquid $\rightleftharpoons$ Vapour

(iii) Solid $\rightleftharpoons$ Vapour

(iv) Solid $\rightleftharpoons$ Liquid $\rightleftharpoons$ Vapour

The Phase diagram of water system is given as

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Phase Diagram of water system

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The phase diagram consists of :

(i) Stable curves: three *OB, OA* and *OC*

(ii) Metastable curve: one OA'

(iii) Areas: three AOB, COB and AOC

(iv) Triple point: One O

(i) Stable curves

OA : It is known as **vapour pressure curve of water**. The curve OA starts from point O i.e., freezing point of water, 0.0098°C under 4.579 mm of Hg pressure and ends at A, the critical temperature (374^0C at 218 atm.). Above critical temp. on the vapour phase exists whatever may be the value of pressure. The vapour pressure of water increases with increase in temperature.

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The rate of increase of its vapour pressure with temperature is relatively higher at higher temperatures and therefore the curve OA slants upwards and slopes away from the temperature axis.

From phase rule,

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

The water vapour system is univariant

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OB : It is the **sublimation curve of ice**. Along this curve, solid ice is in equilibrium with its vapour.

This curve is not the prolngation of curve A but falls of more steeply. Curve OB starts From the temperature 0.0098°C above which solid water *i.e.,* ice cannot exist. The curve terminates at *B i.e.,* absolute zero (- 273°C). At this temperature, no vapour can exist and, therefore, only ice is left. But on other points of the curve O*B,* ice is in equilibrium with vapour. Hence, there are two phases. According to phase rule,

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

Thus, the system is univariant. This means that for each temperature; there may be one pressure and for each pressure there may be one temperature.

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OC : This curve is the **melting point curve or fusion curve of ice.** Along this curve two phases, ice and water are in equilibrium. The inclination of *OC* line towards the pressure axis indicates that the melting point of ice is slightly lowered by increase of pressure. (According to Le Chatelier's principle the increase in pressure causes the water - ice equilibrium to shift in such a direction that there is a decrease in volume.) As the melting point of ice is accompanied by decrease in volume, it should be lowered by the increase of pressure.

The curve *OC* starts from point O but there is no limit for this curve. It goes upto a point corresponding to 2000 atm. and - 20°C. According to phase rule,

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

Thus, the system is univariant. This means that for any given pressure, melting point must have one fixed value.

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(ii) Metastable Curve

OA' : It is a metastable curve shown in continuation *of AO.* When water is cooled below its freezing point (when it is not vigorously stirred) without separation of ice, the water is said to be super cooled. The vapour pressure curve of liquid water *AO* extends below O as shown by the dotted curve *OA'.* Along curve *OA'* liquid water coexists with vapour and vapour pressures are different than over the solid. This equilibrium is called metastable equilibrium as slight disturbance brings it to the stable region *OB* of the phase diagram.

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(iii) Areas

The areas give the conditions of temperature and pressure under which single phase - ice (solid), water (liquid) and vapour (gas) can exist. It is necessary to specify both temperature and pressure to define a system within this area. In the area *BOC, AOC* andAOB exists, ice (solid), water (liquid) and vapour (gas) respectively. In these areas, the degrees of freedom for the system is two or they are bivariant

(iv) The Triple point O

The point O at which the curves *AO, BO* and *CO* meet is called the triple point. At this point all the three phases *viz* , ice, water and vapour co-exist. Thus, *P* =3. According to phase rule, at triple point O,

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

Phase Rule

   Thus, the degree of freedom at triple point is zero, which indicates that there is only one set of variables *P, T* at which all the three phases coexist. If any of the variables is changed, then the number of phases decreases. For example, if the temperature is raised, heat causes more and more of the solid (ice) to melt but no change in temperature or pressure of the system occurs till the whole of the solid has completely changed into liquid (water) and the system becomes a two phase system. On applying the pressure to the system, vapours start condensing to liquid or solid phase. As long as there are three phases, temperature and pressure remains same.

The triple point O is a self defined point corresponding to 0.0075°C temperature and 4.579 mm of Hg pressure (difference from the ordinary freezing point,(0.000^0C at 760mm pressure) because freezing temperature is lower than triple point temperature due to effect of high pressure and dissolved air).