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Topic: Phase equilibrium (part I)

Physical Chemistry

B. Sc. Chemistry (H) 2nd Year

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PHASE:

In general, a "phase" is a homogeneous, physically distinct, mechanically separable portion of a material with a given chemical composition. It is defined as homogeneous part of a system which is physically and chemically different from other part also it is mechanically separable from other part of the system. Completely miscible gas and liquids form a singles phase while immiscible system give different phases i.e., solid +Liquid, solid +gas, have two component. Phases are denoted by P.

Any material can exist as a gas, a liquid or a solid, depending on the relative magnitude of the attractive interatomic or intermolecular forces vs the disruptive thermal forces. It is thus clear that the stability (existence) of the different states of aggregation, which are referred to as phases, is a function of temperature and pressure.

A few examples phase systems:

Ice cubes in water constitute a two-phase system (ice and liquid water), unless we include the vapor above the glass in our system, which would make it a three-phase system. A mixture of oil and water would also be a two-phase system. Just as oil and water represent two distinct liquid phases, two regions of a solid with distinctly different composition or structure separated by boundaries represent two solid phases.

Pure liquids or solutions constitute homogeneous phases, but two immiscible liquids (or solutions) constitute two phases since there is a definite boundary between them.

Mixture of gases always constitutes one phase because the mixture is homogeneous and there are no bounding surfaces between the different gases in the mixture.

Components:

The number of components of a system at equilibrium, the minimum number of independent variable constitutions (chemical species) which are required to express quantitavely the composition of each and every phase either directly or in terms of chemical equation is called components or denoted by C.

Example: (i) Water system consist of 3 phases.

Ice= Water = Vapour

(Solid) (Liquid)(Gasecus)

This system consists of one component only, i.e., it is a one component system because the composition of each of the three phases present can be directly expressed as H_2O

(ii) Sulphur system consisting of four phases- Monoclinic (s), Rhombic(s), Liquid (L) and vapors(g). It is also one component system because the composition of each phase can be expressed in term of one constituent sulphur.

the no. of component is calculated by

$$C = S - E - R$$

Where S= Total No. of constituents or species

E= No. of equation representing equilibrium between the constituents

R= No. of restrictions for electrical neutrality

(iii) Na_2SO_4-H_2O

(a) Assuming no dissociation

S=2

E=0(No chemical reaction/equilibrium)

R=0(No. restriction of electrical neutrality or material balance

C=S-E-R=2-0-0=2 Thus no. of components=2

b) Assuming complete dissociation of the salt.

S=3(Na^+, $SO4^{2-}$ and H_2O)

E=0

R=1(For electrical neutrality, $2Na^+ = SO_4^{2-}$)

C=S-E-R=3-0-1=2, Thus no. of components=2

Degree of Freedom:

It is defined as the no. of independent variables such as temperature, pressure and concentration which must be specified in order to define the system completely. The variables may be changed independently without causing the appearance of a new phase or disappearance of an existing phase

It is denoted by F Greater the no. of component C, greater the degree of freedom F. Greater the No. of phases P, smaller the number of degree of freedom F. Degree of freedom as also known as variance.

PHASE RULE AND EQUILIBRIUM

The phase rule, also known as the ***Gibbs phase rule***, relates the number of components and the number of degrees of freedom in a system at equilibrium by the formula

$$F = C - P + 2$$

where F is the number of degrees of freedom or the number of independent variables, C is the number of components in a system in equilibrium and P is the number of phases. The digit 2 stands for the two variables, temperature and pressure.

- The phase rule applies to dynamic and reversible processes where a system is heterogeneous and in equilibrium and where the only external variables are temperature, pressure and concentration. For one-component systems the maximum number of variables to be considered is two – pressure and temperature. Such systems can easily be represented graphically by ordinary rectangular coordinates. For two-component (or binary) systems the maximum number of variables is three – pressure, temperature and concentration.

For example, in the reaction involving the decomposition of calcium carbonate on heating, there are three phases – two solid phases and one gaseous phase.

$$CaCO_3\,(s) \leftrightarrows CaO\,(s) + CO_2\,(g)$$

There are three different chemical constituents, but the number of components is only two because any two constituents completely define the system in equilibrium. Any third constituent may be determined if the concentration of the other two is known. Substituting into the phase rule we can see that the system is univariant,

F = C – P + 2 = 2 – 3 + 2 = 1. Therefore only one variable, either temperature or pressure, can be changed independently.

References

- Physical chemistry: K.L Kapoor
- Physical chemistry By Atkins.
- Physical chemistry By P.C. Rakshit.
- Principles of chemistry By Puri, Sharma and Pathania.
- NPTEL online materials