

Phase Equilibrium

Asst. Prof. Chandana Pramanik

PHASE (HETEROGENEOUS EQUILIBRIUM)

What is phase?

Ans: According to Gibbs, a phase is defined as a physically distinct homogeneous part of a system having same chemical composition throughout.

A phase is always separated from other portion by definite boundary surface.

- A gas mixture is always a single phase system. Completely miscible liquids together constitute a single phase. Example → water and ethyl alcohol mixed at any proportion constitute a single phase.
- Partially miscible liquid pair (A and B) always do not constitute a single phase. When A is added dropwise to B at first A dissolves into B and forms a homogeneous solution constituting a single phase system. With the addition of more and more A into the given amount of B, the number of phase remains one until the solution becomes saturated with respect to A. After the saturation limit is crossed if more A is added into B, then excess A dissolves B as much as possible to form another saturated solution of B in A. The two saturated solutions are immiscible and being present together in micro level form a two phase heterogeneous system. The mixture then becomes turbid. The two saturated solutions are called conjugate solution. If the addition of A is continued further then the amount of the saturated solution A in B decreases with the increase in the amount of another saturated solution of B in A. In this way at a certain stage two phase heterogeneous system becomes a clear transparent single phase system which is nothing but the solution of B in A.

Completely immiscible liquids when present together then each liquid constitutes a separate phase. Similarly, every solid constitutes a single phase. If powdered CaO and ZnO are intimately mixed up, the system is a two phase system because in the macroscopic sense although the mixture appears to be homogeneous but in the microscopic level a grain is either pure CaO or ZnO . A solid solution or alloy is a single phase system until anything is stated about heterogeneity in chemical composition. When potash alum separates on cooling a hot solution of K_2SO_4 and $Al_2(SO_4)_3$ the solid constitutes a single phase whereas a mixture of solid K_2SO_4 and solid $Al_2(SO_4)_3$ in finely powdered state is a two phase system.

Component:

In a multiphase equilibrium, different phases may contain different or same compounds and a phase may contain more than one compound. To define the composition of all the phases, it is not needed to mention all the compounds always. If the compounds are mutually nonreactive, then to define the composition we have to mention all the compounds present in the system.

To define any system at equilibrium, T , P and the composition are to be defined. Of these state variables T and P are intensive properties. To define the equilibrium state it is not required to define the amount of the system since amount of the system does not change the property of the system. Rather what is needed is the concentration or % composition (w/v) or % (wt/wt) composition mole fraction of the constituents. To know the number of independent concentration terms we must have to know the number of independent chemical individuals by which each phase can be defined.

⇒ Independent chemical individuals by which the composition of each phase can be defined is called component.

or

⇒ Component is defined as the least number of chemically independent species that is required to describe the composition of every phase in the system.

The general principle to have the number of components is that, $\text{Number of components } (C) = \text{number of compounds or constituents } (C') - \text{number of independent chemical equations } (Q) - \text{number of additional restrictions } (R).$

Ex-1: ⇒ Water-vapour equilibrium system is defined by only one-chemical individual namely H_2O although in liquid state it is $(H_2O)_n$ and in vapour state it is H_2O . So, ~~no~~ number of component is one. However if we consider $(H_2O)_n$ and H_2O as separate compounds then the relation between them is to be considered. i.e., $(H_2O)_n \rightleftharpoons nH_2O$. Now both are not independent as one equation or restriction exists between them. So, only one is independent and the number of component is also one.

Ex-2: In case of $NH_4Cl(s)$ dissociation equilibrium, the compounds present are $NH_4Cl(s)$, $NH_3(g)$ and $HCl(g)$. They are related by the equation $NH_4Cl(s) \rightleftharpoons NH_3 + HCl$. Moreover, NH_3 and HCl constitute a single phase and are produced in the mole ratio 1:1 so that in gas phase $X_{HCl} = X_{NH_3} = 1$. So, one is independent. This is additional restriction apart from the equation. So, $C = 3 - 1 - 1 = 1$. This can simply be considered in the ~~number~~ manner that 1:1 NH_3 and HCl vapour is nothing but $NH_4Cl(vap)$. So, basically one chemical individual defines both the phases and hence number of component is one.

However, if $NH_4Cl(s)$ dissociates in presence of $NH_3(g)$ or $HCl(g)$, the additional restriction that NH_3 and HCl are present in the system ~~are~~ in 1:1 mole ratio is not valid. Hence number of components $= 3 - 1 = 2$.

Ex-3: At the dissociation equilibrium of $CaCO_3(s)$, the relation between the constituents of the system is $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$. Now composition

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of each phase can be defined from the composition of other two phases. To define the gas phase we have to mention CO_2 and solid phase by $\text{CaCO}_3(\text{s})$. The composition of the remaining solid phase is known from the two other compounds CaCO_3 and CO_2 . The remaining solid phase is CaO , obtained from CaCO_3 after releasing one mole of CO_2 .

⊗ Degrees of Freedom (F) ⊗

Degrees of freedom (F) represents the minimum number of intensive variables that must be specified to represent the system. In other words, degrees of freedom may be defined as the number of intensive variable that can be changed without altering the system i.e. maintaining the equilibrium condition of the system. The variables are pressure, temperature and composition.

A pure substance in a given phase has a fixed composition. Both the temperature and pressure can be changed at random without altering the phase of the system so long the phase is stable. Under this condition the number of degrees of freedom is two;

Example, we can change the temperature and pressure of a given amount of a gas independently so long it is in the gaseous state. The volume is determined by the magnitude of instantaneous pressure and temperature. Hence the degrees of freedom is two. On the other hand to define the state of a given amount of any gas pressure and temperature are to be defined. Similar is the case of a liquid.

When a liquid remains in equilibrium with its vapour, the vapour pressure changes with the temperature. At a given temperature, liquid has a definite vapour pressure. If at a given temperature pressure is just increased infinitesimally from the equilibrium vapour pressure the vapour phase disappears and if pressure is just reduced infinitesimally from the equilibrium.

pressure the liquid vapour. vapourize completely (fig-3)

If we change the temperature then to maintain liq \rightleftharpoons vap equilibrium pressure is to be changed accordingly following clausius-clapeyron equation. Thus, the degrees of freedom of any two phases of a substance in equilibrium is one. In the pressure-temperature diagram a single phase system is represented by an area while a two phase system in equilibrium is represented by a line (fig-1).

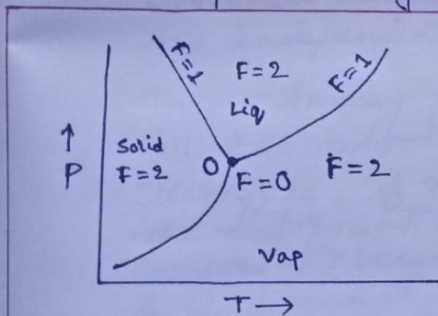
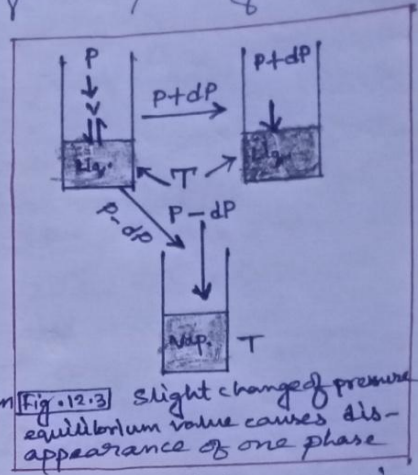


Fig. 12.4 Phase diagram of a pure substance. ($V_s > V_L$)

Three phases of a pure substance remain in equilibrium only at a particular temperature and pressure. If either pressure or temperature is changed the three phases no longer remain in equilibrium. Hence, degree of freedom becomes zero (0). Therefore, a three phase equilibrium is represented by a point (O) in the pressure-temperature diagram.

When system has degree of freedom two, it is called bivariant system. Similarly, system with degree of freedom one or zero is called univariant or non-variant system respectively. In a two dimensional phase diagram a bivariant system is represented by an area, univariant system by a line and nonvariant system by a point. Degree of freedom cannot be negative.

To study heterogeneous equilibrium the relation between the number of phases, components and degrees of freedom was derived by Willard Gibbs and the very famous equation is known as Gibbs-phase rule. For nonreactive constituents phase rule can be derived as follows.

Phase Rule

Let us consider a system having C no. of non reactive constituents in each of P number of phases which are in mutual equilibrium with one another. It is also considered that external fields of forces have no effect on the system. To find out the number of composition variables let us consider at first the phases separately to find out the independent composition variables. When the phase are in equilibrium some restrictions will arise and this will lower the number of independent composition variables considered so far. Finding out the number of dependent variables arising out due to equilibrium between phases, the independent composition variables can be calculated.

In any phase the summation of mole-fraction of all the components is equal to one; i.e. $x_1 + x_2 + \dots + x_c = 1$. Therefore, if molefraction of $(C-1)$ components are known, the molefraction of the remaining constituent (here the component) becomes known. So, for each phase the number of independent composition variables is $(C-1)$. Hence for all the P no. of phases considered separately the total number of composition variable becomes $P(C-1)$.

When different phases containing the same constituent are in equilibrium at a given temperature and pressure then according to Gibbs-Duhem equation, the condition of equilibrium is that the chemical potential of each constituent must be the same in all the phases. i.e., for the i th constituent, present in $\alpha, \beta, \gamma, \dots, P$ phases in equilibrium.

$$\mu_i^\alpha = \mu_i^\beta = \dots = \mu_i^P$$

Therefore if the chemical potential of a component in any one of the P no. of phases is known then its chemical potentials in other $(P-1)$ phases are also known. Moreover, as chemical potential is a function of concentration, if the concentration or molefraction of a constituent in any one phase is known then the other $(P-1)$ concentration or molefraction terms becomes dependent. Therefore, for all the C no. of components the number of dependent concentration term is $C(P-1)$. So number of independent composition variables when all the phases are considered together = $P(C-1) - C(P-1) = C - P$.

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considering pressure and temperature as two other intensive variables, the total number of degrees of freedom becomes,

$$F = C - P + 2$$

For any additional restriction (r), the degree of freedom becomes -

$$F = C - P + 2 - r.$$

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