It follows from the above that for a multiphase system at equilibrium, the chemical potential, μ_i, of a component i is the same in every phase.

Gibbs Phase Rule

The celebrated phase rule, enunciated by J. Willard Gibbs, states that if the equilibrium in a heterogeneous system is not affected by gravity or by electrical and magnetic forces, the number of degrees of freedom, F, of the system is related to the number of components, C and the number of phases, P, existing at equilibrium with one another by the equation

$$F = C - P + 2$$

Derivation of the Phase Rule. Consider a system of C components (C_1, C_2, C_3,..., C_C) distributed between P phases (α, β, γ, δ,····P), as shown in Fig. 1. Assume that passage of a component from one phase to another does not constitute a chemical reaction. The state of each phase of the system is completely specified by the two variables, temperature and pressure and also by the composition of each phase. In other words, the state of each phase is specified by

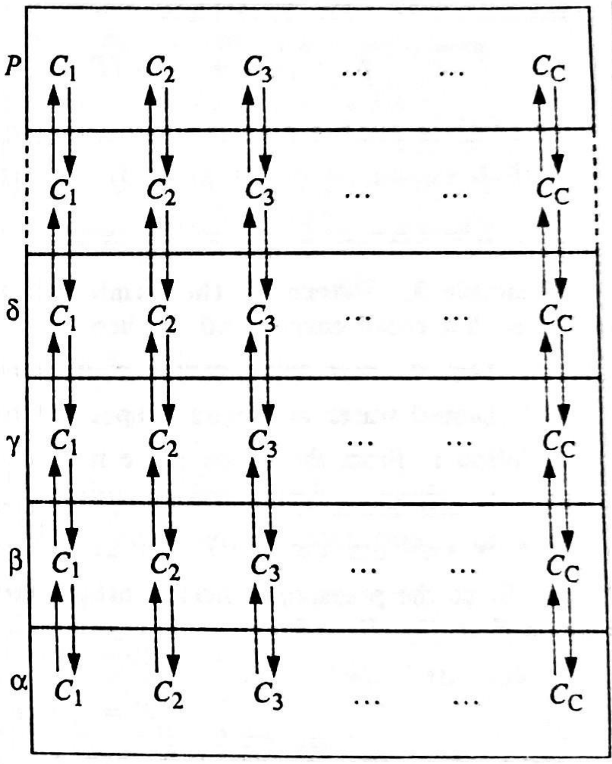

Fig. 1. A system of C components distributed through P phases.

$$T, P, (x_{1,\alpha}, x_{2,\alpha} \ldots\ldots x_{c,\alpha}), (x_{1,\beta}, x_{2,\beta} \ldots\ldots x_{c,\beta}), \ldots\ldots (x_{1,P}, x_{2,P}, \ldots\ldots, x_{c,P}) \qquad \ldots(18)$$

where x_is are compositions of the component. The total number of variables is thus $CP + 2$. However, in Eq. 18 all the variables are not independent since in each phase, the sum of the mole fractions must equal unity, *i.e.*,

$$x_{1,\alpha} + x_{2,\alpha} + x_{3,\alpha} + \cdots\cdots = x_{1,\beta} + x_{2,\beta} + x_{3,\beta} + \cdots\cdots, \text{ etc.} = 1$$

In other words, $\sum_i x_{i,P} = 1 \qquad (i = 1, 2, 3, \cdots\cdots C)$ ...(19)

for all the P phases separately. There are thus P relations of this type.

Again, for complete equilibrium to exist between the phases, the chemical potential of each species must be the same in each phase, *i.e.*,

$$\left.\begin{array}{l} \mu_{1,\alpha} = \mu_{1,\beta} = \mu_{1,\gamma} = \cdots = \mu_{1,P} \\ \mu_{2,\alpha} = \mu_{2,\beta} = \mu_{2,\gamma} = \cdots = \mu_{2,P} \\ \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \\ \mu_{c,\alpha} = \mu_{c,\beta} = \mu_{c,\gamma} = \cdots = \mu_{c,P} \end{array}\right\} \quad \text{(cf. Eq. 17)} \qquad \text{...(20)}$$

We see that there are $P - 1$ separate equations for each component. Hence, for C components, the number of such equations is $C(P - 1)$.

Also, the equilibrium conditions for the chemical reactions require that the chemical affinity, A_f, for each reaction at equilibrium must be zero, *i.e.*,

$$A_{f,i} = 0 \qquad (i = 1, 2, 3, \cdots\cdots, r') \qquad \text{...(21)}$$

This means that there are r' equations of this type.

Hence, total number of restricting conditions is

$$P + C\,(P - 1) + r' \qquad \text{...(22)}$$

The degree of freedom, F, is given by the difference between the number of variables required to specify the state of the system (*i.e.*, $CP + 2$) and the number of restrictions imposed by their interdependence (*i.e.*, Eq. 22). Thus,

$$F = (CP + 2) - (P + CP - C + r') = 2 + (C - r') - P \qquad \text{...(23)}$$

Eq. 23 is known as Gibbs Phase rule. If the system is non-reactive, *i.e.*, no reaction takes place in it, then equations of the type $A_f = 0$ will be absent, *i.e.*, $r' = 0$. Hence, the phase rule becomes

$$F = C - P + 2 \qquad \text{(Eq. 1)}$$