Conditions for the equilibrium between the phases:

1. **Thermal Equilibrium:** All the phases must be at the same temperature otherwise there will be flow of heat from one phase to another. Consider two phases α and β at same temperature T_α and T_β respectively. Let S_α and S_β be the entropies of two phases and let *dq* be the heat transferred from phase α to phase β at equilibrium. Then the entropy change of system is given by:

$$dS = dS_\alpha + dS_\beta = 0$$

Since, $dS_\alpha = -{}^{dq}/_{T}$ and $dS_\beta = {}^{dq}/_{T}$

$$\therefore \left(-{}^{dq}/_{T_\alpha}\right) + \left({}^{dq}/_{T_\beta}\right) = 0$$

$$T_\alpha = T_\beta$$

2. **Mechanical Equilibrium**: All the phases must be under the same pressure otherwise the volume of one phase will increase at the expense of another. We can prove it as follows. Suppose α-phase is expanded in β-phase by the volume change *dV.* Then the change in the Helmholtz free energy at constant temperature is given by

$$dA = -dA_\alpha + dA_\beta = 0$$

But, $dA_\alpha = -P_\alpha dV$ and $dA_\beta = -P_\beta dV$ (at constant T)

Since at equilibrium, $dA_\alpha = dA_\beta$ $and\ hence, P_\alpha = P_\beta$

3. **Chemical equilibrium:** For a system of many phases at equilibrium, the chemical potential of a component *i* is the same in all the phases. We can prove it as follows. Consider a closed system of P phases designated as α, β, γ……. P containing C components designated as 1, 2, 3….., C in equilibrium. It is being considered that all the phases are at same constant temperature and pressure. The Gibbs free energy change can be given as:

$$dG = dG_\alpha + dG_\beta + dG_\gamma + \ \dots\dots\dots$$

For a multicomponent system we have

$$dG = -SdT + VdP + \sum_i \mu_i dn_i$$

$$at\ constant\ T\ \&\ P, dT = 0\ and\ dP = 0$$

Hence, $(dG)_{T,P} = \sum_i \mu_i dn_i$

For a closed system at equilibrium, $dG=0$ and hence summations for all the above equation becomes zero. Thus it can be said that for multiphase system at equilibrium, the chemical potential is same in every phase.

Gibbs Phase Rule

The Gibbs Phase Rule was formulated by Josiah Willard Gibbs and gives the relationship between the number of phases, components, and degrees of freedom of a system at equilibrium. It 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 related system is related to the number of components, C and number of phases, P, existing at equilibrium with one another by the equation:

$$F = C + P - 2$$

At thermodynamic equilibrium:

1. Temperature is the same in all phases.

2. Pressure is the same in all phases.

3. Chemical potential of each component is the same in all phases.

Consider the system of C components (C_1, C_2, C_3…… C_C) distributed between P phases (α, β, γ, ….., P phases. Assume that passage of a component of a component from one phase to another does not constitute the 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

$T, P, (\chi_{1,\alpha}, \chi_{2,\alpha}, \chi_{3,\alpha}, \ldots \chi_{c,\alpha}), (\chi_{1,\beta}, \chi_{2,\beta}, \chi_{3,\beta}, \ldots \chi_{c,\beta}), \ldots\ldots\ldots\ldots\ldots (\chi_{1,P}, \chi_{2,P}, \chi_{3,P}, \ldots \chi_{c,P})$

Where χ_is are the composition of the components. The total number of variables are this *CP+2.*

Since all these variables are not independent since in each phase the sum of the mole fractions must be unity and hence

$$\chi_{1,\alpha} + \chi_{2,\alpha} + \chi_{3,\alpha} + \cdots \ldots \ldots \ldots .. = \chi_{1,\beta} + \chi_{2,\beta} + \chi_{3,\beta} + \cdots \ldots \ldots \ldots .. = etc. = 1$$

Or in other words, $\sum_i \chi_i P = 1 \; (i = 0,1,2,3 \ldots \ldots \ldots C)$

For all the phases separately. Thus there are P relations of this type.

There are P-1 separate equations for each component and for C components the number of such equations are *C(P-1).*

In a chemical reaction equilibrium conditions also satisfy the criteria for chemical affinity to be $A_{f,i} = 0$

i=1,2,3……….r

where r is the number of chemical reactions. Therefore when there is no chemical reaction in the system overall equation for the Gibbs free energy becomes

$$F = (CP + 2) - (P + CP - C) = 2 + C - P$$