(iii) The following equilibria are present:

$$NaCl(s) \xrightleftharpoons{H_2O} Na^+(aq) + Cl^-(aq)$$

$$KCl(s) \xrightleftharpoons{H_2O} K^+(aq) + Cl^-(aq)$$

$$H_2O(l) \rightleftharpoons H_2O(g)$$

$P = 4$

$C = 7 - 3 - 1 = 3$ (3 equilibria and 1 electroneutrality)

$\therefore \quad F = C - P + 2$

$= 3 - 4 + 2$

$= 1$

Example 7.2

Show that the system, $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$, is a one component system when $p_{NH_3} = p_{HCl}$ and a two component system when $p_{NH_3} \neq p_{HCl}$.

Solution:

Number of constituent = 3
Number of equation = 1
Number of restriction = 1 (when $p_{NH_3} = p_{HCl}$)
∴ Number of components = 3 – 1 – 1 = 1

When, $p_{NH_3} \neq p_{HCl}$ there is no restriction.
∴ Number of components = 3 – 1 – 0 = 2

Hence, the number of component = 1, when $p_{NH_3} = p_{HCl}$ and the number of component = 2, when $p_{NH_3} \neq p_{HCl}$.

Example 7.3

Find the number of components and phases and calculate the degrees of freedom in the following equilibria.

(i) An aqueous solution of sucrose.
(ii) A dilute solution of sulphuric acid in water.
(iii) An aqueous solution saturated with respect to both NaCl and KCl and in equilibrium with the vapour phases.

Solution:

(i) An aqueous solution of sucrose contains sucrose dissolved in water.

$P = 1$
$C = 2$
$\therefore F = C - P + 2$
$= 2 - 1 + 2$
$= 3$

(ii) A dilute aqueous solution of sulphuric acid involves the following equilibria:

$$H_2SO_4 + H_2O \rightleftharpoons HSO_4^- + H_3O^+$$

$$HSO_4^- + H_2O \rightleftharpoons SO_4^{2-} + H_3O^+$$

$P = 1$
$C = 5 - 2 - 1 = 2$ (Two equilibria and one electroneutrality)
$\therefore F = C - P + 2$
$= 2 - 1 + 2$
$= 3$

$F = (PC + 2) - \{P + C(P-1)\}$
$= C - P + 2$

or, $F + P = C + 2$ .... (7.1)

This is Gibbs phase rule.

It is seen from Equation (7.1) that for a system of definite number of components, the less is the number of phases, more will be the number of degrees of freedom. Thus for a one component system:

(i) $P = 1$, $F = C - P + 2 = 1 - 1 + 2 = 2$ (Bivariant)

(ii) $P = 2$, $F = 1 - 2 + 2 = 1$ (Univariant)

(iii) $P = 3$, $F = 1 - 3 + 2 = 0$ (Invariant)

Thus, for a one component system, the maximum number of phases that can be at equilibrium is three.

Again, for a system having a given number of phases, the more is the number of components greater will be the number of degrees of freedom.

The phase rule does not depend upon the nature or the amount of the substances present in the system at equilibrium. Phase rule does not take into account external forces like electric, magnetic, gravitational, surface forces, etc. The phase rule is not concerned about the composition of the matter. It merely states that systems having same degrees of freedom behave alike thermodynamically.

Example 7.1

Find the number of components and number of phases in the following equilibria and evaluate the degrees of freedom in each case.

(i) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

(ii) $S_{(\alpha)} \rightleftharpoons S_{(\beta)} \rightleftharpoons S_{(l)} \rightleftharpoons S_{(g)}$

(iii) $Fe(s) + H_2O(g) \rightleftharpoons Fe(s) + H_2(g)$

Solution:

(i) Number of phase = 1

Number of components = 3 − 1 = 2

Number of degrees of freedom, $F = C - P + 2$
$= 2 - 1 + 2$
$= 3$

(ii) Number of phase = 4

Number of components = 1

Number of degrees of freedom, $F = 1 - 4 + 2$
$= -1$

(This means that all the four phases cannot be at equilibrium)

(iii) Number of phase = 3

Number of components = 4 − 1 = 3

Number of degrees of freedom, $F = C - P + 2$
$= 3 - 3 + 2$
$= 2$

Now,

Degree of freedom or the no. of independent variables = Total no. of variables need to be specified − Total no. of equ^ns that are available

∴ from equ^ns (1) & equ^n (3), we have

$$F = (PC + 2) - \{P + C(P-1)\}$$

$$= PC + 2 - P - PC + C$$

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

$$\Rightarrow \boxed{F + P = C + 2} \longrightarrow (4)$$

This is Gibbs Phase Rule

For each phase there is one such equ^n

$\therefore$ For 'P' phases, there are 'P' equ^{ns} like equ^n (2)

Now, the thermodynamic condi^n of phase equ^m is that at const. 'T' & 'P', chemical potential (μ), which is Gibbs free energy per mole, of a particular compt. will have the same value in all phases

$\therefore$ For 2 phases 'α' & 'β' at equ^m then,

$$\mu_\alpha \rightleftharpoons \mu_\beta$$

$\therefore$ For 3 phases α, β, & 'γ' at equ^m then,

$$\mu_\alpha \rightleftharpoons \mu_\beta \rightleftharpoons \mu_\gamma$$

$\therefore$ For each compt, we will have 'P-1' equ^{ns}

$\therefore$ " 'C' " , " " " $= C(P-1)$ equ^{ns}

$\therefore$ total no. of equ^{ns} that are available $= P + C(P-1)$ $\longrightarrow$ (3)

Gibbs Phase Rule & Its Derivation:

Rule is, $F + P = C + 2$

$F \rightarrow$ Degree of freedom
$P \rightarrow$ No. of phases
$C \rightarrow$ No. of compts

Let's consider a heterogeneous system of 'P' phases
→ all at equilibrium
— All phases contain 'C' compts

i.e. In one phase, no. of compts $= C$
∴ In 'P' phases, " " $= CP$

In addn, there are 2 more variables = Temp. & Pressure

∴ Total no. of variables need to be specified $= CP + 2$ → (1)

Again,
sum of mole fractions of compts in a phase $= 1$

$$\therefore x_1 + x_2 + \cdots + x_i = \sum_i x_i = 1$$
→ (2)

7.1.3 Degree of Freedom or Variance

*The **degree of freedom or variance** of a system is the minimum number of independent variables such as temperature, pressure and concentration, that must be ascertained so that a given system at equilibrium can be completely defined. Alternatively, the degree of freedom of a system may be defined as the number of factors, such as temperature, pressure and concentration, which can be varied independently without altering the number of phases.*

Let us consider a gaseous system. To describe completely the state of the system only two of the three variables need to be specified as the third one is automatically known because these three variables are linked through the equation of state. Hence, the system is bivariant, i.e., degrees of freedom is two.

If, on the other hand, a liquid is in equilibrium with its vapour, only one variable needs to be specified. Thus, if temperature is fixed, its vapour pressure is automatically fixed. So, it is necessary to specify either the temperature or the pressure to define the state of the system completely. Hence, the system is univariant and degree of freedom is one.

When three phases, say, ice, water and water vapour are at equilibrium at the triple point both the temperature and the pressure are fixed. For ice-water-water vapour system the temperature at the triple point is 0.0075^0 C and the pressure is 4.58 torr. The change in either the temperature or the pressure will disturb the equilibrium and will change the three phase system into two phase system. The system is said to the invariant or non-variant and the degree of freedom is zero.