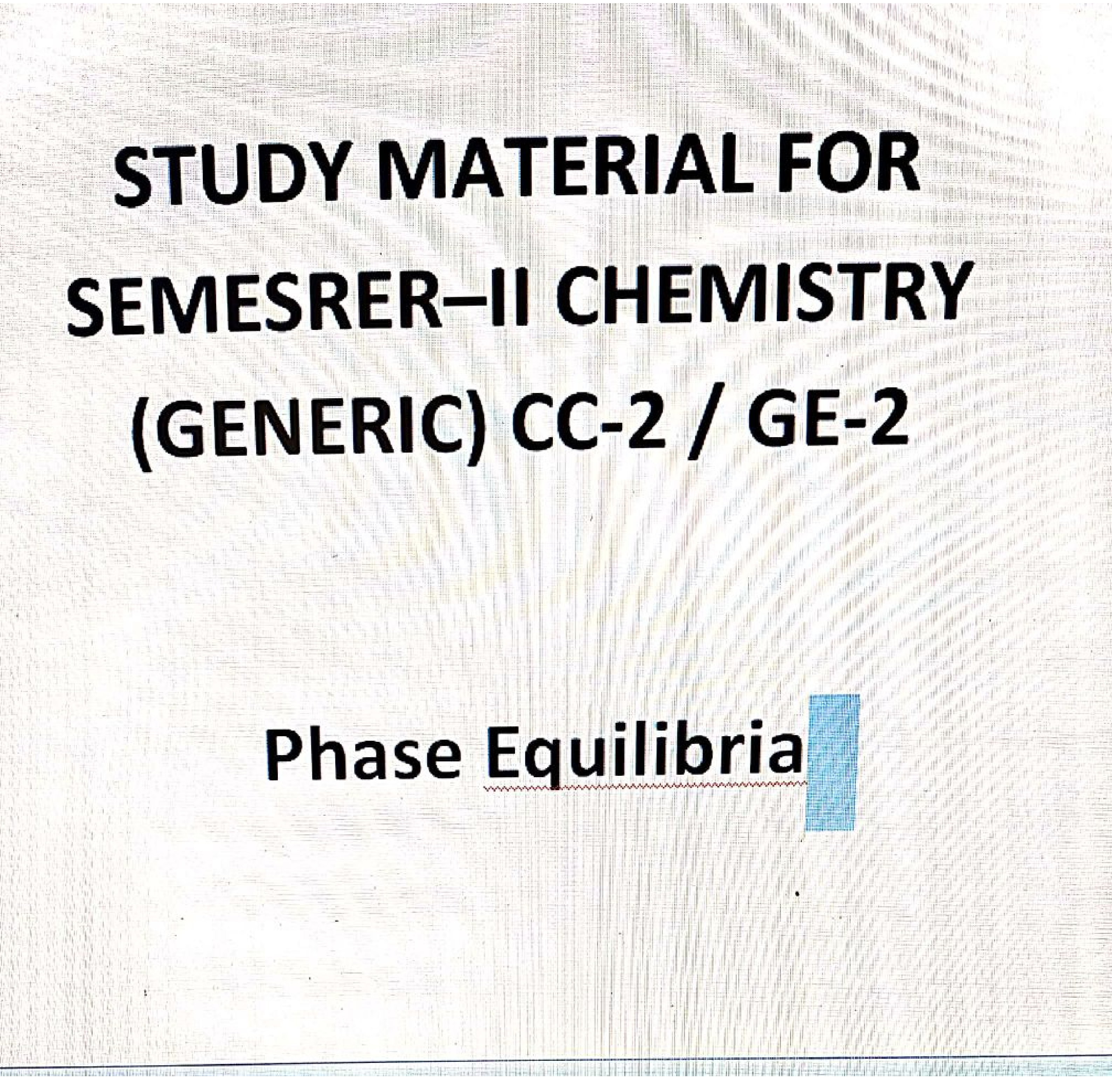

STUDY MATERIAL FOR SEMESRER–II CHEMISTRY (GENERIC) CC-2 / GE-2

Phase Equilibria

Phase Rule

3.1 Introduction and Definitions

The various conditions of equilibrium between phases, such as the number of phases, the number of components and the degrees of freedom (or the variance), can be correlated with one another with the help of a general rule, known as the *phase rule.* This rule was deduced theoretically by J.W. Gibbs. Before proceeding with the deduction of the rule, it is necessary to define and explain the terms involved, viz., phase, component and degrees of freedom.

PHASE

A phase is defined as any homogeneous and physically distinct part of a system which is separated from other parts of the system by definite bounding surfaces. The term homogeneous means that the system has identical physical properties and chemical composition throughout the whole of the system.

In general, we have:

(i) *For gaseous system*: Only one phase is possible since gases are completely miscible with one another in all proportions.

(ii) *For liquid system*: The number of phases is equal to the number of layers present in the system. For completely miscible liquids, the number of phases is equal to one.

(iii) *For solid system*: In general, every solid constitutes a single phase except when a solid solution is formed. Thus the number of phases in the solid system is equal to the number of solids present. In solid solution, the number of phases is equal to one. Each polymorphic form and allotropic modification constitutes a separate phase.

NUMBER OF COMPONENTS

It is the smallest number of independent chemical constituents by means of which the composition of each and every phase can be expressed. The independent chemical constituent is the one whose concentration can be varied independent of other constituents of the system. Some typical examples are given below.

(i) *One-component system*: The water system is a typical example of one-component system. We can have the following equilibria between the different phases of water;

solid water (ice) $\rightleftharpoons$ liquid water
solid water $\rightleftharpoons$ water vapour
liquid water $\rightleftharpoons$ water vapour
solid water $\rightleftharpoons$ liquid water $\rightleftharpoons$ water vapour

The composition of any one phase (solid, liquid or vapour) can be expressed in terms of the single constituent water and hence the number of components is one. The variable could be either H_2 or O_2 since specification of one fixes the other through the formula H_2O. However, this choice is never considered since H_2 or O_2 does not exist as the individual constituent in the above equilibrium.

(ii) *Two-component system*: The typical example of a two-component system is the salt hydrate system such as sodium sulphate-water, copper sulphate-water, etc. In Na_2SO_4-H_2O system, the various phases that may occur are Na_2SO_4, $Na_2SO_4 \cdot 7H_2O$, $Na_2SO_4 \cdot 10H_2O$, an aqueous solution of Na_2SO_4, water present as ice, liquid and vapour. The composition of any of the above phases can be stated in terms of the two constituents, namely, sodium sulphate and water:

Na_2SO_4 : $Na_2SO_4 + 0H_2O$
$Na_2SO_4 \cdot 7H_2O$: $Na_2SO_4 + 7H_2O$
$Na_2SO_4 \cdot 10\,H_2O$: $Na_2SO_4 + 10H_2O$
Na_2SO_4 (aq) : $Na_2SO_4 + x\,H_2O$
H_2O (s), H_2O (l), H_2O (g) : $0Na_2SO_4 + H_2O$

It can be seen that the composition of some of the phases can be represented by only one component while the others necessarily require two components. Since two components are the smallest number by which the composition of all the phases can be defined, the number of components in sodium sulphate-water system is two.

Another example is the equilibrium between $CaCO_3$(s), CaO(s) and CO_2 (g) as represented by the equation

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

Here the number of phases are three, viz., solid $CaCO_3$, solid CaO and gaseous CO_2. The number of components in the above system is two since two species out of the three are sufficient to express the composition of all the three phases. It is immaterial which of the two are selected for this purpose. For example:

(a) If CaO and CO_2 are chosen, then

$CaCO_3$ (s) : $CaO + CO_2$
CaO (s) : $CaO + 0\,CO_2$
CO_2 (g) : $0\,CaO + CO_2$

(b) If $CaCO_3$ and CaO are chosen, then

$CaCO_3$ (s) : $CaCO_3 + 0\,CaO$
CaO (s) : $0\,CaCO_3 + CaO$
CO_2 (g) : $CaCO_3 - CaO$

and so on.

Thus it is the number and not the nature that is important for determining the components of the system.

Another example, which makes a clear distinction between the one-component system and the two-component system, is the dissociation of ammonium chloride:

$$NH_4Cl\ (s) \rightleftharpoons NH_3\ (g) + HCl\ (g)$$

This system has two phases, viz., solid NH_4Cl and gaseous phase containing ammonia and hydrochloric acid. If the dissociation is carried out in vacuum, then the number of components of the system is one. This is due to the fact that in the gaseous phase both HCl and NH_3 are always present in equal amounts and thus its composition can be represented by NH_4Cl ($= x\,NH_3 + x\,HCl$). But if the dissociation is carried out in the presence of arbitrary amounts of NH_3 or/and HCl, then the number of components of the system becomes two:

Solid NH_4Cl : $NH_3 + HCl$
Gaseous phase : $x\,NH_3 + y\,HCl$

DEGREES OF FREEDOM

The degree of freedom or variance of the system is the minimum number of independent variables such as temperature, pressure and concentration, that must be ascertained so that a given system in equilibrium is completely defined. For an illustration, we cite an example of water system. If only one phase is present (solid, liquid or gas), then we have to describe values of at least two parameters, namely, temperature and pressure, in order to define the system. For example, we can have liquid water under different conditions of temperature and pressure. Thus the water system has two degrees of freedom or it is bivariant. Now consider two phases in equilibrium, for example, solid and liquid water, i.e.

$$\text{solid water} \rightleftharpoons \text{liquid water}$$

It is well known that the temperature at which a solid melts depends upon external pressure. Thus if the value of one of the variables is fixed, the other will automatically have a definite value. The usual melting point of 0°C is referred to one atm external pressure. In order to describe the above equilibrium completely, we need to specify only one variable—either temperature or pressure; hence the system has one degree of freedom, i.e., it is an univariant system.

Alternatively, *the degree of freedom of the 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.* For a single phase system, both temperature and pressure can be varied independently of each other and thus the system is bivariant. For two phases in equilibrium, only one variable can be varied as the other one will automatically have a fixed value and thus the system is univariant.

Consider now the situation at the triple point of water where all the three phases are in equilibrium with each other. This equilibrium is achieved at a temperature of 0.009 8°C and a pressure of 4.58 mmHg. Any change in the values of these variables, converts the three-phase system into either two-phase or one-phase system. Thus, none of the variables can be changed so long as we want to have all the three phases in equilibrium. Thus the system has zero degree of freedom, or it is nonvariant (or invariant).

3.2 Derivation of Phase Rule

Phase rule is a general rule which is applicable to all types of reactive and nonreactive systems. In a nonreactive system, we simply have the distribution of various components in different phases without any complications such as the chemical reaction between the components. We derive the rule, first, for the nonreactive system and then show how the same rule can be used for the reactive system.

NONREACTIVE SYSTEM

Consider a heterogeneous system of P phases at equilibrium containing in all C components. Let us start with the assumption that all the C components are present in all P phases. The system at equilibrium can be completely described if we know the values of the variables listed in Table 3.2.1.

TABLE 3.2.1 THE VALUES OF THE VARIABLES TO BE KNOWN TO DEFINE A GIVEN SYSTEM COMPLETELY

Variables	*Number*
(i) Temperature of the system	1
(ii) Pressure of the system	1
(iii) Concentration (or mole fraction) of each and every component in all the P phases. For each phase, we will have to specify the values of C concentration terms and thus for P phases, we will have to specify in all PC values	PC
Total number of variables that need to be specified	$PC+2$

Values of these variables can be obtained by solving the equations which are applicable when the system is at equilibrium. There are two types of equations which are available (Table 3.2.2).

Mathematically, we know that the number of variables that can be obtained from a set of equations is equal to the number of equations. Thus if there are as many equations as there are variables, then the temperature, pressure and composition of the whole system in equilibrium can be determined. Such a system, as stated earlier, is the *nonvariant* system. If the number of variables exceeds the number of equations by one, then the equilibrium of the system cannot be determined until one of the variables is arbitrarily chosen. Such a system is called *monovariant* (*or univariant*) and has one degree of freedom. Thus we see that the excess of variables over

TABLE 3.2.2 TYPES OF EQUATIONS WHICH ARE AVAILABLE

Equations	Number
(i) Condition of sum of the mole fractions in any phase being equal to one, i.e., $x_1^{(1)}+x_2^{(1)}+\ldots+x_c^{(1)} = 1$ $x_1^{(2)}+x_2^{(2)}+\ldots+x_c^{(2)} = 1$ .... $x_1^{(P)}+x_2^{(P)}+\ldots+x_c^{(P)} = 1$ There will be as many equations as the number of phases. Thus their total number will be P	P
(ii) Thermodynamic condition of phase equilibria: According to this, the species will be distributed in such a manner that value of G of the system at equilibrium is minimum. The condition for this is that the chemical potential of any component will have the same value in all the P phases, i.e., $\mu_1^{(1)} = \mu_1^{(2)} = \mu_1^{(3)} = \ldots = \mu_1^{(P)}$ $\mu_2^{(1)} = \mu_2^{(2)} = \mu_2^{(3)} = \ldots = \mu_2^{(P)}$ $\ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots$ $\mu_c^{(1)} = \mu_c^{(2)} = \mu_c^{(3)} = \ldots = \mu_c^{(P)}$ For each component, we will have $(P-1)$ equations and thus for C components, the number of equations will be $C(P-1)$	$C(P-1)$
Total number of equations that are available	$P+C(P-1)$

equations, which is called the variance F of the system, is given as

$$\text{Variance} = \begin{pmatrix}\text{Total number of variables}\\ \text{that need to be specified}\end{pmatrix} - \begin{pmatrix}\text{Total number of equations}\\ \text{that are available}\end{pmatrix}$$

Thus, from Tables 3.2.1 and 3.2.2, we have

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

or

$$F = C-P+2$$

or

$$F+P = C+2 \tag{3.2.1}$$

Equation 3.2.1 is the phase rule which connects the number of phases and components with the variance of the system. Let us verify the rule by calculating the variance of a one-component system:

(i) *One phase only*: $P = 1,\ F = 1-1+2 = 2$
(ii) *Two phases in equilibrium*: $P = 2,\ F = 1-2+2 = 1$
(iii) *Three phases in equilibrium*: $P = 3,\ F = 1-3+2 = 0$

Thus, we see that the calculated degrees of freedom agree with experimentally observed values of the one-component water system.

The condition that all the components must be present in every phase, which has been used above in deriving the phase rule, is not altogether essential. The rule is applicable even if any component is missing in any of the phases. Say, for example, the component number 1 is missing from the phase number 1. We can once again derive the phase rule by following the procedure described earlier. Tables 3.2.3 and 3.2.4 describe the number of variables and equations for the present case.

TABLE 3.2.3 VALUES OF VARIABLES TO BE KNOWN TO DEFINE A GIVEN SYSTEM COMPLETELY

Variables	*Number*
(i) Temperature	1
(ii) Pressure	1
(iii) Concentration of components in different phases: For the first phase, $(C-1)$ concentration terms and for the remaining $(P-1)$ phases, C terms for each phase	$(C-1)+C(P-1)$
Total number of variables that need to be specified	$(C-1)+C(P-1)+2$ $= CP+1$

TABLE 3.2.4 TYPES OF EQUATIONS AVAILABLE

Equations	*Number*
(i) Condition of mole fraction: $x_2^{(1)}+x_3^{(1)}+\dots x_c^{(1)} = 1$ $x_1^{(2)}+x_2^{(2)}+\dots x_c^{(2)} = 1$ ……………………………… $x_1^{(P)}+x_2^{(P)}+\dots+x_c^{(P)} = 1$ There will again be in all P equations	P
(ii) Condition of thermodynamic equilibrium: For the component 1 $\mu_1^{(2)} = \mu_1^{(3)} = \dots = \mu_1^{(P)}$	$(P-2)$
For other components $\mu_2^{(1)} = \mu_2^{(2)} = \mu_2^{(3)} = \dots = \mu_2^{(P)}$ ……………………………… $\mu_c^{(1)} = \mu_c^{(2)} = \mu_c^{(3)} = \dots = \mu_c^{(P)}$	$(C-1)(P-1)$
There will be $(P-2)$ equations for the component number 1, one less as compared to others as it is absent in the phase number 1	
Total number of equations that are available	$P+(P-2)+(C-1)(P-1)$ $= \{P+C(P-1)\}-1$

From Tables 3.2.3 and 3.2.4, we have

$$\text{Variance of the system} = \begin{pmatrix}\text{Total number}\\ \text{of variables}\end{pmatrix} - \begin{pmatrix}\text{Total number of}\\ \text{equations}\end{pmatrix}$$

$$F = CP+1-[P+C(P-1)-1]$$

$$F = C-P+2$$

3.3 Some Typical Examples to Compute the Number of Components

We have earlier defined the number of components as the minimum number of independent chemical constituents required to express the composition of each and every phase of a system. This definition is completely in harmony with the definitions given below for the reactive and the nonreactive systems.

For nonreactive system: Number of components = Number of constituents

For reactive system: Number of components = (Number of constituents) − (Number of chemical reactions) − (Number of restricting conditions)

Let us illustrate the above consistency with the help of a few typical examples.

SODIUM SULPHATE—WATER SYSTEM

As stated earlier, it is a two-component system. It can be shown that so long as no precipitate is formed by virtue of a reaction between salt and water, the number of components is always two no matter what else is assumed to take place in the solution. We consider below four typical assumptions regarding the nature of the system.

(i) *Neglecting all Dissociations*: There are two constituents, no chemical reaction, and no restricting equation. Hence

$$C' = C - r - Z = 2 - 0 - 0 = 2$$

(ii) *Complete Dissociation of the Salt*: The total number of constituents present in the solution are three: Na^+, SO_4^{2-} and H_2O. Since there is one restricting condition:

$$x_{Na^+} = 2\,x_{SO_4^{2-}}$$

we have

$$C' = C - r - Z = 3 - 0 - 1 = 2$$

(iii) *Partial Dissociation of the Salt*: The dissociation may be represented as

$$Na_2SO_4 \rightleftharpoons 2Na^+ + SO_4^{2-}$$

Now the system possesses four constituents, namely, Na_2SO_4, Na^+, SO_4^{2-} and H_2O. There is one reaction and one restricting condition:

$$x_{Na^+} = 2\,x_{SO_4^{2-}}$$

Thus, we have

$$C' = C - Z - r = 4 - 1 - 1 = 2$$

(iv) *Dissociation of Water also*: We have the following two equilibrium reactions:

$$Na_2SO_4 \rightleftharpoons 2\ Na^+ + SO_4^{2-}$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

The different constituents are Na_2SO_4, Na^+, SO_4^{2-}, H_2O, H^+ and OH^-, a total of six. There are two reactions and two restricting conditions :

$$x_{Na^+} = 2\ x_{SO_4^{2-}}$$

$$x_{H^+} = x_{OH^-}$$

Thus

$$C' = C - Z - r = 6 - 2 - 2 = 2$$

SODIUM DIHYDROGEN PHOSPHATE—WATER SYSTEM

It can be shown that this system is a two-component system irrespective of whatever chemical changes may be considered in the solution except that no precipitate is formed.

(i) *Neglecting all Dissociations*: There are two constituents, no chemical reaction and no restricting equation. Hence

$$C' = C - Z - r = 2 - 0 - 0 = 2$$

(ii) *Single Dissociation of the Salt*: We may represent the dissociation as

$$NaH_2PO_4 \rightarrow Na^+ + H_2PO_4^-$$

There are four constituents (NaH_2PO_4, H_2O, Na^+ and $H_2PO_4^-$), one chemical reaction and one restricting equation:

$$x_{Na^+} = x_{H_2PO_4^-}$$

Hence

$$C' = C - Z - r = 4 - 1 - 1 = 2$$

(iii) *Multiple Dissociation of the Salt*: The multistep dissociation may be represented as

$$NaH_2PO_4 \rightleftharpoons Na^+ + H_2PO_4^-$$

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$$

$$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$$

There are seven constituents, NaH_2PO_4, Na^+, $H_2PO_4^-$, H^+, HPO_4^{2-}, PO_4^{3-} and H_2O.

Number of chemical reactions = 3

Number of independent restricting equations = 2:

$$x_{Na^+} = x_{PO_4^{3-}} + x_{HPO_4^{2-}} + x_{H_2PO_4^-}$$

$$x_{H^+} = 2\ x_{PO_4^{3-}} + x_{HPO_4^{2-}}$$

Thus

$$C' = C - Z - r = 7 - 3 - 2 = 2$$

(iv) *Dissociation of Water also*: Besides the dissociation given in part (iii), we also have

$$H_2O \rightleftharpoons H^+ + OH^-$$

There are total eight constituents, NaH_2PO_4, Na^+, $H_2PO_4^-$, H^+, HPO_4^{2-} PO_4^{3-}, OH^- and H_2O.

Number of chemical reactions = 4

Number of restricting equations = 2 :

$$x_{Na^+} = x_{PO_4^{3-}} + x_{HPO_4^{2-}} + x_{H_2PO_4^-}$$

$$x_{H^+} = 2\, x_{PO_4^{3-}} + x_{HPO_4^{2-}} + x_{OH^-}$$

Thus

$$C' = C - Z - r = 8 - 4 - 2 = 2$$

ALUMINIUM CHLORIDE—WATER SYSTEM

In this case, $AlCl_3$ combines with water according to the equation:

$$AlCl_3 + 3H_2O = Al(OH)_3 + 3HCl$$

Some of the $Al(OH)_3$ is precipitated out. The dissociation of the various species will be as follows:

$$AlCl_3 \rightleftharpoons Al^{3+} + 3Cl^-$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$Al(OH)_3 \rightleftharpoons Al^{3+} + 3OH^-$$

$$HCl \rightleftharpoons H^+ + Cl^-$$

Total number of constituents = 8:

$AlCl_3$, H_2O, $Al(OH)_3$, HCl, Al^{3+}, Cl^-, H^+ and OH^-

Number of chemical reactions = 4

Since some of the $Al(OH)_3$ has precipitated out, there is only one restricting equation, namely, that expressing the electrical neutrality of the solution

$$3\, x_{Al^{3+}} + x_{H^+} = x_{OH^-} + x_{Cl^-}$$

Thus the number of components = 8 − 4 − 1 = 3.

If we assume complete dissociation of $AlCl_3$ and that of HCl, we will have

$$C = 6,\ r = 2 \text{ and } Z = 1$$

Thus

$$C' = C - Z - r = 6 - 1 - 2 = 3$$

PROBLEM 3.3.1 Show that an aqueous system containing K^+, Na^+ and Cl^- is a three-component system whereas K^+, Na^+, Cl^- and Br^- is a four-component system. What are the number of components if the salts are present in equal amounts?

(a) K^+, Na^+, Cl^- *and* H_2O *system:* In this case, we have

Number of reactions, $r = 3$:

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$KCl \rightleftharpoons K^+ + Cl^-$$

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

Number of constituents, $C = 8$:

$$H_2O,\ KCl,\ NaCl,\ H^+,\ OH^-,\ K^+,\ Cl^- \text{ and } Na^+$$

Number of restricting equations, $Z = 2$:

(i) Electrical neutrality

$$x_{Na^+} + x_{K^+} + x_{H^+} = x_{Cl^-} + x_{OH^-}$$

(ii) Water dissociation

$$x_{H^+} = x_{OH^-}$$

Hence

Number of components, $C' = C - r - Z = 8 - 3 - 2 = 3$

If the salts are present in equal amounts, then one more restricting equation exists, i.e.,

$$x_{Na^+} = x_{K^+}$$

Hence, here

Number of components, $C' = C - r - Z = 8 - 3 - 3 = 2$

Alternatively, leaving KCl and NaCl on the basis that they are strong electrolytes, we have

Number of constituents, $C = 6$:

$$H_2O,\ H^+,\ OH^-,\ Na^+,\ K^+,\ Cl^-$$

Number of reactions, $r = 1$:

$$H_2O \rightleftharpoons H^+ + OH^-$$

Number of restricting equations, $Z = 2$:

$$x_{H^+} = x_{OH^-}$$

$$x_{Na^+} + x_{K^+} = x_{Cl^-}$$

Hence

Number of components, $C' = C - r - Z = 6 - 1 - 2 = 3$

If the salts are present in equal amounts, then one more restricting equation exists, i.e.,

$$x_{Na^+} = x_{K^+}$$

Hence, here

Number of components, $C' = C - r - Z = 6 - 1 - 3 = 2$

(b) K^+, Na^+, Cl^-, Br^- *and* H_2O *system:* In this case, we have

Number of reactions, $r = 5$;

$$H_2O \rightleftharpoons H^+ + OH^-$$
$$KCl \rightleftharpoons K^+ + Cl^-$$
$$NaBr \rightleftharpoons Na^+ + Br^-$$
$$NaCl \rightleftharpoons Na^+ + Cl^-$$
$$KBr \rightleftharpoons K^+ + Br^-$$

Number of constituents, $C = 11$

H_2O, H^+, OH^-, KCl, K^+, Cl^-, $NaBr$, Na^+, Br^-, $NaCl$ and KBr

Number of restricting equations, $Z = 2$:

(i) Electrical neutrality

$$x_{Na^+} + x_{K^+} + x_{H^+} = x_{Cl^-} + x_{Br^-} + x_{OH^-}$$

(ii) Water dissociation

$$x_{H^+} = x_{OH^-}$$

Hence

Number of components, $C' = C - r - Z = 11 - 5 - 2 = 4$

If the salts are present in equal amounts, then we have three independent restricting equations:

$$x_{Na^+} = x_{K^+}$$
$$x_{Cl^-} = x_{Br^-}$$
$$x_{H^+} = x_{OH^-}$$

Hence

Number of components, $C' = C - r - Z = 11 - 5 - 3 = 3$

Alternatively, leaving KCl, NaBr; NaCl and KBr as they are strong electrolytes, we have:

Number of constituents, $C = 7$:

H_2O, H^+, OH^-, Na^+, K^+, Cl^- and Br^-

Number of reactions, $r = 1$:

$$H_2O \rightleftharpoons H^+ + OH^-$$

Number of restricting conditions, $Z = 2$:

$$x_{H^+} = x_{OH^-}$$
$$x_{Na^+} + x_{K^+} = x_{Cl^-} + x_{Br^-}$$

Hence

Number of components, $C' = C - r - Z = 7 - 1 - 2 = 4$

If the salts are present in equal amounts, then we have three independent restricting equations:

$$x_{Na^+} = x_{K^+}$$
$$x_{Cl^-} = x_{Br^-}$$
$$x_{H^+} = x_{OH^-}$$

Hence

Number of components, $C' = C - r - Z = 7 - 1 - 3 = 3$

PROBLEM 3.3.2 Show that $NH_4Cl(s)-NH_3(g)-HCl(g)$ system in which $p_{NH_3} = p_{HCl}$ is a one-component system whereas when $p_{NH_3} \neq p_{HCl}$ is a two-component system.

(a) $NH_4Cl(s)-NH_3(g)-HCl(g)$ *when* $p_{NH_3} = p_{HCl}$: The condition of $p_{NH_3} = p_{HCl}$ would arise only when the gases are obtained by the sublimation of $NH_4Cl(s)$. Thus, we have

Number of reactions, $r = 1$:

$$NH_4Cl(s) \rightleftharpoons NH_3(g)+HCl(g)$$

Number of constituents, $C = 3$:

$$NH_4Cl(s),\ NH_3(g) \text{ and } HCl(g)$$

Number of restricting equations, $Z = 1$:

$$p_{NH_3} = p_{HCl}$$

Hence

Number of components. $C' = C-Z-r = 3-1-1 = 1$.

(b) $NH_4Cl(s)-NH_3(g)-HCl(g)$ *when* $p_{NH_3} \neq p_{HCl}$: Here, we have

Number of reactions, $r = 1$
Number of constituents, $C = 3$
Number of restricting equations, $Z = 0$
Hence
Number of components, $C' = C-Z-r = 3-0-1 = 2$

PROBLEM 3.3.3 Determine the number of components in a system containing $NH_4Cl(s)$, $NH_4^+(aq)$, $Cl^-(aq)$, $H_2O(l)$, $H_3O^+(aq)$, $H_2O(g)$, $NH_3(g)$, $OH^-(aq)$, and $NH_4OH(aq)$.

We have:
Number of constituents, $C = 9$
Number of equilibrium reactions, $r = 5$:

$$NH_4Cl(s) \rightleftharpoons NH_4^+(aq)+Cl^-(aq)$$

$$NH_4^+(aq)+2H_2O \rightleftharpoons NH_4OH(aq)+H_3O^+(aq)$$

$$NH_3(g)+H_2O(l) \rightleftharpoons NH_4OH(aq)$$

$$2H_2O(l) \rightleftharpoons H_3O^+(aq)+OH^-(aq)$$

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

Number of restricting conditions, $Z = 1$:

$$x_{NH_4^+} + x_{H_3O^+} = x_{Cl^-} + x_{OH^-} \qquad \text{(condition of electroneutrality)}$$

Hence
Number of components, $C' = C-r-Z = 9-5-1 = 3$

PROBLEM 3.3.4 Consider a homogeneous mixture of four ideal gases capable of undergoing the reaction

$$\nu_1A_1+\nu_2A_2 \rightleftharpoons \nu_3A_3+\nu_4A_4$$

Determine the components if we start with (a) arbitrary amounts of A_1 and A_2 only, (b) arbitrary amounts of all the four gases, and (c) ν_1 moles of A_1 and ν_2 moles of A_2 only.

(a) Number of constituents, $C = 4$:

$$A_1,\ A_2,\ A_3 \text{ and } A_4$$

Number of reactions, $r = 1$

Number of restrictions, $Z = 1$:

$$[A_3]:[A_4]::\nu_3:\nu_4$$

Hence

Number of components, $C' = C-r-Z = 4-1-1 = 2$

(b) Number of constituents, $C = 4$
Number of reactions, $r = 1$
Number of restrictions, $Z = 0$
Number of components, $C' = C-r-Z = 4-1-0 = 3$

(c) Number of constituents, $C = 4$
Number of reactions, $r = 1$
Number of restrictions, $Z = 2$

$$[A_1]:[A_2]::\nu_1:\nu_2$$

and

$$[A_3]:[A_4]::\nu_3:\nu_4$$

Hence

Number of components, $C' = C-r-Z = 4-1-2 = 1$

REVISIONARY PROBLEMS

3.1 (a) Explain with suitable examples the terms involved in the phase rule

$$F+P = C+2$$

(b) What do you understand by the reactive and nonreactive systems?

3.2 (a) Derive the expression of phase rule as applicable to a nonreactive system.

(b) Prove that the expression of phase rule remains unchanged even if one of the components is missing in some of the phases present at equilibrium.

3.3 (a) What is the difference between the number of constituents and the number of components of a given system?

(b) Show that for the reactive systems, the form of the phase rule remains unaltered provided we define the number of components as

$$C' = C-r-Z$$

where C is the number of constituents present, r is the number of independent reactions, and Z is the number of independent restricting equations.

TRY YOURSELF PROBLEMS

3.1 Show without using the phase rule explicity that the two-component system has (1) $F = 3$ if $P = 1$; (2) $F = 2$ if $P = 2$; (3) $F = 1$ if $P = 3$; and (4) $F = 0$ if $P = 4$.

3.2 Show that it is not possible to have more than three phases at equilibrium for a one-component system.

3.3 Blue copper sulphate crystals decompose and release their water of hydration when heated. How many phases and components are present in an otherwise empty heated vessel?

3.4 The absence of a few components in some phases does not alter the phase rule relation, $F+P=C+2$. Derive the above conclusion by taking the following system of three components distributed over five phases:

$$\underset{\text{Phase 1}}{A+B} \rightleftharpoons \underset{\text{Phase 2}}{B+C} \rightleftharpoons \underset{\text{Phase 3}}{A+B+C} \rightleftharpoons \underset{\text{Phase 4}}{A} \rightleftharpoons \underset{\text{Phase 5}}{A+C}$$

3.5 How many degrees of freedom, number of phases and number of components are present in each of the following systems:

components by two, provided that the only significant external factors acting are temperature and pressure (*i.e.,* no surface effect, gravitational effect, *etc.* are present), or stated in symbols,

$P + F = C + 2$, or the more usual form, $C - P + 2 = F$ ... (17.7)

where C is the number of components, P the number of phases and F the degrees of freedom.

Some deductions from Phase Rule are shown below in tabular form. Application to some typical systems follows.

	No. of phases, P	No. of Degrees of Freedom, F	Example
One-Component System $C = 1$	2	1	Ice—Vapour ; Water—Vapour ; Rhombic S—Monoclinic S ; Sulphur—Vapour ; $NH_4Cl(s)$—$NH_4Cl(g)$
	3	0	Triple point of Ice-Water-Vapour; Triple points in Sulphur System
Two-Component System $C = 2$	1	3	$NH_4Cl(g)+NH_3(g)$ or HCl (g)
	2	2	Salt Solution—Vapour ; Satd. salt soln.—Solid ; $NH_4Cl(g)+NH_3(g)+NH_4Cl(g)$;
	3	1	$CaCO_3(s)+CaO(s)+CO_2(g)$; Satd. Soln.—Solid—Vapour ; Liquid 1—Liquid 2—Vapour

PHASE EQUILIBRIA OF ONE-COMPONENT SYSTEMS

Thermodynamic Consideration ▌ The basic thermodynamics has already been discussed (Chapter 12). According to this, if the same substance exists in a number of phases (I, II, *etc.)* in mutual equilibrium, its chemical potential must be the same in all the phases, *i.e.*,

Condition of Phase Equilibrium : $\mu\ (\mathrm{I}) = \mu\ (\mathrm{II})$ ... (17.8)

Note that μ is an intensive (as opposed to extensive) property and so the equilibrium is independent of the amount of the phases present. However, it is far simpler to understand such equilibrium from pressure-temperature diagrams (P–T diagram) which involves directly observable quantities, rather than μ–T diagrams, and this will be done here.

Phase Diagram of Water ▌ The phase diagram of water (*i.e.*, the vapour pressure *versus* temperature diagram) is shown in Fig. 17.3. The curve AO (full line) is the vapour pressure curve of ice which indicates that ice has a small but definite vapour pressure at each temperature like water. OB is the vapour pressure curve of water. The curve OB terminates at B, the critical temperature (374°C), because above this temperature the distinction between a liquid and its vapour vanishes.

Along OA, ice is in equilibrium with its vapour and each temperature has a definite vapour pressure. This is in agreement with phase rule because this is a one-component system with two phases ($C=1, P=2$; $\therefore$ $F=1-2+2=1$) and so there is only one degree of freedom, *i.e.*, if the temperature is fixed, all other properties are fixed. The same remarks apply along *OB* (water-vapour equilibrium).

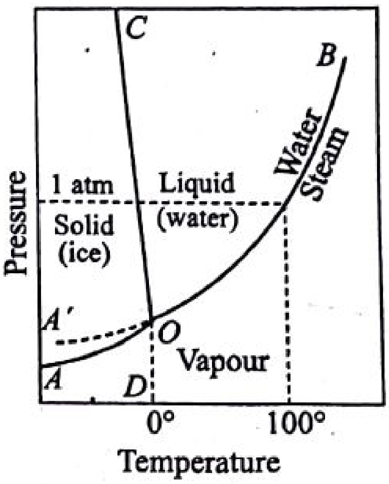

Fig. 17.3 : *Phase diagram of water (not to scale)*

The point of intersection of these two curves, *viz.* the point *O*, is called a TRIPLE POINT, because the three phases, ice-water-vapour are in equilibrium. It is really the melting point of ice under its own vapour pressure ; its value is very near to 0°C, to be exact 0.0098°C under 4.58 mm pressure (*i.e.*, 273.16 K & 6.11×10^2 Nm^{-2} which are the internationally accepted values). The interesting point to note is that it is a fixed point and admits of no change in temperature, pressure or any other property. This is also expected from phase rule because $C = 1$, $P = 3$ and, therefore, the degree of freedom, $F = 1 - 3 + 2 =$ zero.

The dotted portion *OA'*, which is the continuation of the curve *BO* below 0°C, is the vapour pressure curve of water when super-cooled below 0°C. This curve runs above the vapour pressure curve for ice in harmony with the fact that ice is stabler than water below 0°C. The curve *OC* represents the change of melting point of ice with pressure. It is inclined towards the pressure axis in conformity with the well-known fact that the melting point of ice is lowered by an increase of pressure.

[According to Clausius-Clapeyron equation, $\dfrac{dP}{dT} = \dfrac{\Delta H_{\text{fus}}}{T\Delta V_{\text{fus}}}$. For, solid $\rightleftharpoons$ liquid equilibrium in case of H_2O, ΔH_{fus}, T are positive, while ΔV_{fus} is negative. Hence, P vs. T curve (*OC*) has a negative slope.]

To sum up, the curves divide the whole region into three portions, in each of which, as indicated in the figure, only one phase is present. The temperature and pressure can both be varied in these single-phase regions, because the degree of freedom, $F=2$. The vapour pressure curves are the common lines of intersection of these regions and hence along them two phases are in equilibrium with $F=1$. At the triple point *O*, three phases co-exist in equilibrium ($F = 0$) ; also, since the two curves, *AO* and *BO* intersect at one point, there is only one triple point for the system.

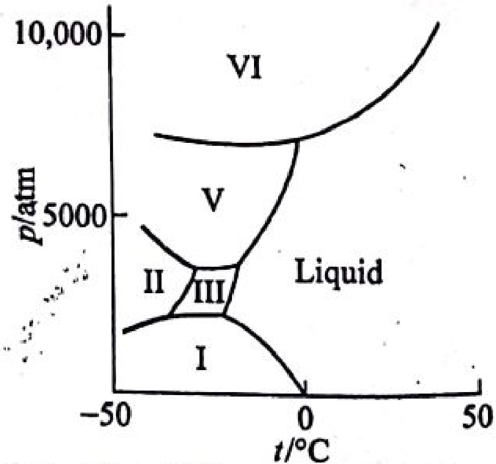

Fig. 17.3a : *Different phases of ice*

Other Forms of Ice ▌ The ice shown in Fig. 17.3a is really Ice (I). Many other forms of ice (Ice II, Ice III, ... Ice VII) are found to exist at high pressure. The point to note is that, under such conditions only either three solid forms of water or two solid forms and a liquid water can co-exist, because *phase rule does not permit the co-*

existence of more than three phases in a one-component system (vide Table). If four phases of a one-component system would have co-existed, $P = 4$, $C = 1$. Hence, $F = 1 - 4 + 2 = -1$. But F cannot be negative. The minimum value of F is zero.

Phase Diagram of Carbon Dioxide ▌ The phase diagram of CO_2 is similar to that of water (Fig. 17.4), where *OA* is the solid $\rightleftharpoons$ vapour line and *OB* is the liquid $\rightleftharpoons$ vapour line, '*O*' being the triple point. One essential difference is that the solid $\rightleftharpoons$ liquid transition line *OC* is inclined to the right, signifying an increase of melting point with pressure, whereas for water (Fig. 17.3), it is inclined to the left which is rather exceptional. This is because for most of the one-component system, ΔH_{fus} is positive, hence for solid $\rightleftharpoons$ liquid equilibrium, slope of *P* vs. *T* curve is positive (for most substances). The triple point pressure of CO_2 is 5.2 atmosphere and the solid CO_2 has a vapour pressure of 1 atm at a temperature as low as –76°C. Therefore, under atmospheric pressure, the solid will directly pass into the vapour state (*i.e.*, it would sublime) instead of melting to liquid. Because of this property, solid CO_2 is sold commercially as "dry ice" which is free from the messiness of the admixed liquid under ordinary conditions. However, if the external pressure is more than 5.2 atm, solid CO_2 would melt into a liquid just like any other solid ; this is shown by the fact that any horizontal line at above 5.2 atm cuts the solid-liquid transition line *OC*, but below this pressure it cuts the solid-gas transition line but not the former.

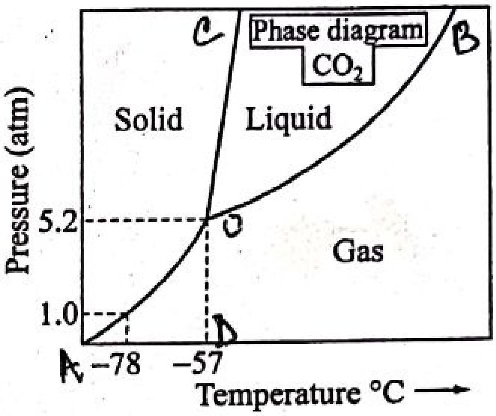

Fig. 17.4 : *Phase Diagram of* CO_2

Principle of Sublimation ▌ From the above diagram, it is clear that, if a vapour below its triple point pressure (*OD*) is cooled, it will be directly converted to the solid state. The reverse is also equally true. If a solid is heated and the vapour pressure above it is not allowed to exceed the triple point pressure, the solid will be directly converted to the vaporous state. The above is the principle of sublimation. Thus, iodine with a triple point of 114°C and 90 mm pressure, is easily sublimed on slow heating, provided P_{I_2} is maintained below 90 mm. However, if the heating is too rapid in an almost closed space, P_{I_2} exceeds 90 mm and iodine melts to a mobile liquid. Similarly, ice can be sublimed in a good vacuum below the triple point pressure and this makes it possible to dry substances by the *freeze-drying technique* ; for example, the dehydration of frozen blood plasma under vacuum for preservation.

For those substances, whose triple point pressures exceed one atmosphere, the condition for sublimation is automatically maintained and hence they pass directly into the vapour state on heating This is the case with *solid carbon dioxide*—commercially known as *'dry ice'* and extensively used for refrigeration by ice-cream vendors—which passses directly into the vaporous state, because its triple point pressure is 5.2 atmospheres (Fig. 17.4) as discussed in the previous Section.

The Sulphur System ▌ Another one-component system, which is slightly more complex than the previous ones, is the sulphur system, the phase diagram of which