CHAPTER 2

Phase Rule

The ‘phase rule’ generalization was given by J.W. Gibbs in 1874 and further studied by H.W.B. Roozeboom 1884. The phase rule is able to predict the conditions necessary to be specified for a heterogeneous system to exhibit equilibrium. During the study of chemical systems, we usually deal with the systems containing two or more phases in equilibrium, which are called heterogeneous or polyphase systems. Phase rule was based on the basis of the principles of thermodynamics. The phase rule is able to predict qualitatively, by means of diagram, the effect of changing temperature, pressure, or concentration on a heterogeneous system in equilibrium. In this chapter we will study the phase rule and its various applications in the daily life.

1 GIBB’S PHASE RULE

Phase rule may be defined as:

When a heterogeneous system in equilibrium at a definite temperature and pressure, the number of degrees of freedom is equal to by 2 the difference in the number of components and the number of phases provided the equilibrium is not influenced by external factors such as gravity, electrical or magnetic forces, surface tension etc.

It is applicable for all the universally present heterogeneous systems.

Mathematically, the rule is written as

$$\boxed{F = C - P + 2}$$

Where F = Number of degrees of freedom,

C = Number of components

P = Number of phases of the system

For understanding the various applications of phase rule a clear understanding of the various terms, *phases (P), components (C)* and *degrees of freedom (F)* present in the phase rule, is essential which have their specific meanings.

[2] Components (C)

The minimum number of independently variable constituents in terms of which the composition of each phase of a heterogeneous system can be expressed directly or in the form of a chemical equation are called the components of system (C).

For example, a system consisting of a solution of sugar in water *($P = 1$ i.e. solution phase)* is a two-component system because the solution phase present in the system consists of two constituents—water and sugar.

Some common examples related to the components are as follows:

(a) Consider the following system consisting of ice, water and vapour in equilibrium.

$$\text{Ice}\ (s) \rightleftharpoons \text{Water}\ (l) \rightleftharpoons \text{Vapour}\ (g)$$

The system consists of three phases *ice, water* and *vapour phase.* The chemical substance present in each phase is H_2O. Therefore, the composition of each phase is expressed in terms of H_2O. Hence, it is called *one-component system.*

(b) The saturated solution of sodium chloride consists of three *phases—solid sodium chloride, salt solution* and *water vapour* in equilibrium.

$$\text{NaCI}\ (s) \rightleftharpoons \text{NaCI}\ (aq) \rightleftharpoons \text{Water Vapour}\ (g)$$

$$\text{Ca}\ CO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

The chemical composition of each phase of the system can be expressed if we consider two chemical constituents NaCI and water as shown below.

Phase *Components*

(i) NaCI (s) = $\text{NaCI} + 0H_2O$

(ii) NaCI(aq) = $y\text{NaCI} + xH_2O$

(iii) $H_2O(g)$ = $0\text{NaCI} + H_2O$

Hence, it is a *two-component system.*

(c) The system, $CuSO_4.5H_2O\ (s) \rightleftharpoons CuSO_4.3H_2O\ (s) + 2H_2O\ (g)$ is a three-phase and *two component system.* It requires two constituents $CuSO_4$ and H_2O to express the composition of each phase of the system.

[3] Degree of Freedom (F)

The smallest number of independently variable factors such as temperature, pressure and concentration which must be required in order to define the system completely are called the degree of freedom. Degree of freedom of a system is also known as variance.

When a system having no degree of freedom

$F = 0$ it is called *non-variant system* or *invariant system.*

When a system having only one degree of freedom

$F = 1$ it is a *univariant* or a *monovariant system.*

Similarly, a system having two degrees of freedom

$F = 2$ is a *bivariant system and so on.*

The term degree of freedom can be understood with the help of following examples:

(a) *The system ice* $\rightleftharpoons$ *water* $\rightleftharpoons$ *vapour* has no degree of freedom *(i.e.,* $F = 0$).
The three phases of water *i.e.* ice, liquid water and vapour can exist together in equilibrium only at a particular-temperature and pressure (corresponding to the freezing point) and no factor is necessary to be specified to define the system. Hence, *a system consisting of ice, water and vapour in equilibrium has no degree of freedom i.e. it is a non-variant system.*

(b) *For a mixture of gases,* the number of degrees of freedom is three *(i.e.,* $F = 3$). Such a system can be completely defined when the temperature, pressure and composition are fixed. In this case, the remaining factor i.e., volume gets automatically fixed. For example, a gaseous mixture consisting of 70% N_2 and 30% O_2 at 22°C and 1 atm pressure is completely defined and does not require any other information for its description. Hence, *a system consisting of a mixture of gases has three degrees of freedom i.e. it is a trivariant system.*

(c) *For a saturated LiCl solution,* the number of degrees of freedom is one *(i.e.,* $F = 1$). This is because the system can be completely defined by specifying the temperature only. The other two factors *i.e.* composition and vapour pressure get automatically fixed when the temperature is fixed. *Hence, a system consisting of a saturated LiCl solution is a univariant system.*

2 DERIVATION OF PHASE RULE EQUATION

The Gibb's phase rule can be derived on the basis of thermodynamic principle as follows.

Let us consider a heterogeneous system consisting of $P(P_1, P_2, P_3 \ldots P)$ number of phases and $C(C_1, C_2, C_3 \ldots C)$ number of components in equilibrium. *Let us assume that the system is non-reacting i.e. the passage of a component from one phase to another does not involve any chemical reaction.* When the system is in equilibrium state it can be explained completely by specifying the following variables:

(i) Pressure (ii) Temperature

(iii) Composition of each phase.

(a) *Total number of variables required specifying the state of system:*

(i) Temperature: same for all phases

(ii) Pressure: same for all phases

(iii) Concentration

Independent concentration variables for one phase with respect to the C components = $C - 1$ [$\because$ Conc. of last component is independent]

$\therefore$ Independent concentration variables for P phases with respect to the C components = $P(C - 1)$

Total number of variables = $P(C - 1) + 2$ ...(1)

(b) *The total number of equilibria:*

The various phases present in the system can remain in equilibrium only when the *chemical potential* (μ) of each component is the same in each phases, *i.e.*

$$\begin{array}{llllllllll}
\mu_1, P_1 & = & \mu_1, P_2 & = & \mu_1, P_3 & = & \dots & = & \mu_1, P & \text{Component 1} \\
\mu_2, P_1 & = & \mu_2, P_2 & = & \mu_2, P_3 & = & \dots & = & \mu_2, P & \text{Component 2} \\
\vdots & & \vdots & & \vdots & & & & \vdots & \\
\vdots & & \vdots & & \vdots & & & & \vdots & \\
\vdots & & \vdots & & \vdots & & & & \vdots & \\
\mu_C, P_1 & = & \mu_C, P_2 & = & \mu_C, P_1 & = & \dots & = & \mu_C, P & \text{Component C}
\end{array}$$

(a) For each component the no of equilibria for P phases = $(P - 1)$

(b) For C component the no of equilibria for P phases = $C(P - 1)$

Total no. of equilibria involved (E) = $C(P - 1)$ ...(2)

From eq. 1 & 2 we get

$$F = [P(C - 1) + 2] - [C(P - 1)]$$

$$F = [CP - P + 2 - CP + C]$$

$$\boxed{F = C - P + 2}$$

This above equation is Gibb's phase rule equation.

Some conclusions from the phase rule equation:

(a) *For a system having a specified number of components, the greater the number of phases, the lesser is the number of degrees of freedom.* For example,

(i) When the system consists of only one phase, we have

$$C = 1 \quad \text{and} \quad P = 1$$

So, according to the phase rule,

$F = C - P + 2 = 1 - 1 + 2 = 2$. The system has two degrees of freedom.

(ii) When the system consists of two phases in equilibrium, we have

$$C = 1 \quad \text{and} \quad P = 2$$

$F = C - P + 2 = 1 - 2 + 2 = 1$. The system is *monovariant.*

(b) *A system having a given number of components and the maximum possible number of phases in equilibrium is non-variant.*

For a one component system, the maximum possible number of phases is three. When a one-component system has three phases in equilibrium, it has no degree of freedom or non-variant system.

(c) *For a system having a given number of phases, the larger the number of components, the greater will be the number of the degrees of freedom of the system.*

For example,

For one-component system: $C = 1, \quad P = 2$

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

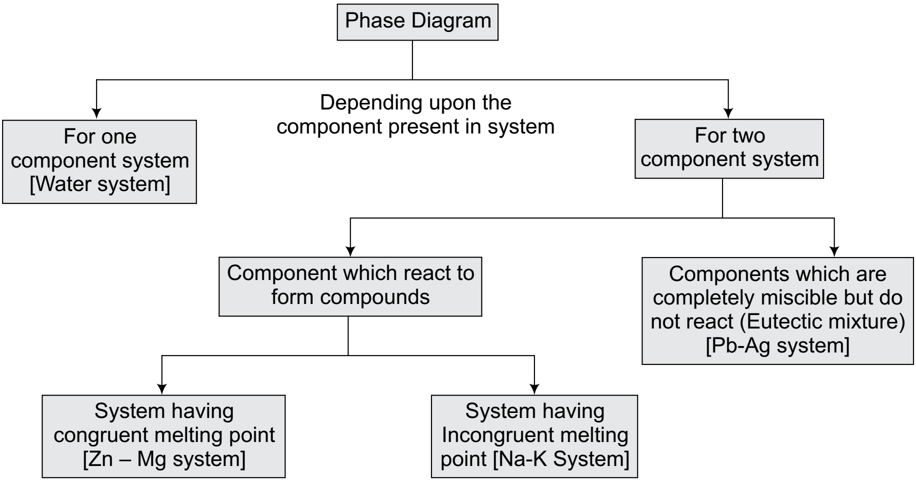
For two-component system: $C = 2, \quad P = 2$

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

The two-component system has a higher number of degrees of freedom.

3 PHASE DIAGRAMS

The graphical presentation giving the conditions of pressure and temperature under which the various phases are existing and transform from one phase to another is known as the phase diagram of the system. A phase diagram consists of *areas, curves* or *lines* and *points.*



4 PHASE RULE FOR ONE-COMPONENT SYSTEMS

The least number of phases possible in any system is one. So, according to the phase rule equation, a one-component system should have a maximum of two degrees of freedom.

When $C = 1, \quad P = 1$

So, $F = C - P + 2 = 1 - 1 + 2 = 2$

Hence, a one-component system requires a maximum of two variables to be fixed in order to define the system completely. The two variables are temperature and pressure. So, phase diagrams for one component system can be obtained by plotting P vs T.

In case of a one-component system, phase diagram consists of *areas, curves* or *lines* and *points* which provide the following informations regarding the system:

Point on a phase diagram represents a non-variant system.

Area represents a bivariant system

Curve or a *line* represents a univariant system.

Water system and the sulphur system are the example of one component systems.

[1] Water System

Water is a one component system which is chemically a single compound involved in the system. The three possible phases in this system are: ice (solid phase), water (liquid phase) and vapour (gaseous phase).

Hence, *water constitutes* a *three-phase, one-component system.* Since water is a three-phase system, it can have the following equilibria:

$$\text{ice} \rightleftharpoons \text{vapour},$$

$$\text{ice} \rightleftharpoons \text{water};$$

$$\text{water} \rightleftharpoons \text{vapour}$$

The existence of these equilibria at a particular stage depends upon the conditions of temperature and pressure, which are the variables of the system. If the values of vapour pressures at different temperatures are plotted against the corresponding temperatures, the phase diagram of the system is obtained.

The phase diagram of the water system is shown in Fig. 2.1. The explanation of the phase diagram of water system is as follows:

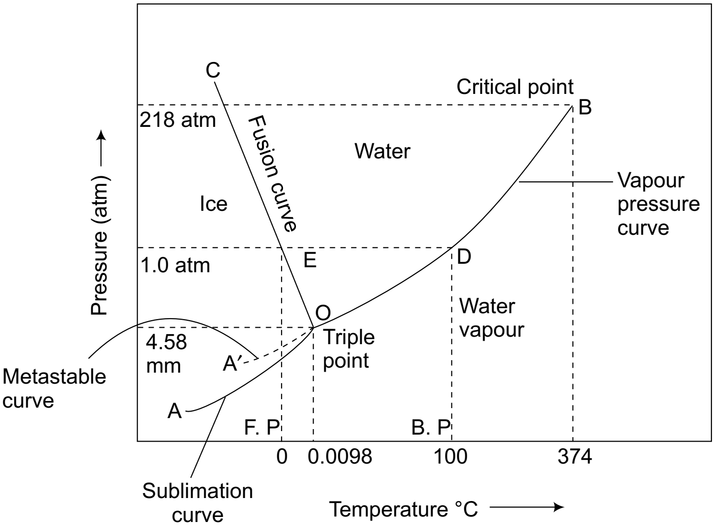


Fig. 2.1 Phase diagram of water system

(a) Curves

The phase diagram of the water system consists of three stable curves and one metastable curve, which are explained as follows:

(i) Curve *OB*: The curve *OB* is known as *vapour pressure curve of water* and tells about the vapour pressure of water at different temperatures. Along this curve, the two phases—*water* and *vapour* exist together in equilibrium.

At point *D,* the vapour pressure of water become equal to the atmospheric pressure (100°C), which represents the boiling point of water. The curve *OB* finishes at point B (temp. 374°C and pressure 218 atm) where the liquid water and vapour are indistinguishable and the system has only one phase. This point is called the *critical point.*

Applying the phase rule on this curve,

$$C = 1 \quad \text{and} \quad P = 2$$

$$F = C - P + 2 = 1 - 2 + 2 = 1$$

Hence, the curve represents a *univariant system.* This explains that only one factor (either temperature or pressure) is sufficient to be fixed in order to define the system.

(ii) Curve *OA*: *It is known as sublimation curve of ice* and gives the vapour pressure of solid ice at different temperatures. Along sublimation curve, the two phases *ice* and *vapour* exist together in equilibrium. The lower end of the curve *OA* extends to absolute zero (–273°C) where no vapour exists.

	Area	*Phase exits*	*Component*
(i)	Area *AOC*	ice	H_2O
(ii)	Area *COB*	water	H_2O
(iii)	Area below *BOA*	vapour	H_2O

Thus, for every area contains

$$C = 1 \quad \text{and} \quad P = 1$$

Therefore, applying phase rule on areas

$$F = C - P + 2 = 1 - 1 + 2 = 2$$

Hence, each area is a *bivariant system.* So, it becomes necessary to specify both the temperature and the pressure to define a one phase-system.

Table 2.1: Some salient features of the water system

Curve/ area/ point	*Name of the system*	*Phases in equilibrium*	*No. of phase (P)*	*Degree of the freedom (F)*
Curve *OB*	Vapourisation curve	Liquid & vapour	02	01(Univariant)
Curve *OA*	Sublimation curve	Solid & vapour	02	01(Univariant)
Curve *OC*	Fusion curve	Solid & liquid	02	01(Univariant)
Curve *OA′*	Metastable vaporization curve	Liquid & vapour	02	01(Univariant)
Area *AOC*		Ice	01	02(Bivariant)
Area *BOC*		Water	01	02(Bivariant)
Area *AOB*		Vapour	01	02(Bivariant)
Point *O*		Ice & water & vapour	03	0(Invariant)

5 TWO-COMPONENT SYSTEMS

When the two independent components are present in a heterogeneous system, the system is referred to as a *two-component system.* Hence, according to the phase rule, for a two-component system having one phase,

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

Therefore, the two component system having one phase will have three degrees of freedom or three variables would be required to define the system. The three variables are pressure *(P),* temperature (*T*) and concentration *(C).* This will require a three-dimensional phase diagram for the study of a two-component system. However, in order to simplify the study, a two-component system is usually studied in the form of a condensed system. A condensed system can be studied by reducing a comparatively less important variable. This reduces the degree of freedom of the system by 1 and the system can easily be studied with the help of a two-dimensional phase diagram.

It can have a maximum of following four phases:

Solid lead, Solid silver, Solution of molten silver & lead and Vapours

The boiling points of silver and lead are considerably high and the vapour pressure of the system is very low. So, the vapour phase can be ignored and the system can be studied as a *condensed system.* This system thus can be easily studied with the help of a two dimensional $T - C$ diagram and the reduced phase rule equation, $F' = C - P + 1$, can be used. This system is generally studied at constant pressure (atmospheric). The phase diagram of Lead-Silver system is shown in Fig. 2.2.

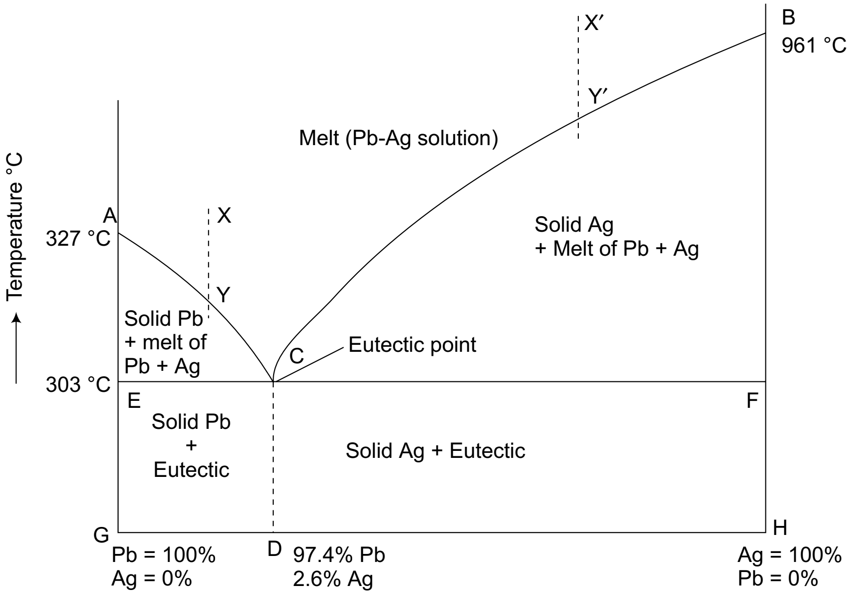


Fig. 2.2 Phase diagram of Pb-Ag system

(a) Curves

The phase diagram of the lead-silver system consists of following curves, which are explained as follows:

(i) Curve *AC (Freezing point curve of lead):* The *AC* curve shows the variation of the melting point of lead on addition of silver. The pure lead melts at 327°C (point *A*). Addition of silver lowers its melting point along curve *AC*. The added silver dissolves in molten lead to form Ag-Pb solution with the separation of some part of solid lead. Therefore, the two phases, solid lead and Ag-Pb solution remain together in equilibrium along the curve *AC*.

Hence, $P = 2$, (solid Pb and melt of Ag-Pb)

$C = 2$(Pb and Ag)

So, $C = 2$ and $P = 2$,

On applying the reduced phase rule

$$F' = C - P + 1 = 2 - 2 + 1 = 1 \text{ The system is univariant.}$$

(iii) Area *BCF:* The area consists of two phases—solid Ag and a solution of Pb and Ag. Hence it is also univariant.

(iv) Area *DCFH*: This area also has the two phases which are solid Ag crystals and solid eutectic crystals. Hence $C = 2$ and $P = 2$, the system is *univariant.*

(iv) Area *CEGD*: The area also has the solid Pb crystals and solid eutectic crystals phases. The system is *univariant.*

Table 2.2: Some salient features of the Pb-Ag system.

Curve/ area/ point	*Name of the system*	*Phases in equilibrium*	*No. of phase (P)*	*Degree of freedom (F)*
Curve AC	Freezing curve of Pb	Pb & Melt (Pb+Ag Solution Pb & Ag)	02	01(Univariant)
Curve BC	Freezing curve of Ag	Ag & Melt Pb & Ag)	02	01(Univariant)
Area ACE	.....	Pb & melt	02	01(Univariant)
Area BCF	.....	Ag & melt	02	01(Univariant)
Area above ACB	.....	Liquid (melt)	01	02(Bivariant)
Area ECF	.....	Pb & Ag both in solid	02	01(Univariant)
Point O	Eutectic point	Pb, Ag & melt	03	0(invariant)

Desilverisation of Argentiferrous Lead (Pattinson's Process)

The process, which is used for the recovery of silver from argentiferrous lead is called *Pattinson's process* and involves the *desilverisation of lead* in accordance to the phase diagram of lead-silver system.

The argentiferrous lead contains a small percentage of silver (less than 0.1%). For its recovery, the argentiferrous lead is heated above its melting point when a liquid melt consisting of silver-lead solution is obtained. Now if the silver lead solution is cooled, then Pb continues to separate out and is regularly removed. In the end, a eutectic solution containing 2.6% Ag (corresponding to point *C*) is obtained. Thus, the above process increases the percentage of silver in the argentiferrous lead. Therefore, the eutectic mixture containing 2.6% silver can be treated for the recovery of silver profitably.

(B) Systems having Congruent Melting Point

A binary system is said to possess a congruent melting point when it melts at a sharp temperature to give a liquid of the same composition as that of the solid.

The components of a binary mixture at a certain stage enter into chemical combination and form one or more compounds (inter-metallic compounds) in *stochiometric* proportions. These compounds melt sharply at a constant temperature into a liquid having the same composition as that of the solid. The temperature at which such a compound melts is called the congruent melting point.

Some common examples of this type of system are zinc-magnesium system, mercury-thallium system, gold-tin system and ferric chloride-water system etc.

1 Zn-Mg system

Zn-Mg System is a two-component system and possess a congruent melting point. The phase diagram of Zn-Mg system is shown in Fig. 2.3. In this system, the two components are zinc and magnesium, which melt at 419°C and 650°C respectively which are represented as point *B* and *A* in the phase diagram of the system. Both metals enter into chemical combination and form an intermetallic compound $MgZn_2$ and melts at 590°C to give a liquid of the same composition. Hence, 590°C is the congruent melting point of the system.

In the reduced form, the system has the following four phases:

Solid magnesium, solid zinc, solid $MgZn_2$ and liquid solution of Zn and Mg.

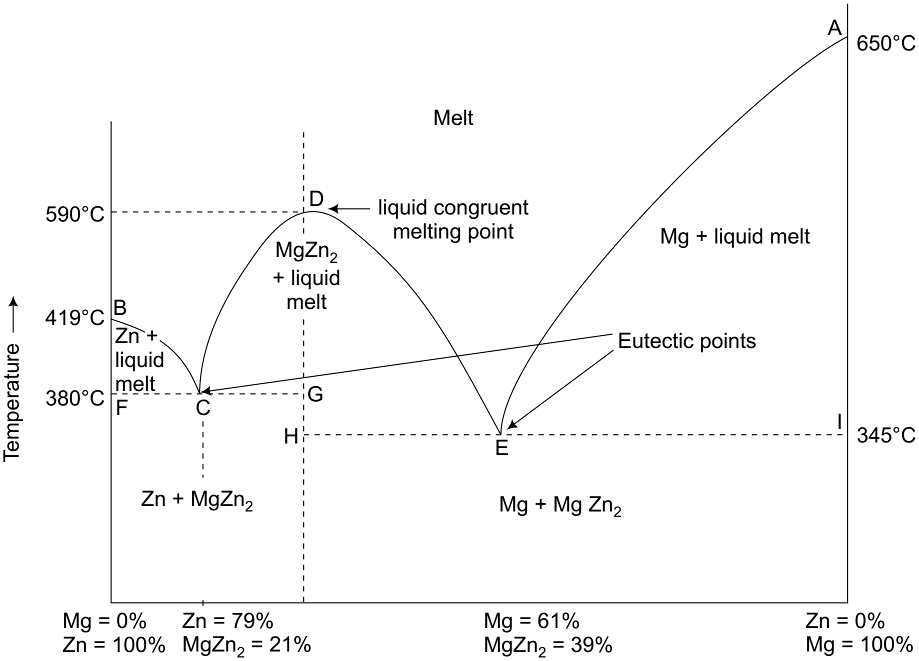


Fig. 2.3 Phase diagram of Zn-Mg system [Congruent melting point system]

On applying the reduced phase rule

$$F' = C - P + 1 = 1 - 2 + 1 = 0$$

Therefore, at point D constitutes a *non-variant* system.

(ii) Point E (Eutectic point): Point E represents the eutectic point of the system at a temperature of 345°C which is the least melting point of Mg-$MgZn_2$ system. Here, also three phases existing together in equilibrium at point E are solid Mg, solid $MgZn_2$ and liquid $MgZn_2$.

Hence, $C = 2$ and $P = 3$,

$F' = C - P + 1 = 2 - 3 + 1 = 0$ The system is *non-variant.*

(iii) Point C (Eutectic point): This point also represents the eutectic point (380°C) which is the least melting point of Zn-$MgZn_2$ system. At this point, the three phases—solid Zn, solid $MgZn_2$ and liquid $MgZn_2$ exist together in equilibrium. Therefore,

$$C = 2 \text{ and } P = 3$$

$$F' = C - P + l = 2 - 3 + 1 = 0$$

Hence, point C represents a *non-variant system.*

(c) Areas

The phase diagram of zinc-magnesium system consists of many areas. The area above the curve *BCDEA* constitutes a single phase system. The phase present in this area is a liquid melt consisting of a liquid solution of zinc and magnesium.

Hence $C = 2$ and $P = 1$,

$F' = \mathrm{C} - P + 1 = 2 - 1 + 1 = 2$ that the system is *bivariant.*

Most of the other areas of the Zn-Mg system consists of two phases and they are *univariant systems* as represented in the phase diagram. These areas are explained in datail in table 2.3.

Table 2.3: Some salient features of the Zn-Mg system

Curve/ area/ point	*Phases in equilibrium*	*No. of phase(P)*	*Degree of the freedom (F)*
Curve BC (Freezing curve of Zn)	Zn & Melt (Containing Zn & $MgZn_2$)	02	01(Univariant)
Curve AE (Freezing curve of Mg)	Mg & Melt (Containing Zn & $MgZn_2$)	02	01(Univariant)
Curve CD	$MgZn_2$ & melt (Containing Mg & $MgZn_2$)	02	01(Univariant)
Curve DE	$MgZn_2$ & melt (Containing Zn & $MgZn_2$)	02	01(Univariant)
Curve CDE	$MgZn_2$ & melt	02	01(Univariant)
Area above BCDEA	Liquid (Melt of Zn, Mg & $MgZn_2$)	01	02(Bivariant)

Area BCF	Zn & Melt(Containing Zn & $MgZn_2$)	02	01(Univariant)
Area DCG	$MgZn_2$ & Melt(Containing Zn & $MgZn_2$)	02	01(Univariant)
Area DEH	$MgZn_2$ & Melt(Containing Mg & $MgZn_2$)	02	01(Univariant)
Area AEI	Mg & melt (containing Mg + $MgZn_2$)	02	01(Univariant)
Area below line FCG	Zn & $MgZn_2$ (both solid)	02	01(Univariant)
Area below line HEI	Mg & $MgZn_2$ (Both solid)	02	01(Univariant)
Point C (Eutectic)	Zn, $MgZn_2$ & Melt(Containing Zn & $MgZn_2$)	03	0(invariant)
Point E (Eutectic)	Mg, $MgZn_2$ & Melt(Containing Mg & $MgZn_2$)	03	0(invariant)

(C) Incongruent Melting Point System

There are several systems in which components combine together to form one or more compounds which are unstable and do not possess congruent melting points.

A system (compound) is said to possess incongruent melting point, if on heating it decomposes much below its melting point and forms a new solid phase and a solution having different composition from the corresponding solid state. It has no sharp melting point. The decomposition at this temperature is known as transition or meritectic or peritectic rection and the temperature (the incongruent melting point) is known as transition or meritectic or peritectic temperature.

$$\text{Original solid} \rightleftharpoons \text{new solid} + \text{solution (melt)}$$

Examples: Following are some examples of the binary systems which possess incongruent melting point:

(i) Gold-antimony system
(ii) Sodium-bismuth system
(iii) Sodium-potassium system
(iv) Sodium sulphate-water system
(v) Potassium chloride-copper chloride system

1 Na-K system

This is a two-component system having incongruent melting point. The melting points of sodium and potassium are 97.8°C and 63.8°C respectively which are shown in the phase diagram in Fig. 2.4. Both elements chemically combine together in the ratio of 2:1 to form a compound Na_2K. But this compound is unstable and decomposes into solid Na and melt at a temperature of 70°C. It is the incongruent melting point or peritectic temperature of this system. This system consists of four phases i.e. Solid K, Solid Na, Solid Na_2K and Liquid of Na and K.

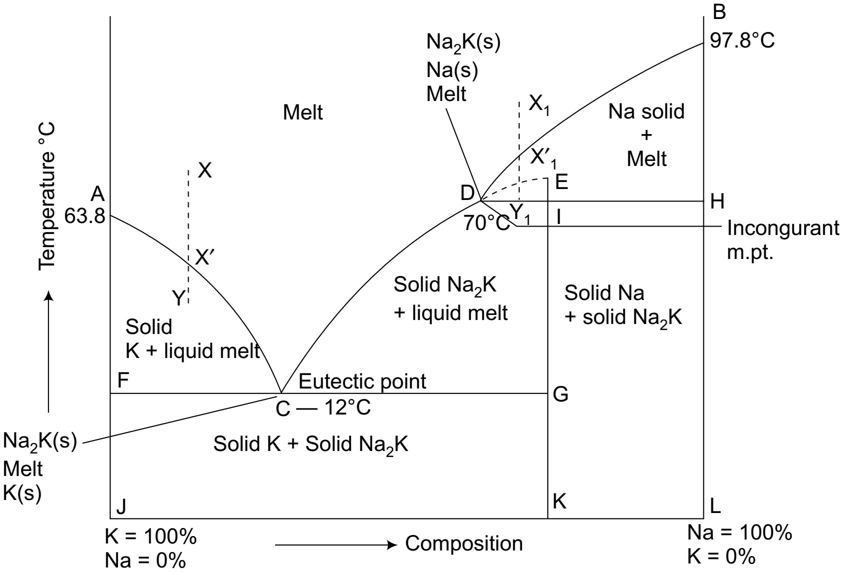


Fig. 2.4 Phase diagram of Na-K [Incongruent melting point system]

As the pressure does not have any effect on this type of equilibria hence the degree of freedom for such a system is reduced by one, So, reduced phase rule is applicable on the Na-K system. ($F' = C - P + 1$)

The phase diagram contains the following curves, points and areas.

1 Curves

(i) *Curve AC.* (Freezing point curve of potassium): This curve shows the lowering in freezing point of potassium by addition of sodium and continues till the point '*C*' is reached. Along this curve, potassium (K) separates out as solid phase. A new phase Na_2K separates out at point *C*. The two phases exist in equilibrium along this curve.

$P = 2$, [K(solid) and liquid (Na-K melt)] and $C = 2$

On applying the reduced phase rule

$F' = C - P + 1 = 2 - 2 + 1 = 1$ Hence, the system is univariant along this curve.

(ii) *Curve CD.* (Fusion curve of Na_2K): Along this curve the two phases exists in equilibrium. The Na_2K is stable along this curve. [If further the compound would be stable as having congruent melting point then the curve may be plotted up to the stable melting point *E* of the compound, which is shown in the phase diagram of the Na-K system].

$$Na_2K(s) \rightleftharpoons \text{Liquid}$$

$P = 2$ [Na_2K(s) and liquid] and $C = 2$

Hence $P = 3, \quad C = 2$

So, according to the phase rule

$$F' = C - P + 1 = 2 - 3 + 1 = 0$$

Thus, the system is invariant at point D.

3 Areas

(i) *Area above ACDB*: The area above the *ACDB* contains only liquid phase i.e. melt of Na, K and Na_2K.

Hence $P = 1, \quad C = 2$

On applying the reduced phase rule

$$F' = C - P + 1 = 2 - 1 + 1 = 2$$

Thus, the system is bivariant in the area above *ACDB*.

(ii) *Area ACF:* It consists of two phases solid K and liquid.

(iii) *Area ECG:* This area consists of two phases solid Na_2K and liquid.

(iv) *Area BDH:* It consists of the two phases, which exist in equilibrium i.e. solid Na and liquid.

(v) *Area below FCG:* It consists of solid K and solid Na_2K.

(vi) *Area IHLK:* This area consists of two phases solid Na and solid Na_2K.

All areas from (ii) to (vi) are having two phases and two components

Hence $P = 2, \quad C = 2$

On applying the reduced phase rule

$$F' = C - P + 1 = 2 - 2 + 1 = 1$$

$$F' = 1$$

Therefore, all the above areas represent univariant systems.

Table 2.4: Some salient features of the Na-K system.

Curve/ area/ point	*Phases in equilibrium*	*No. of phase(P)*	*Degree of the freedom (F)*
Curve AC (Freezing curve of K)	K & Melt (Containing K & Na_2K)	02	01(Univariant)
Curve BD (Freezing curve of Na)	Na & Melt (Containing Na & Na_2K)	02	01(Univariant)
Curve CD	Na_2K & Melt (Containing K & Na_2K)	02	01(Univariant)
Area above ACDB	Liquid (Melt of Na, K & Na_2K)	01	02(Bivariant)
Area ACF	K & Melt (Containing K & Na_2K)	02	01(Univariant)

Area BDH	Na & Melt (Containing Na & Na_2K)	02	01(Univariant)
Area CDIG	Na_2K & Melt (Containing K & Na_2K)	02	01(Univariant)
Area below line FGC	Na_2K & K (both solid)	02	01(Univariant)
Area below line IH	Na_2K & Na (Both solid)	02	01(Univariant)
Point C (Eutectic)	K, Na_2K & Melt (Containing K & Na_2K)	03	0(invariant)
Point I (Eutectic)	Na, Na_2K & Melt (Containing Na & Na_2K)	03	0(invariant)

6 APPLICATIONS OF THE PHASE RULE

Phase rule has wide applications in electronic industries, pharmaceutical science, medical science, etc. Some major applications of phase rule are as follows:

[1] Solders

Solder is an alloy, which is homogenous mixture having melting point lower than that of the corresponding metal pieces, which have to be joined together. Solders have compositions somewhat different from the eutectics so that the freezing occurs *over a range* of temperatures. The quality of solder depends upon the formation of a surface alloy between the solder and parts of metals being used. The selection of solder alloy is based upon the melting point desired and the pieces of metals to be joined. Some essential qualities of the solder are as follows:

(1) Melting point of the solder should be less than the material to be soldered.

(2) Solder should spread in liquid form and also form homogeneous mixture with the metals.

Some common solders which are available in the market are:

(i) 'Soft solder' alloy of Pb and Sn.

(ii) 'Plumber alloy' contains Pb = 67% and Sn = 33%.

(iii) 'Half-half alloy' contains Pb = 50% and Sn = 50%

Half-half alloy is commonly used for soldering the pipes with a bright surface finishing after soldering but very expensive. Also due to high contents of tin, it is not widely applicable for several electric appliances. The solder which contains about 60% Pb is used in the electrical wires.

[2] Safety Plug

Safety plugs are also known as the safety fuses. It is an alloy having low melting point, used to ensure the safe working and avoid accidents. Safety fuses are used in buildings to protect them against fires. One alloy is woods metal, which is used in the safety fuses. This alloy melts at 65°C and consists of the composition woods metal Bi = 50%, Pb = 25%, Sn = 12.5% and Cd = 12.5%.

and the frozen liquid (ice) is directly converted into a gaseous state. The removed water is stored again through the condensers. The material or tissue is left almost as a skeleton and original matter can be obtained by adding water. By this process shrinkage of flowers is eliminated or minimized.

All botanical samples, fruits and vegetables can be freeze-dried. This technique is also used in pharmaceutical industry, museums, taxidermy, floral industry and camping/hiking food processors.

QUESTIONS FOR EXAMINATION

[A] Short Answer Type Questions

1. What is the phase rule?
2. Define phase with some examples.
3. What are the components of a system? Explain with examples.
4. How many phases are present in a homogeneous system?
5. How many phases and components are present in each of the following systems:
    (i) $NH_4CI\ (s) \rightleftharpoons NH_3\ (g) + HCI\ (g)$
    (ii) An aqueous solution of salt (NaCl)
    (iii) Toluene in equilibrium with its vapour
6. Define degree of freedom of a system and explain with examples.
7. How many degrees of freedom are possible for a mixture of gases?
8. Calculate the maximum possible number of phases and degrees of freedom for a one-component system.
9. Is it possible to have a quadruple point (point having $P = 4$) in the phase diagram of a one-component system?
10. What is metastable equilibrium? Explain with reference to the water system.
11. What do you understand by a triple point? What is the variance of a one-component system at this point?
12. What is a condensed or reduced system? Explain with some example.
13. Can the phase rule equation in its original form be applied to a condensed system? Write the reduced phase rule equation.
14. What do you understand by a eutectic point?
15. Draw the phase diagram for Pb-Ag system.
16. What is the Pattinson's process?
17. Define congruent melting point and name a system, which forms a compound with such a melting point.