B.Sc. (Chemistry)

Semester-VI

US06CCHE23 Physical Chemistry

Unit-3 Phase Equilibria

Introduction to phase rule:

Gibbs phase rule may be expressed as: $P + F = C + 2$,

where 'P' is the number of phases, 'F' is the number of degrees of freedom and 'C' is the number of components in a system at equilibrium. Mass of phase has no influence on the state of equilibrium, so it is not involved in the phase rule.

The phase rule may be stated as:

"In a heterogeneous system in equilibrium, the number of degrees of freedom plus the number of phases are equal to the number of components plus two."

Phase: It is defined as any homogeneous and physically distinct part of a system which is bounded by a surface and is mechanically separable from other parts of the system.

A phase may be gas, liquid or solid.

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Examples of different phases are:

(i) In a system consisting of ice, water and vapour, there are three phases, solid, liquid and gas. Each phase is homogeneous and can be separated mechanically from other phases.

(ii) A gaseous mixture consists of one phase only irrespective of the number of gases present in the mixture. This is due to the fact that all gases are completely miscible.

(iii) Two or more liquids which are completely miscible with each other constitute a single phase because there is no bounding surfaces separating different liquids.

For example, alcohol and water are completely miscible, so it constitut one phase only.

(iv) A solid mixture has number of phases equal to number of solids present in the mixture.

Consider decomposition of calcium carbonate into CO_2 and CaO.

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$$

Here, there are two solid phases and one gaseous phase. So, it is a three phase system.

Component : A component is an element or a compound present in a system. The concentration of this component can be changed independtly. But in phase rule the component doesn't mean total number of constituents of the system. In phase rule, component is defined as, "minimum number of molecular species in terms of which the composition of all the phases may be expressed quantitatively."

Let us consider actual cases to understand meaning of the term component.

(i) Consider water system having three phases.

$$\text{Ice} \rightleftharpoons \text{water} \rightleftharpoons \text{Vapour}$$

Each phase has the same chemical compound H_2O, so, this system is one component system.

(ii) Consider the dissociation of $CaCO_3$ by heat

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$$

There are three phases, two solids and one gas. At first sight, it seems that it is a three component system. However, due to existence of equilibrium, the number of components is only two. If we choose CaO and CO_2, then the composition of $CaCO_3$ can be given by $CaO + CO_2$. If we consider $CaCO_3$ and CO_2, composition of CaO can be given by $CaCO_3 - CO_2$. If we consider $CaCO_3$ and CaO, composition of CO_2 can be given by $CaCO_3 - CaO$.

Thus, the composition of all the three phases can be expressed by taking any two constituents. Thus, number of components for the system is two.

(iii) Consider the dissociation of ammonium chloride in a closed vessel which is in equilibrium with ammonia and hydrochloric acid.

$$\underset{\text{solid}}{NH_4Cl} \rightleftharpoons \underset{\text{gas}}{NH_4Cl} \rightleftharpoons NH_3 + HCl$$

This is one component system because the composition of both the solid and gaseous phases can be given in terms of

NH_4Cl only.

Phase	component
Solid	NH_4Cl
Gaseous	$x\,NH_3 + x\,HCl$ or, $x\,NH_4Cl$

If a small amount of NH_3 or HCl is added to the equilibrium mixture then the number of components becomes two. Suppose y moles of HCl is added, then the gaseous mixture will contain x moles of NH_3 + x moles of HCl + y moles of HCl. Therefore, the composition of two phases of NH_4Cl can be given as

Phase	component
Solid NH_4Cl	NH_4Cl
Gas	$x\,NH_3 + x\,HCl + y\,HCl$ $= x\,NH_4Cl + y\,HCl$

Similarly, if we add NH_3 to the equilibrium mixture, it behaves as two component system.

Degree of freedom or variance of the system : It is defined as the least number of variable factors such as temperature, pressure and concentration which should be arbitrarily fixed in order to define the system completely.

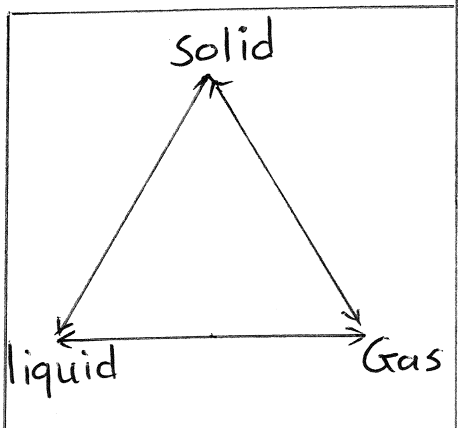
For example, a gaseous mixture of

carbon dioxide and nitrogen is completely defined by three variables temperature, pressure and concentration. Thus, the degree of freedom is three, or trivariant.

A system consisting of unsaturated water vapour, pressure and temperature are to be specified to define the system because pressure may have any value at a particular temperature. Degree of freedom for this system is two or it is bivariant.

- Phase reactions:

Physical or chemical reactions in which there is appearance or disappearance of a phase are known as phase reactions. For excample, change of solid to liquid, liquid to solid, liquid to gas, gas to liquid, solid to gas, gas to solid. These reactions can be indicated by the figure.



All processes of vapourization, sublimation, freezing, melting, solidification, crystallization, and precipitation are phase reactions.

All chemical processes may not be phase reactions. For example, the combination of gaseous ammonia and gaseous hydrogen chloride to form solid ammonium chloride is a phase reaction because the reactants and products are in different phases. The reaction between gaseous hydrogen and gaseous chlorine to form gaseous hydrogen chloride is not a phase reaction as all the substances are in one phase.

- Conditions for equilibrium between phases.

(a) Thermal equilibrium :

Temperature of all the phases must be the same. If temperature is not the same there is flow of heat from one phase to another.

It can be proved thermodynamically.

Consider two phases α and β at temperatures T_α and T_β respectively. If heat dq is transferred from phase α to phase β, entropy of phase α will be increased by amount dS_α and entropy of phase β will be increased by amount dS_β.

We know that,

$$dS_\alpha = -\frac{dq}{T_\alpha} \quad \text{and} \quad dS_\beta = \frac{dq}{T_\beta} \quad ; \quad \text{-----(1)}$$

Now, change in entropy of the system is zero at equilibrium.

$$dS = dS_\alpha + dS_\beta = 0 \qquad \text{------(2)}$$

Upon substituting equation (1) into equation(2),

$$-\frac{dq}{T_\alpha} + \frac{dq}{T_\beta} = 0$$

$$\therefore \; T_\alpha = T_\beta.$$

Thus, the temperatures of all the phases in equilibrium is the same.

(b) Mechanical equilibrium:

Mechanical equilibrium means all the phases must have the same pressure.

If pressures of different phases are not the same, one phase would increase its volume at the cost of another phase.

Suppose, there is increase in volume dV of a phase α at the cost of phase β.

We know that,

$$dA_\alpha = P_\alpha dV \quad \text{and} \quad dA_\beta = -P_\beta dV \qquad \text{----(1)}$$

where dA_α and dA_β are Helmholtz free energy changes for phase α and phase β respectively. P_α and P_β are pressures of phase α and phase β respectively..

If temperature is constant, the change in Helmholtz free energy of the system will be zero at equilibrium.

$$dA = dA_\alpha + dA_\beta = 0 \qquad \text{------(2)}$$

Upon substituting equation (1) into equation(2)

$$dA = P_\alpha dV + (-P_\beta dV) = 0.$$

This is possible only if $P_\alpha = P_\beta$.

Thus, it is clear that the phases in equilibrium are under the same pressure

(c) Chemical equilibrium:

Chemical equilibrium means the chemical potential of any component 'i' is the same in all the phases at equilibrium.

Consider a closed system of 'p' phases indicated by $\alpha, \beta, \gamma, \ldots\ldots$ having total of 'c' components indicated by 1, 2, 3.... in equilibrium and at constant pressure and temperature.

Gibbs free energy (G) of each phase is a function of temperature, pressure and composition.

$$\left.\begin{array}{l} G_\alpha = f(T, P, n_i)_\alpha \\ G_\beta = f(T, P, n_i)_\beta \\ \text{--- --- --- ---} \\ G^P = f(T, P, n_i)_P \end{array}\right\} \quad \text{.....(1)}$$

where $i = 1, 2, 3, \text{......} c$.

The free energy change of the system is the sum of change of free energies of all the phases.

$$dG = dG_\alpha + dG_\beta + dG_\gamma + \text{......} \quad \text{---(2)}$$

For a multicomponent system, we know

$$dG = -SdT + VdP + \sum \mu_i dn_i \quad \text{---(3)}$$

At constant temperature $dT=0$ and at constant pressure $dP=0$

$$\therefore (dG)_{T,P} = \sum \mu_i dn_i \quad \text{----(4)}$$

If there is a transfer of mass from one phase to another, we can write

$$dG = \sum_{i=1}^{c} \mu_{i\alpha}\, dn_{i\alpha} + \sum \mu_{i\beta}\, dn_{i\beta} + \dots\dots \quad \text{--(5)}$$

At equilibrium for a closed system $dG=0$

$$\sum \mu_{i\alpha}\, dn_{i\alpha} + \sum \mu_{i\beta}\, dn_{i\beta} + \dots = 0$$

At equilibrium for a closed system, total mass of each component is constant.

$$\left.\begin{aligned}
&dn_{1\alpha} + dn_{2\beta} + dn_{3\gamma} + \dots\dots + dn'_{1P} = 0 \\
&dn_{2\alpha} + dn_{2\beta} + dn_{2\gamma} + \dots\dots + dn_{2P} = 0 \\
&\dots \quad \dots \quad \dots \quad \dots \\
&dn_{i\alpha} + dn_{i\beta} + dn_{i\gamma} + \dots\dots + dn_{iP} = 0 \\
&\dots \quad \dots \quad \dots \quad \dots \\
&dn_{c\alpha} + dn_{c\beta} + dn_{c\gamma} + \dots\dots + dn_{cP} = 0
\end{aligned}\right\} \text{—(6)}$$

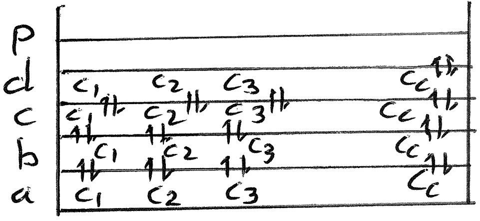
From equations (5) and (6), we can say,

$$\begin{aligned}
&\mu_{1\alpha} = \mu_{1\beta} = \mu_{1\gamma} = \dots\dots = \mu_1^P \\
&\mu_{2\alpha} = \mu_{2\beta} = \mu_{2\gamma} = \dots\dots = \mu_2^P \\
&\dots \quad \dots \quad \dots \quad \dots \\
&\mu_{c\alpha} = \mu_{c\beta} = \mu_{c\gamma} = \dots\dots = \mu_c^P
\end{aligned}$$

Thus, for any component 'i' in the system, the value of chemical potential must be the same in every phase if the system is in equilibrium at constant temperature and pressure.

- Derivation of phase rule:

Let us consider a heterogeneous system of 1, 2, 3 ..... c components distributed between a, b, c, ... P phases as shown in figure.



Now,

$$\text{Degree of freedom} = \left\{\begin{array}{l}\text{Total number of intensive}\\ \text{variables which define the}\\ \text{given system completely}\end{array}\right\} - \left\{\begin{array}{l}\text{Total number of intensive}\\ \text{variables of a given system}\\ \text{at equilibrium}\end{array}\right\}$$

- Total number of intensive variables which define the given system completely:

For above multicomponent system, we consider that all the components are present in each phase. It is necessary to give 'c−1' concentration variables to define the composition of each phase because the concentration of last component will be fixed automatically.

Total number of concentration variables are P(C−1) as there are 'p' number of phases in the system. In addition to this temperature and pressure must be specified. Thus, total number of intensive variables to define the given system completely are P(C−1)+2.

- Total number of intensive variables of a given system at equilibrium

We consider the closed system in equilibrium at a definite temperature and pressure. Suppose component C_1 is distributed in three phases a, b and c.

According to thermodynamic generalization, " When a heterogeneous system is in equilibrium at a given temperature and pressure, chemical potential of any component has the same value in all phases."

we can write,

$$\mu_1(a) = \mu_1(b) = \mu_1(c)$$

where μ_1 is chemical potential of component C_1

If phase 'a' is considered as standard

$\mu_1(a)=\mu_1(b)$ and $\mu_1(a)=\mu_1(c)$, two equations are required. In general for P phases $(P-1)$ equations are required. We have 'c' components, so number of equations are $c(P-1)$. Thus, total number of intensive variables of a given system at equilibrium is $c(P-1)$.

Now, Degree of freedom =

$$P(c-1)+2-c(P-1)$$

$$= Pc-P+2-Pc+c$$

$$\therefore\ F = c-P+2$$

This is Gibb's phase rule. This rule is applicable even if any component is missing from any of the phases.

- Advantages of phase rule:

(i) It gives a simple method of classifying equilibrium states of systems.

(ii) It confirms that the different systems having the same number of degrees of freedom behave in a similar manner.

(iii) It predicts the behaviour of systems when temperature, pressure and volume are changed.

(iv) The phase rule is applicable to macroscopic system. It is not necessary to consider molecular structures.

(v) It is applicable to physical as well as to chemical phase reactions.

(vi) Phase rule takes no account of nature of the reactants or products in phase reactions.

(vii) Phase rule predicts that a number of substances will remain in equilibrium or not if new substance is formed.

Limitations of the phase rule :

(i) Phase rule is applicable to systems which are in equilibrium. For systems which are slow in reaching the equilibrium state, this rule has no use.

(ii) This rule is applicable to a single equilibrium state, so it never tells about the number of other equilibrium possible in the system.

(iii) Temperature, pressure and composition are variables in phase rule. Electric and magnetic influences are not considered. If these variables are to be considered, the factor 2 of phase rule should be adjusted accordingly.

(iv) All the phases in the system must be present under the same pressure, temperature and gravitational force.

(v) No liquid or solid phases should be finely divided otherwise their vapour pressures will differ from their normal values.

• One Component systems :

When one component is the smallest number by means of which the composition of each phase is expressed, it is known as a one component system.

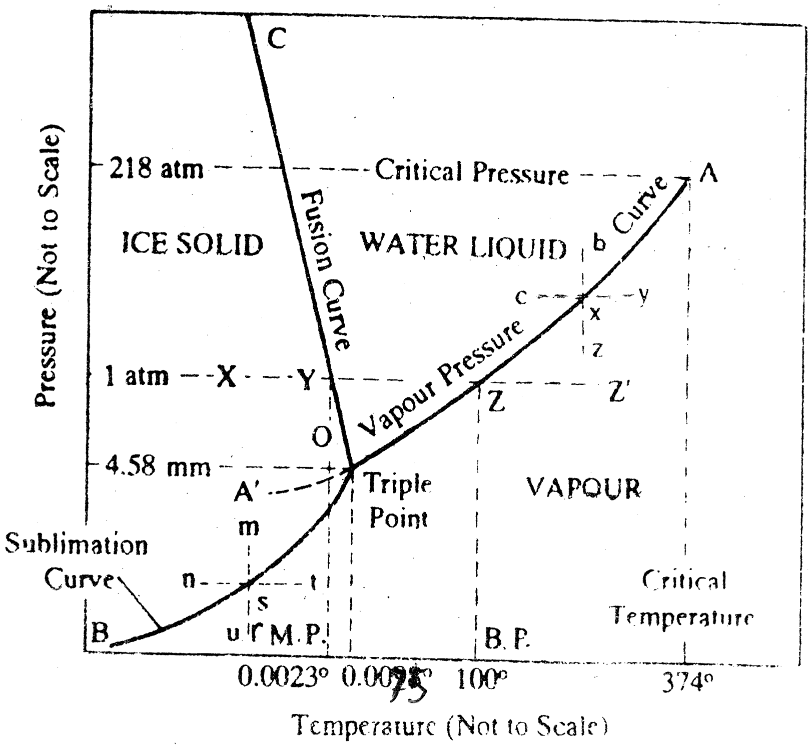
Maximum number of phases - When F is minimum, P becomes maximum. The minimum number of degrees of freedom possible in a system is zero. According to the phase rule, $P = C - F + 2 = 1 - 0 + 2 = 3$

Thus, the maximum number of phases of one component system having zero degree of freedom will be three.

Maximum number of degree of freedom - When number of phases is minimum, degree of freedom will be maximum. As the minimum number of phases in any system is one, maximum number of degree of freedom in one component system are two. $F = C - P + 2 = 1 - 1 + 2 = 2$.

- The water system:

It is one component system as H_2O is the only chemical compound involved. Water has three phases solid, liquid and vapour. The phase diagram of this system is given in the figure.



This diagram consists of three curves OA, OB and OC, triple point 'O' and three areas AOC, AOB and BOC.

Curve AO is known as the vapour pressure curve as it gives the vapour pressure of water at different temperatures. The curve starts from 'o' which is the freezing point of water and ends at point 'A' which is the critical temperature of water (374 °C). Beyond this temperature two phases, liquid and water vapour merge into each other.

From this curve, it is clear that for any given temperature, there is a fixed value of pressure. Similarly, for each vapour pressure, temperature has also a fixed value. The degree of freedom on any point of this curve is one or we can say it is univariant.

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

Curve 'OB' is the sublimation curve. Along this curve, solid and vapour are in equilibrium with each other. Thus, this curve gives variation of vapour pressure of ice at various temperatures, so this curve is also known as vapour pressure curve of ice.

This curve starts at point 'o' and

ends at point 'B', absolute zero (−273°C). At this temperature, no vapour can exist therefore only solid is there. But on the other points of the curve 'OB', solid is in equilibrium with vapour. There are two phases, so according to phase rule,

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

The system has one degree of freedom or it is univariant. It means each vapour pressure has a fixed temperature.

Curve 'OC' is the fusion curve of ice. This curve shows the effect of pressure on melting point of ice. The inclination of this curve towards the pressure axis indicates that the melting point of ice decreases upon increasing pressure. At any point on the curve 'OC' two phases solid and liquid water are in equilibrium. According to phase rule,

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

The system has one degree of freedom or it is univariant. It means for any given pressure, melting point must have one definite value.

Three curves OA, OB and OC meet at a point 'O' which is known as triple point. At this point solid, liquid and vapour co-exist and in equilibrium with each other. Applying phase rule,

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

Thus, degree of freedom at triple point is zero. It is non-variant. It means that three phases can co-exist in equilibrium only at a definite temperature and pressure. For water system the values of temperature and pressure for triple point is 0.0075 °C and 4.58 mm.

If temperature and pressure changes from the values for triple point, three different cases may arise:

(i) If pressure is increased at fixed temperature, solid and vapour will be convertedinto liquid.

(ii) If pressure is decreased at fixed temperature ice and liquid will be converted into the vapour.

(iii) If temperature and pressure both

are changed, curve OA, OB or OC will be followed.

In the area AOB only vapour exists. In the area AOC only liquid exists. In the area BOC only solid exists. According to phase rule,

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

All these areas are bivariant. That means to locate any point in the area, temperature and pressure must be defined.

Sometime it is possible to cool water below its freezing point without the separation of solid ice. Thus, the curve AO can be extended to A'. Along the curve OA' the liquid is in equilibrium with the vapour. This equilibrium is known as metastable equilibrium. If small ice piece is kept in contact with the supercooled liquid, it changes into solid ice and the curve merges in OB.

From phase diagram it is clear that the curve OB is below the curve OA'. Thus the metastable system has higher vapour pressure than the stable system at the same temperature.

Effect of change of temperature and pressure on equilibrium:

The real significance of phase diagram can be understood if we study the changes that are occuring due to temperature-pressure change. Suppose we are interested to study the effect of heating ice at 1 atm pressure and at a temperature represented by the point X in the figure. At point X, there is only solid phase. This point is bivariant, so the temperature can have any value at the same pressure. Therefore, heating the ice slowly at constant pressure will cause the system to move along XY. Upto point Y there is only ice phase. Beyond the point Y, fusion starts means liquid phase appears. At point beyond Y, there are two phases ice and water. The system becomes univariant. Due to one degree of freedom the temperature cannot be changed without changing the pressure. The effect of continuous heating is the conversion of solid into liquid. At point Z, there is only liquid phase and the system is bivariant. Beyond the point Z, vaporization starts. Number of phases becomes two. System becomes univariant. Pressure is kept constant, so continuous heating will not change the temperature. The only effect of further heating is conversion of liquid into vapour. The temperature will increase along the line ZZ'.

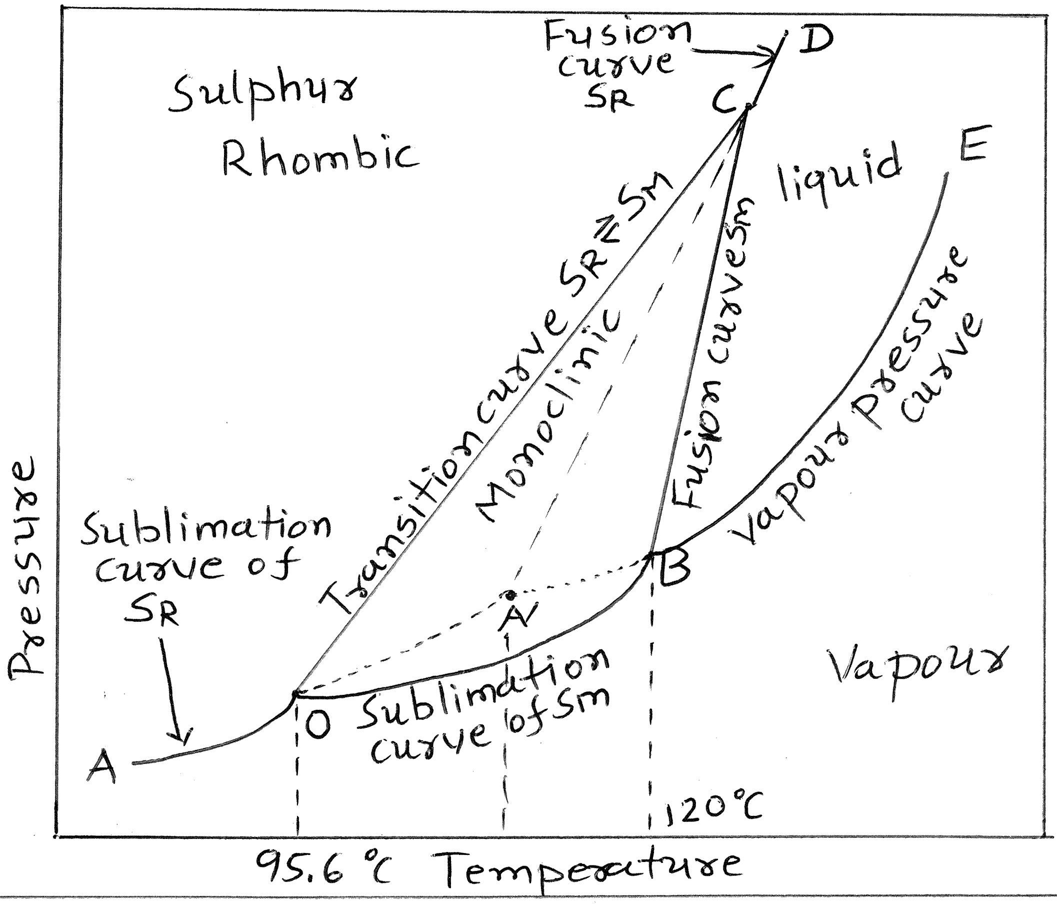
It is interesting to see the effect of temperature and pressure on the system at the triple point. If we do heating at this point, solid will convert into liquid but temperature and pressure remains constant until the whole ice has completely converted into liquid. The system has now two phases. ~~liquid and~~ Further heating will result into increase in temperature & the equilibrium is shifted along the curve OA.

Now, if we apply pressure to the

system at the triple point 'O', no change in temperature or pressure will occur as long as all the three phases are present. Upon applying pressure, vapour will be converted into solid or liquid. Further ~~increase~~ application of pressure will cause increase of pressure with change of temperature along the curve 'OC'.

- The Sulphur system:

Sulphur exists in two crystalline forms, rhombic and monoclinic, one liquid and one vapour phase. The phase diagram of this system is given below.



Curve AO is the sublimation curve of rhombic sulphur. This gives the variation of vapour pressure of rhombic sulphur at different temperatures. Thus, along this curve, two phases rhombic and vapour are in equilibrium. According to phase rule, $F=C-P+2=1-2+2=1$, the system is univariant along this curve. It means that there is only one vapour pressure value at one temperature.

Point 'O' is a triple point. There are three phases - rhombic, monoclinic and vapour in equilibrium. At this point rhombic sulphur changes into monoclinic sulphur. This is known as transition temperature (95.6 °C). There are three phases so according to phase rule $F=C-P+2=1-3+2=0$. Thus, 'O' is a non-variant.

Curve 'OB' is the sublimation curve of monoclinic sulphur. It gives the variation of vapour pressure of monoclinic sulphur at different temperatures. At any point on this curve two phases monoclinic sulphur and vapour are in equilibrium. There are two phases so according to phase rule $F = C-P+2 = 1-2+2 = 1$. The system is univariant.

Point ‘B’ is the melting point of monoclinic sulphur (120° C). This is another triple point. At this point three phases-monoclinic sulphur, liquid and vapour are in equilibrium. According to phase rule $F = C-P+2 = 1-3+2 = 0$. Thus, this is a non-variant point.

Curve ‘BE’ is the vapour pressure curve of liquid sulphur. This curve starts at point ‘B’ which is the melting point of monoclinic sulphur and curve ends at point ‘E’ which is the critical temperature. Beyond this temperature, there is only vapour phase.

Along this curve liquid and vapour are in equilibrium. According to phase rule $F = C-P+2 = 1-2+2 = 1$. This means at any point on the curve for the fixed value of pressure, temperature has a fixed value. Degree of freedom 1 means it is univariant.

Curve 'OC' is the transition curve of rhombic to monoclinic sulphur. It gives the effect of pressure on transition point. Both phases are solids. The system is monovariant. This curve terminates at point c beyond which monoclinic form disappears. As the transition point increases with increase of pressure, the curve 'oc' slopes away from the pressure axis.

Curve 'BC' is the fusion curve for monoclinic sulphur. It gives the effect of pressure on melting point of monoclinic sulphur. Melting point increases with pressure, so this curve slopes slightly away from the pressure axis. At any point on this curve, two phases - monoclinic sulphur and liquid are in equilibrium with each other. This curve has one degree of freedom. Point 'c' is another triple point where three curves 'OC', 'BC' and 'CD' meet. At this point three phases rhombic, monoclinic and liquid are in equilibrium.

Curve 'CD' is the fusion curve for rhombic sulphur. Along this curve rhombic sulphur and liquid are in equilibrium. According to phase rule $F = C - P + 2 = 1 - 2 + 2 = 1$. This system is monovariant.

In sulphur system in addition to stable equilibrium, there are certain metastable equilibria.

Curve OA' - If the temperature of rhombic sulphur is not increased extremely slowly at the transition temperature 95.6 °C, the conversion of rhombic to monoclinic does not take place at point 'O'. But this curve is extended to A', the melting point of rhombic sulphur. The curve OA' is metastable curve of rhombic sulphur.

Curve BA' - If liquid sulphur is not allowed to cool extremely slowly, solid will not separate out at point 'B'.

Thus, the curve EB will be extended to A'. Thus, the curve BA' represents metastable equilibrium between liquid and vapour.

Curve CA' - It is the metastable curve of rhombic sulphur. Along this curve, rhombic sulphur is in metastable equilibrium with liquid sulphur. This curve gives the effect of pressure on the melting point of rhombic sulphur in metastable state.

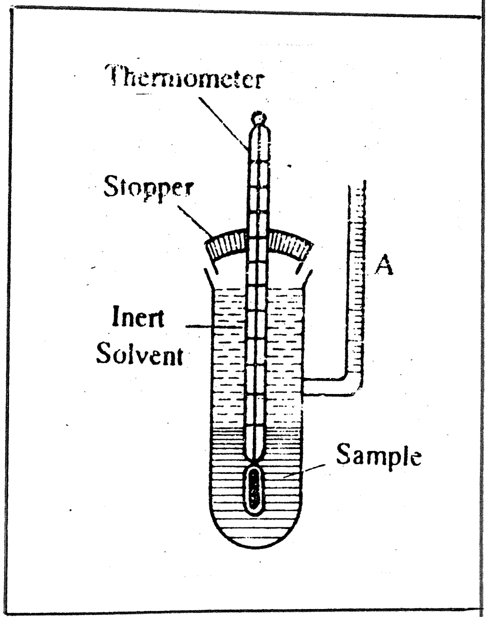
Point A' is the triple point where rhombic sulphur, liquid and vapour co-exist in the equilibrium. This point is non-variant.

There are four areas. Area AOCD contains only rhombic sulphur. Area AOBE contains only vapour phase. Area DCBE contains only liquid phase. Area OCB contains only monoclinic phase. All these areas contain only one phase, so according to phase rule $F = C - P + 2$ $= 1 - 1 + 2 = 2$. It means both temperature and pressure are required to define any point in all the areas.

· Experimental determination of transition point :

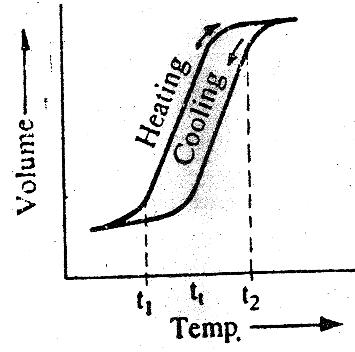
(1). Dilatometric method:-

This method is based on the principle that volume changes due to the transition of one form into another because each form has a different density.



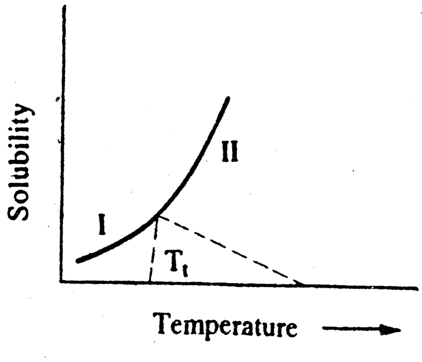
The apparatus used to determine transition point is known as dilatometer. It consists of a wide tube having a graduated capillary, side tube A. The substance whose transition temperature is to be measured is filled in the lower half of the tube. Rest of the tube is filled with an inert solvent such as xylene. The stopper carrying the thermometer is inserted into the tube. The dilatometer is kept in a thermostat. The level of xylene in the capillary is noted. The temperature is increased slowly. As soon as the transition point is reached, volume changes suddnely and level will be fall or rise. The same thing happens on cooling.

The heating curve and cooling curve do not coincide due to a lag. A mean of the temperature is the transition temperature.



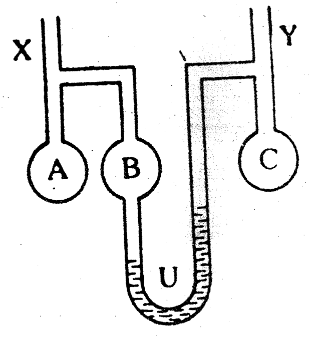
(2). The solubility method :-

At a given temperature each form has a different solubility. But both the forms have the same solubility at the transition temperature. The solubility curves for both the forms are plotted against temperature. The point where two curves intersect is transition temperature.



(3). The vapour pressure method:-

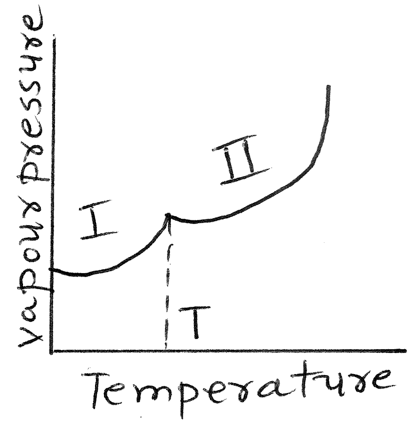
This method is based on the principle that the vapour pressure of two forms becomes equal at the transition temperature. Bremer and Frowein used the apparatus known as tensimeter to measure the vapour pressure.



Tensimeter consists of a U-tube containing mercury. Two limbs of U-tube are connected to bulbs B and C. Bulb B is fused to bulb A having side-let X. The bulb C has side-let Y.

In bulb A, water is kept and then it is sealed at X. The pure hydrated substance is kept in the bulb C. An exhaust pump is connected to Y. The pump is started to reduce the pressure in the apparatus by removing all the air from it. Now, the bulb C is also sealed at Y. Mercury level in the U-tube is to be noted. Then, bulb C is heated to start dehydration by keeping the apparatus in a thermostat. When the equilibrium is attained, the difference in mercury level is noted with travelling microscope.

$P_1 - P_2$ = difference in mercury level where P_1 is decomposition pressure of the substance kept in the bulb C, and P_2 is saturation pressure due to the water present in bulb A. Various values of P_1 are plotted against temperature. The sharp break in the curve will give transition temperature.



(4). Thermometric method:

This method is based on the principle that each form possesses different energy content. If the substance is heated, its temperature increases. At transition temperature one form is converted to another form and this temperature remains constant.

- Two component systems:-

When two components denote the smallest number by means of which composition of each phase can be expressed, it is known as a two component system.

when degree of freedom F is minimum, number of phases P becomes maximum. The minimum degree of freedom is zero. Applying phase rule $F = C - P + 2$

$$0 = 2 - P + 2$$

$$P = 4.$$

Thus, the maximum number of phases for two component system is four.

When number of phase P is minimum, degree of freedom F becomes maximum. Minimum P is 1 $F = C - P + 2 = 2 - 1 + 2 = 3$. Thus, maximum number of degree of freedom for two component system is 3.

In order to have simple phase-diagram for two component systems, pressure is kept constant. The phase-rule for such system becomes $F' = C - P + 1$. This phase rule is known as reduced phase rule.

- Types of two component systems:

Solid-liquid systems of two components.

Condensed systems:- A system in which only solid and liquid phases are there and the experiments are carried out at atmospheric pressure is known as a condensed system. For such system phase rule becomes, $F' = C - P + 1$. This phase rule is known as condensed phase rule.

Solid-liquid equilibria of different types are

Type I:- Two components are completely miscible in liquid phase, and the solid phase consists of pure components. Examples are (i) lead-antimony, (ii) lead-silver, (iii) KI-water.

Type II:- Two components combine to

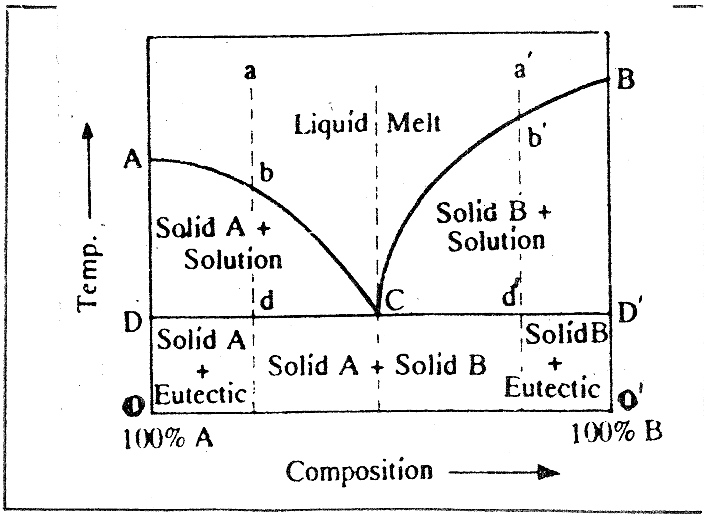
give a compound. There are two sub-types of this system.

II A :- Two components form a compound with congruent melting point. Examples are (i) zinc-magnesium, (ii) $FeCl_3$- water.

Type II B :- Two components form a compound with incongruent melting point. Examples are (i) picric acid-benzene, (ii) gold-antimony, (iii) sodium sulphate- water.

• Simple eutectic system:

Consider two components A and B which are completely miscible in liquid state and do not form any compound.



Curve AC is known as freezing point curve of component A in component B. Upon gradual addition of B to A, the freezing point of A is lowered along this curve. Along this curve, solid A is in equilibrium with the solution of B in A at different temperatures. Number of phases are two, so according to condensed phase rule $F' = C - P + 1 = 2 - 2 + 1 = 1$. It is univariant. It means that only composition changes along this curve.

Curve BC - Gradual addition of A to B decreases the freezing point along this curve. Solid B is in equilibrium with the solution of A in B at different temperatures along this curve. Number of phases two, so $F' = C - P + 1 = 2 - 2 + 1 = 1$. It is univariant. It means that only composition changes along this curve.

At point C, two curves AC and BC meets. Solid A, solid B and liquid are in equilibrium. Number of phases are three so $F' = C - P + 1 = 2 - 3 + 1 = 0$. It is non-variant. This means that there is only one temperature at which this equilibrium occurs. Point C is the lowest temperature so known as eutectic point. It represents the lowest melting point of mixture of A and B.

Above area ABC two components A and B exist as a homogeneous liquid solution. Number of phase is one. $F' = C - P + 1 = 2 - 1 + 1 = 2$. It is bivariant. It means that to define any point both, temperature and composition are required.

In the area OO'D'D only solid exist as the liquid phase can not exist below the eutectic temperature.

Any point in the area ADC represents equilibrium between solid A and liquid.
Any point in the area CD'B represents equilibrium between solid B and liquid.

It is possible to predict the behaviour of any system by heating or cooling. This type of study is important in the study of alloys in metallurgy.

Consider a liquid corresponds to point 'a'. Allow it to cool. Temperature decreases untill the point 'b' on curve AC is reached. At this point, solid A starts to separate out. Here, number of phases are two, so

$F' = C - P + 1 = 2 - 2 + 1 = 1$. It is univariant means only composition changes. If the solid A continues to separate out along the curve bc, solution becomes richer in B.

In the area ACD, solid A is in equilibrium with solution of different compositions depending upon different temperatures.

At point C, there are three phases. $F' = C - P + 1 = 2 - 3 + 1 = 0$. It is non-variant. On further cooling, solid A and B separates out in the fixed ratio so that the composition of the liquid mixture remains constant.

In the area OO'D'D has mixture of solid A and B. In this area $F' = 1$.

Similar explanation can be given by considering point a'.

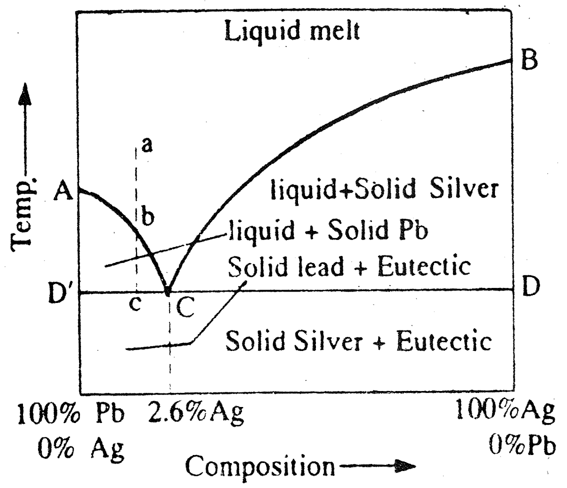
Some examples of eutectic systems are antimony-lead, Si-Al, Bi-Cd, KCl-$CaCl_2$, benzene-methyl chloride, KI-H_2O, lead-silver.

- Lead-silver system:

It is a two component system. Both lead and silver are completely miscible in the liquid state and do not form any compound.

As the pressure is constant the condensed phase rule is applied,

$F' = C - P + 1$.



Curve AC - 'A' is the melting point of lead (327 °c). Addition of silver into lead, lowers melting point of lead along this curve.

It is freezing point curve of lead. Along this curve, solid lead is in equilibrium with liquid melt. Number of phases along this curve is two. Applying condensed phase rule,

$F' = C - P + 1 = 2 - 2 + 1 = 1$. The system is univariant. It means only composition changes along the curve AC.

Curve BC - Point 'B' represents the melting point of pure silver (961 °c). Addition of lead into silver lowers the melting point of silver along this curve. It is freezing point curve of silver. Along this curve, solid silver is in equilibrium with liquid melt. Number of phases along this curve is two. Applying condensed phase rule, $F' = C-P+1 = 2-2+1 = 1$. The system is univariant. It means only composition changes along the curve BC.

Eutectic point 'c' - Two curves AC and BC meet at the eutectic point 'c'. At this point three phases-lead, silver and liquid melt are in equilibrium with each other. According to phase rule $F' = C-P+1 = 2-3+1 = 0$. Thus, point 'c' is invariant. This point C (308 °C) lies at a temperature which is lower than melting points of silver as well as lead. The composition of an alloy of lead (97.4 %) and silver (2.6 %) at this point is fixed. Therefore, point 'c' is known as eutectic point i.e. lowest temperature at which the liquid melt can exist. The temperature corresponding to this point is known as eutectic temperature and composition to this point is known as eutectic composition.

In area above curves AC, and BC silver and lead are present as a homogeneous liquid solution. Thus, there is only one phase in this area. Applying condensed phase rule $F' = C - P + 1 = 2 - 1 + 1 = 2$. The system in this area is bivariant. It means that both-temperature and composition are required to define any point in this area.

In the area ACD', solid lead is in equilibrium with liquid melt. In the area BCD solid silver is in equilibrium with liquid melt.

Significance of phase diagram of lead-silver system;- The phase diagram is used to separate silver from lead in Pattinson's process.

Suppose 'a' in the phase diagram

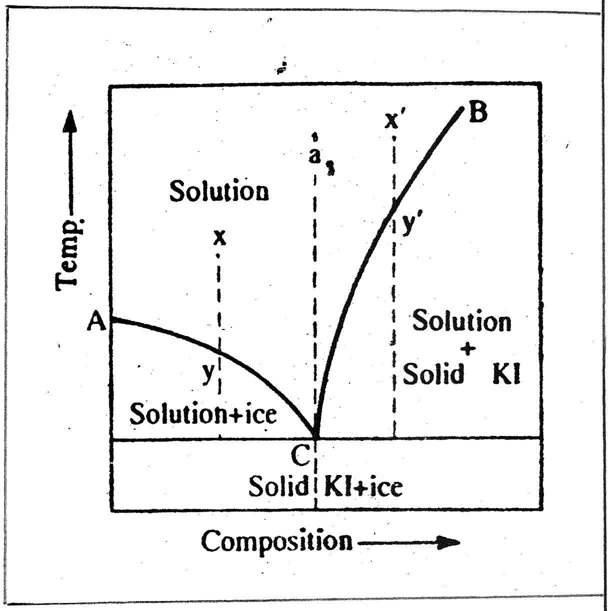
represents the molten argentiferous lead containing a small amount of silver. Now allow the liquid to cool. Temperature of the liquid melt decreases with no change in the concentration till the point 'b' on the curve 'AC' is reached. Upon further cooling, lead will separate out and the solution becomes richer in silver. Further cooling will continue along the curve 'bc'. Lead continues to separate out and is constantly removed by ladels. The liquid melt becomes richer and richer in silver till the point 'c' is reached. At point 'c' alloy containing 2.6% of silver is obtained. This alloy is then subjected to cupellation process.

The above process of increasing the concentration of silver in argentiferous lead is known as Pattinson's process.

- Potassium iodide- water system:

This system is a example of a two component system which forms a eutectic mixture. In the phase diagram melting point of potassium iodide is not shown because it is very high.

Curve AC: Point 'A' represents the freezing point of water at 1 atm pressure. This temperature is 0 °C.



When increasing quantities of potassium iodide are added, the freezing point of water decreases along the curve, AC. Thus, curve AC is known as freezing point curve of water. Along the curve AC there are two phases. According to phase rule,

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

The system is univariant. It means that for each temperature, there is a definite composition. When further quantities of potassium iodide are added, the lowering of freezing point continues along the curve AC till the point 'C' is reached. At this point the solution becomes saturated and freezes at a constant temperature −23°C and fixed composition (52% KI, 48% water).

Curve BC is known as the solubility curve of potassium iodide in water at different temperatures. The solubility increases with increase in temperature. The solubility becomes maximum at the point 'B'. Point 'B' is the boiling point of the saturated solution. If we allow a saturated solution of potassium iodide, the solution freezes along the curve BC, and solid potassium iodide separate out. This crystallization of KI continues till the point C is reached. Along the curve BC, solid KI is in equilibrium with solution. Applying phase rule, $F' = C - P + 1 = 2 - 2 + 1 = 1$. The system is univariant. The steep rise of curve BC indicates that the solubility of KI increases slowly with increase of temperature.

Point C is known as eutectic point or

cryohydric point. At this point two curves AC and BC meets. At this point temperature (−23 °C) and composition (52 %KI + 48 % ice) are definite. At this point 'C' ice, solution and solid KI are in equilibrium. Applying phase rule $F' = C - P + 1 = 2 - 3 + 1 = 0$. Thus, this point is non-variant.

Area above AOB - Above the curve BC, dilute solution of KI is there and above the curve BC there is concentrated solution of KI.

Consider a dilute solution represented by the point 'x' in the phase-diagram of KI- water system. Upon cooling, the temperature of solution decreases along 'xy' without change in composition. At point 'y' ice starts to separate. Here the system is univariant and further cooling takes place along the curve yC. At point 'C' ice and KI freeze with fixed composition, i.e. eutectic mixture.

Now let us consider point x' which represents concentrated solution. Allow this solution to cool. This cooling continues without any change in composition along the curve x'y'. At the point y' solid KI separates out. Further cooling takes place along the curve y'c. At point 'c' ice and KI freeze with fixed composition, i.e. eutectic mixture. (52% KI + 48% ice).

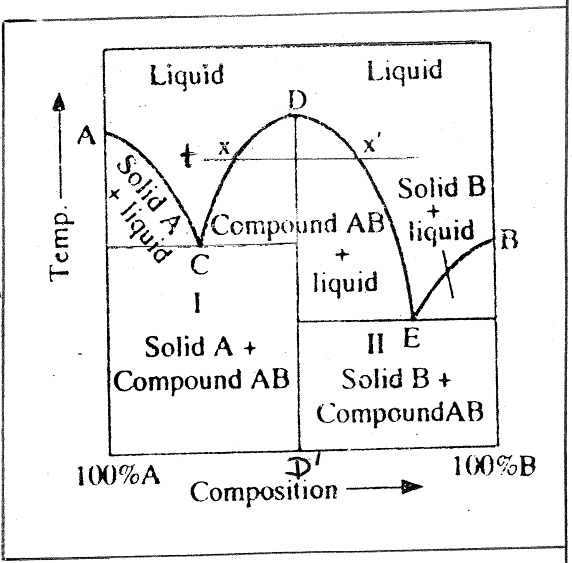
Consider a solution which is represented by the point 'a'. This point lies vertically above the eutectic point 'c'. When the solution is allowed to cool, temperature of the solution decreases along the curve 'ac' until the eutectic point 'c' is reached. At this point, ice and KI separate out simultaneously.

This mixture of potassium iodide and ice deposited at the eutectic point is known as cryohydrate.

- Solid-liquid equilibrium in which two components form a compound with congruent melting point :

A compound is said to have a congruent melting point when it melts sharply at a constant temperature into a liquid of the same composition as that of solid from which it is derived.

Suppose A and B are two components and AB is the compound formed by chemical combination of A and B.



Curve AC : Point A represents the melting point of component A. By gradual addition of B into A decreases the freezing point of A along the curve AC. Thus, this curve represents the freezing point curve of the component A. Along this curve, solid A is in equilibrium with the solution of the component B in A. Applying phase rule $F' = C-P+1 = 2-2+1 = 1$. Thus, the system is univariant, i.e. only the composition varies along AC.

Curve BE - Point B represents the melting point of pure component B. When A is added to B, freezing point of B decreases along curve BE. This curve is freezing point curve of component B. Along this curve, solid B is in equilibrium with the solution of the component A in B. Number of phases are two so $F' = C-P+1 = 2-2+1=1$. The system is univariant, i.e. only the composition varies along BE.

Curve CDE is known as freezing point curve of compound AB. Along this curve, the solid AB is in equilibrium with liquid. Point 'D' is congruent melting point of the compound AB as the solid and liquid both have the same ~~temper~~ composition. Here, two component system becomes one component because both the liquid and solid contain the same compound AB. Applying phase rule $F' = C-P+1 = 1-2+1=0$. Thus, point D is non-variant. It means point D represents a definite melting point.

Eutectic point C - Two curves AC and CDE meet at the point C. Here solid A, compound AB and liquid are in equilibrium. Number of phases three. $F' = C-P+1 = 2-3+1=0$. The system is invariant, i.e. solid A, compound AB and liquid can exist at a definite temperature and composition.

Eutectic point E - Two curves BE and CDE meet at the point E. Here, Solid B, compound AB and liquid are in equilibrium. Number of phases three. $F' = C - P + 1 = 2 - 3 + 1 = 0$. The system is invariant, i.e. solid B, compound B and liquid can excist at a definite temperature and composition.

In this phase-diagram of congruent melting point system, point D is above points A and B. In reality it may be above, below or in between A and B. Compound AB contains equimolar amounts of A and B. This is not always so.

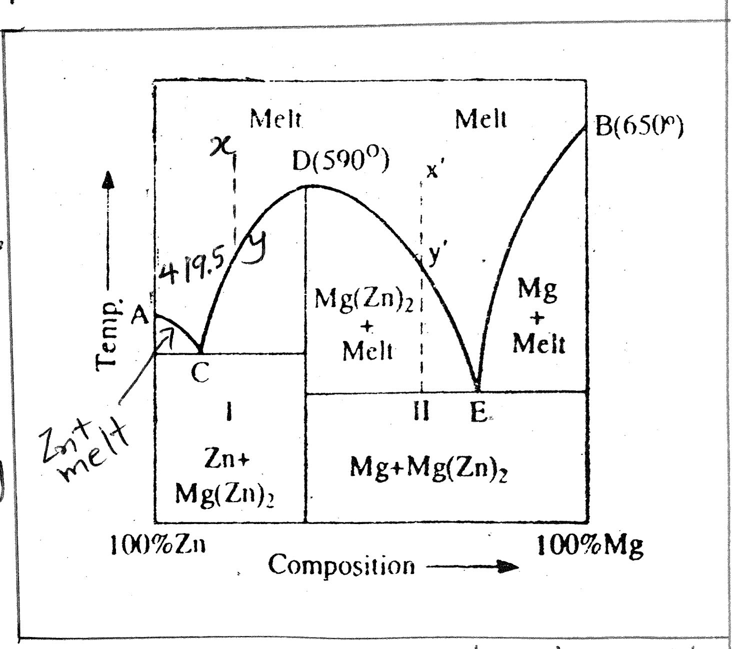
~~Draw a~~ Line xx' in the phase diagram indicates that at a certain temperature 't', the liquid phase can have two compositions. In other words, compound AB has two solubilities at the same temperature. AB is made up of two parts, left half of the diagram is two component system of solid A and AB and right half is two component system of B and AB. The curve DC represents the freezing point curve of solid AB when A is added to it. Similarly, curve DE represents the freezing point curve of AB when B is added to it.

When two components form more than one compound, the phase-diagram will have curves analogous to CDE.

Systems with congruent melting point are- (i) Zinc-magnesium (ii) aluminium-magnesium (iii) mercury-thorium (iv) gold-tin (v) phenol-aniline (vi) ferric chloride-water.

• Zinc-Magnesium system:

This is a two component system in which two metals form a compound $Mg(Zn)_2$ having congruent melting point 590 °C which lies between the melting points of two metals. The composition of $Mg(Zn)_2$ by weight is Mg = 79% and Zn = 21%.



Melting point of Zn is 420 °C and that of Mg is 650 °C. The melting point of $Mg(Zn)_2$ is 590 °C. This compound is stable and it melts without change of composition.

Point A represents the melting point of

pure zinc.

Curve AC - By gradual addition of Mg to Zn, the melting point of zinc is lowered along this curve. Along this curve, solid zinc is in equilibrium with solution. Applying phase rule, $F' = C - P + 1 = 2 - 2 + 1 = 1$. The system is univariant, i.e. only the composition varies along this curve.

Point B represents melting point of Mg.

Curve BE - When zinc is added to Mg the melting point of Mg is lowered along this curve. Along this curve solid Mg is in equilibrium with liquid. This curve is freezing or melting point curve of Mg. $F' = C - P + 1 = 2 - 2 + 1 = 1$, i.e. only composition varies along this curve.

Curve DC - When further quantities of zinc are added melting point of $Mg(Zn)_2$ decreases along this curve. This curve represents the lowering of melting point of compound $Mg(Zn)_2$ upon addition of Zn.

Curve DE represents lowering of melting point of $Mg(Zn)_2$ when Mg is added.

Point D - At this point, liquid and solid have the same composition, i.e. $Mg(Zn)_2$ melts without decomposition. Thus, the temperature corresponding to this point is the congruent melting point of $Mg(Zn)_2$.

Two curves AC and CD meets at the point C. There are three phases, solid zinc, compound $Mg(Zn)_2$ and melt. $F' = C - P + 1 = 2 - 3 + 1 = 0$. This point is eutectic point.

Two curves BE and DE intersect at the point E. There are three phases, solid Mg, $Mg(Zn)_2$ and melt. This point is invariant and eutectic.

Consider a melt of composition 'x'. Allow the melt to cool along line xy. At point 'y' the solid $Mg(Zn)_2$ starts to separate out. At this point, there are two phases, $F' = C - P + 1 = 2 - 2 + 1 = 1$, it is univariant. It means if temperature is further lowered, composition changes. This cooling occurs along yC. At point 'C' zinc will separate out. There are three phases, $F' = C - P + 1 = 2 - 3 + 1 = 0$. It is non-variant. It means if cooling is continued there will be no change in temperature and composition. Similarly, consider point x'. Allow the liquid to cool. The temperature decreases along $x'y'$. At point y', solid $Mg(Zn)_2$ separates. Further cooling will takes place along $y'E$. At the point E, magnesium also separates out.

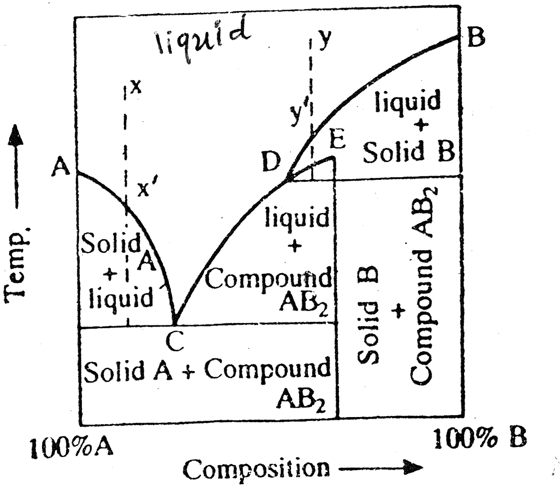
· Solid-liquid equilibria in which two components form a compound with incongruent melting point :

In many two component systems, the compound formed is unstable so instead of melting, it decomposes to form a new solid and a solution of the solid at a temperature which is below its melting point. Such compound is said to have incongruent melting point. The decomposition of this compound is known as transition or meritectic or peritectic reaction.

This type of reaction is represented by

$$S_1 \rightleftharpoons S_2 + \text{Solution}$$

original Solid   new solid



A peritectic reaction has the following characteristics:

(i) It takes place at a constant temperature.

(ii) It is a thermodynamic reaction which involves lattice of morphotropic changes.

(iii) It doesn't involve breaking and making of chemical bonds, it is not considered as a chemical reaction.

Suppose two components A and B combine to form a compound AB_2.

Points A and B represent the melting points of components A and B.

'AC' is the fusion curve of component A. Along this curve, solid A and liquid are in equilibrium.

'CD' is the fusion curve of compound AB_2. Along this curve, compound AB_2 and liquid are in equilibrium.

'D' is the incongruent melting point. At this temperature, compound AB_2 and decomposes and gives a new compound and the liquid. Point D is below point E which is a hypothetical melting point of the compound.

Consider a point 'x' in the liquid region above ACDB. Allow the liquid to cool. Temperature of the liquid decreases without change of composition till the point x' on the curve AC is reached. At the point x', solid A starts to separate out. On further cooling, composition changes along the curve $x'C$. At point C, the compound AB_2 starts to separate out. At point C, there are two solids and one liquid are in equilibrium. Applying the reduced phase rule, $F' = C - P + 1 = 2 - 3 + 1 = 0$. Thus, it is non-variant.

Consider a point y in the liquid region above ACDB. Allow the liquid to cool. Temperature of the liquid decreases without change of composition till the point y' on the curve BD is reached. At the point y', solid B starts to separate out. On further cooling, composition changes along the curve y'D. When point D is reached, the following meritectic reaction occurs.

$$\text{Solid B} \rightleftharpoons \text{Solid } AB_2 + \text{Solution.}$$

At point B solid AB_2 separates out. Point D is nonvariant ($F=C-P+1=2-3+1=0$), means this reaction occurs at constant temperature. This process, continues till whole of the solid B disappears. Therefore, point D is also known as peritectic point.

Some examples of two component system forming a compound with incongruent melting point. (i) picric acid - benzene, (ii) gold-antimony (iii) sodium-bismuth (iv) sodium sulphate-water, (v) potassium chloride-copper chloride, (vi) acetamide-salicylic acid.