Phase Rule

It help us to predicts quantitatively equilibrium existing between different phases of a heterogeneous systems

This rule was first put forward by J. Willard Gibbs, an American Chemist, in the year 1876 The full implications of this rule was understood by chemists only when Roozeboom, Ostwald and van't Hoff applied it to some well-known physical and chemical equilibria.

<u>Dynamic equilibria:</u> When the reactants in a closed vessel at a particular temperature react to give products, the concentrations of the reactants keep on decreasing, while those of products keep on increasing for some time after which there is no change in the concentrations of either of the reactants or products. This stage of the system is the **dynamic equilibrium** and the rates of the forward and reverse reactions become equal. Also called equilibrium **EQUILIBRIUM IN PHYSICAL PROCESSES:** If we examine some physical processes. The most familiar examples are **phase transformation processes**, *e.g.*, Solid – liquid, I iquid – gas, solid – gas, solid1 – solid2

S-L: Melting /fusion, L-G: Vaporization/condensation, S-G: Condensation/Deposition S1-S2: Transition

<u>Phase reactions:</u> Any physical/chemical change associated with appearance/disapperance of phases is termed as phase reaction

• Equilibrium conditions:

- The system is said to be under thermal/Mechanical/Chemical equilibrium if
- 1.Thermal: All phases exist in equilibrium are at same temperature (Temp not changes)
- 2. Mechanical: All phases exist in equilibrium are at same pressure(No exchange of particles into surrounding)
- 3.Chemical: all phases exist in equilibrium are at same Chemical potential. (Composition not changes)

Statement of Phase rule

- In heterogeneous system at equilibrium sum of degree of freedom & phases greater than component by two
 i.e F + P = C + 2
- F=C-P+2
- Where
- P = Phases of system
- C = Component &
- F = Degree of freedom
- 2 stands for the intensive variables pressure, P and temperature
- Terms in phase rules
- <u>Phase: (P):</u> A phase is defined as number of any homogeneous and physically distinct part of a system which is separated from other parts of the system by interfaces/ boundary surface.
- A phase may be gas, liquid or solid.
- A gas or a gaseous mixture is a single phase.
- Totally miscible liquids constitute a single phase.
- In an immiscible liquid system, each layer is counted as a separate phase.
- Every solid constitutes a single phase except when a solid solution is formed
- A solid solution is considered as a single phase.
- Each polymorphic form constitutes a separate phase.
- The number of phases does not depend on the actual quantities of the phases present. It also does not depend on the state of subdivision of the phase

Examples of phases

- Counting the number of phases
- a) Liquid water, pieces of ice and water vapour are present together.
- The number of phases is 3 as each form is a separate phase. Ice in the system is a single phase even if it is present as a number of pieces.
- b) Calcium carbonate undergoes thermal decomposition.
- The chemical reaction is: CaCO₃(s) ↔ CaO(s) + CO₂ (g)
- Number of phases = 3
- This system consists of 2 solid phases, CaCO₃ and CaO and one gaseous phase, that of CO₂
- c) Ammonium chloride undergoes thermal decomposition. The chemical reaction is: NH₄Cl(s) → NH₃ (g) + HCl (g) Number of phases = 2
- This system has two phases, one solid, NH₄Cl and one gaseous, a mixture of NH₃ and HCl.
- d) A solution of NaCl in water Number of phases = 1
 - e) A system consisting of monoclinic sulphur, rhombic sulphur, liquid sulphur and sulphur Number of phases = 4 This system has 2 solid phases and one liquid and vapour phase. Monoclinic and rhombic sulphur, polymorphic forms, constitute separate phases.

- <u>Component (C):</u> Def: Minimum number of molecular species involved by means of which chemical composition of every phase in a system is expressed OR
- It should be noted that the term "constituents" is different from "components",
- which has a special definition. When no reaction is taking place in a system, the number of components is the same as the number of constituents. For example, pure water is a one component system because all the different phases can be expressed in terms of the single constituent water. In order to find out minimum number of C zero &/or –ve quantity of composition be consider.

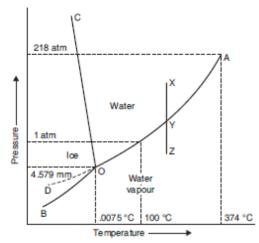
Examples of Component

- a) The sulphur system is a one component system. All the phases, monoclinic, rhombic, liquid and vapour can be expressed in terms of the single constituent sulphur.
- b) A mixture of ethanol and water is an example of a two component system. We need both ethanol and water to express its composition.
- c) An example of a system in which a reaction occurs and an equilibrium is established is the thermal decomposition of solid CaCO₃. In this system, there are three distinct phases: solid CaCO₃, solid CaO and gaseous CO₂. Though there are 3 species present, the number of components is only two, because of the equilibrium
- CaCO₃ (s) \rightarrow CaO(s) + CO₂(g)
- Any two of the three constituents may be chosen as the components. If CaO and CO₂ are chosen, then the composition of the phase CaCO₃ is expressed as one mole of component CO₂ plus one mole of component CaO. If, on the other hand, CaCO₃ and CO₂ were chosen, then the composition of the phase CaO would be described as one mole of CaCO₃ minus one mole of CO₂
- A system in which ammonium chloride undergoes thermal composition. $NH_4Cl(s) \rightarrow NH_3(g) + HCl(g)$
- There are two phases, one solid-NH₄Cl and the other gas a mixture of NH₃ and HCl. There are three constituents. Since NH₃ and HCl can be prepared in the correct stoichiometric proportions by the reaction: NH₄Cl \rightarrow NH₃+HCl
- The composition of both the solid and gaseous phase can be expressed in terms of NH₄Cl alone. Hence the number
 of components is one.
- If additional HCl (or NH₃) were added to the system, then the decomposition of NH₄Cl would not give the correct composition of the gas phase. A second component, HCl (or NH₃) would be needed to describe the gas phase it become two component system
- Degrees of freedom (F) (or variance)
- The degrees of freedom or variance of a system is defined as the minimum number of variables such as temperature, pressure, concentration, which must be arbitrarily fixed in order to define the system completely
- Examples of Degree of freedom
- a) A system having only liquid water has two degrees of freedom or is <u>bivariant</u>. Both temperature and pressure need to be mentioned in order to define the system.
- b) In water system containing liquid water, pieces of ice are added and this system with 2 phases is allowed to come to equilibrium, then it is an <u>univariant</u> system. Only one variable, either temperature or pressure need to be specified in order to define the system. If the pressure on the system is maintained at 1 atm, then the temperature of the system gets automatically fixed at 0°C, the normal melting point of ice.
- c) In water system mentioned above, a small quantity of water is allowed to evaporate and then the system is allowed to come to equilibrium, then the number of phases in equilibrium will be three. This system has no degrees of freedom or it is *invariant*. Three phases, ice, water, vapour can coexist in equilibrium at 0.0098°C and 4.6mm of Hg pressure only. A change in temperature or pressure will result in one or two phases disappearing.
- <u>Hence the degree of freedom of a system may also be defined as the number of variables, such as temperature, pressure and concentration that can be varied independently without altering the number of phases</u>
- True and metastable equilibrium
- True equilibrium is obtained when the free energy content of a system is at a minimum for the given set of variables
- A state of true equilibrium is said to exist in a system when the same state can be obtained by approaching from either direction.
- An example of such an equilibrium is ice and liquid water at 1 atm pressure and 0°C.At the given pressure, the
 temperature at which the two phases are in equilibrium is the same whether the state is attained by partial
 freezing of liquid water or by partial melting of ice
- Liquid water at 4 °C is said to be in a state of metastable equilibrium because this state of water can be obtained by only careful cooling of the liquid and not by fusion of ice. If an ice crystal is added to this system, then immediately solidification starts rapidly and the temperature rises to 0°C.
- A state of metastable equilibrium is one that is obtained only by careful approach from one direction and may be
 preserved by taking care not to subject the system to sudden shock, stirring or "seeding" by solid phase.
- Phase equlibria of one component systems water, and S systems

- Applying the phase rule to a one component system, we write F = C-P+2 = 1-P+2 = 3-P Three different cases are possible with P taking values 1, 2 and 3.
- a) System having only one phase, i.e., P=1 F=3-P=3-1=2
- This is a bivariant system. We need to state the values of 2 variables in order to define the system completely.
 These are temperature and pressure. The given component may exist in any of the three phases, solid, liquid or vapour.
- b) System having 2 phases, i.e. P=2 F=3-P=3-2=1 This is a univariant system and hence the value of either of the 2 variables, temperature or pressure, would define the system completely. The two phases in equilibrium with each other may be solid-solid, solid-liquid, liquid-vapour and solid-vapour.
- c) System having 3 phases, i.e. P=3. F=3-P=3-3=0 The system is invariant and three phases can exist in equilibrium only at definite values of temperature and pressure. The three phases in equilibrium with each other may be solid-liquid-vapour, solid-solid-liquid, and solid-solid-vapour.
- Thus, we see that the maximum number of phases existing in equilibrium in a one component system is **three**.
- For a one component system, as the maximum number of degrees of freedom is two,
- The equilibrium conditions can be represented by a phase diagram in two dimensions choosing <u>pressure</u> and temperature variables.

Water system

- The simplest case of a one component system is one in which there is only one solid phase.
- In a system having more than one solid phase, there are a number of possible equilibria and the phase diagram gets quite complicated.
- In the case of "water" system, above –20°C and below 2000 atm pressure, there is only one solid phase, namely, ordinary ice



- Water system is one component system since all three phases are represented with same chemical formula H₂O
- There are three phases
- Water Ice –Solid, Water liquid liquid, Water Vapour Gas
- It is one component system Hence Phase diagram of one component system will be Shown by Temperature & Pressure Variable which is as shown in above figure
- Phase diagram of water system consist of
- A)Curves: There are three stable curves namely BO,AO,OC & one metastable curve OD'
- Curve BO: It is sublimation curve It starts B(at -273°C) and ends at O (at 0.0098 °C) The two phase Solid & Vapour
 are in equilibrium along this curve each point gives Vaporization temperature of Ice w.r.t pressure Hence system
 along curve is uni variant.
- Curve AO: it is Vaporisation curve It starts A(at 374°C) and ends at O (at 0.0098 °C) The two phase Liquid & Vapour are in equilibrium along this curve each point gives Vapour pressure temperature above 374 it exist in vapour phase Hence system along curve is univariant
- Curve CO: it is Freezing curve It starts O(at 0.0098 °C) and ends at A The two phase Solid & Liquids negative slope
 means Melting temperature falls as the pressure is raised Hence system along curve is univariant
- Metastable Curve: OD': By sudden cooling of water below 0°C allows existence of liquid water up to D' i.e. -4°C Here at temperature below that of triple point liquid water has a vapour pressure higher than sublimation pressure of ice & hence the supercooled liquid unsable at these temperature w.r.t. ice. System is uni variant.
- B) Area: These three curves split phase diagram in 3 areas Each area shows existence of single phase
- BOC- ICE(S), AOC-Water(L), AOB- Water Vapour(G)
- To define any point in area both Temperature & Pressure must be known i.e system is bivariant
- i.e T&P may be changed independently without changing no, of phases

• C) Triple point: (In heterogeneous system a point at which three phases of system are in equilibrium/ point in phase diagram where three phases are in equilibrium) There is only one triple point since no of phases of system is three

At this point phase S,L,V are in equilibrium, corresponding temperature is 0.0098°C & pressure is 4.568mm, It occurs at single definite variable, which is characteristic of substance Hence system is non variant

Application of water system

- We have seen in the water system, the fusion curve OC is almost vertical with a slight tilt (bend) towards the pressure axis. This indicates that an increase in pressure decreases the melting point of ice
- A property that contributes to making skating on ice a possibility. The pressure exerted by the weight of the skater through the knife edge of the skate blade lowers the melting point of ice. This effect along with the heat developed by friction produces a lubricating layer of liquid water between the ice and the blade. It is of interest to note that the skating is not good if the temperature of ice is too low.
- In boiler industry demands dry vapour which possible above critical level (Temp: 374 & Pressure 218atm)

The phase diagram for sulphur

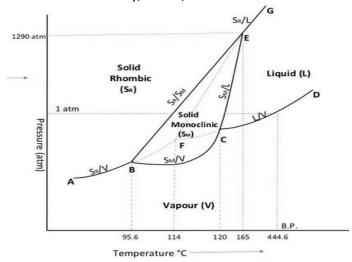
• Sulphur exists in two solid modifications, the rhombic form stable at ordinary temperatures and the monoclinic form at higher temperatures. Substances that can exist in more than one crystalline form, each form having its own characteristics vapour pressure curve, are said to exhibit the phenomenon of polymorphism. Two types of polymorphism are observed, enantiotropy (Greek: opposite change) and monotropy (Greek: one change).

Enantiotropy

• Two crystalline modifications of a substance are said to be enantiotropic (or to exhibit enantiotropy) when each has a definite range of stability and conversion from one modification to the other takes place at a definite temperature in either direction. This temperature is the **transition point** and it is the only temperature at which the two modifications can coexist in equilibrium at a given pressure. A change in this temperature results in the complete transformation of one modification into the other, one being stable above the **transition point** and the other below it.

Monotropy

• If one crystalline form is stable and the other form metastable over the entire range of their existence, the substance is said to exhibit Monotropy. The transformation from one form into another takes place in one direction only, that is, from metastable to stable form.



- Sulphur system is one component system since all four phases are represented with same chemical formula S
- Four are three phases Sr(S),SM(S),SL(L),SV(G)
- It is one component system Hence Phase diagram of one component system will be Shown by Temperature & Pressure Variable which is as shown in above figure
- · Phase diagram of sulphur system consist of
- A)Curves: There are Six stable curves namely AB,BC,CD,BE,CE & FE & three metastable curve BF,CF,EF <u>Curve AB</u>: it is sublimation curve for SR. It starts at A and ends at B. above which SR doesnot exist. The two phase SR& SV are in equilibrium along this curve. Each point on curve gives Vaporization temperature of SR w.r.t pressure Hence applying phase rule system along curve is uni variant
- <u>Curve BC</u>: it is sublimation curve for SM. It starts at B the transition temperature of SR and ends at C The melting point for SM. The two phase SM& SV are in equilibrium along this curve. Each point on curve gives Vaporization temperature of SM w.r.t pressure Hence applying phase rule system along curve is uni variant.
- <u>Curve BE</u>: it is Transition curve for SR. It starts at B and ends at E(Fusion/Melting temp. of SR at corresponding P)
 The curve depicts effect of pressure on transition temperature. *An increase in pressure increases transition temperature* The two phase SR & SV are in equilibrium. Hence system along curve is uni variant

- <u>Curve CE:</u> It is melting point curve for SM. Starts at C(M.P.of SM) ends at E. gives effect of pressure on melting point. Two phases SM&SL are in equilibrium along the curve system is univariant
 <u>Curve EG:</u> It is melting point curve for SR at 1290atm transition temp. equals melting temperature hence SM is not formed beyond point E. The two phases SR&SL are in equilibrium along the curve. System is univarient
- Metastable Curve: There are three metastable curves BF,CF, EF By sudden heating SR above 96 ^oC SR is retained up to point F giving curve BF. Similarly rapid cooling of SL allow existence of SL up to F giving Curve CF, It metastable SR & supercooled SL are formed it gives cuve FE wher SR&SL are in equilibrium no SM is present. But it needs careful heating of SR & careful cooling of SL. The system along three curves is also uni variant.
- B) Area: Six curves split phase diagram in 4 areas Each area shows existence of single phase
- ABCD- SV ABEF- SR, BCE- SM, DCEF- SL
- To define any point in area both Temperature & Pressure must be known i.e system is bivariant
- i.e T&P may be changed independently without changing no, of phases
- <u>C) Triple point:</u> There are three stable triple point and one metastable triple point since no of phases of system is four **1. point B**: At this point phases SR,SM,SV are in equilibrium. The corresponding temp. is 96 &Pis 0.006mm. changing this the system may follow any curve or area hence nonvarient **2. point C**: At this point phases SL,SM,SV are in equilibrium. The corresponding temp. is 120 &Pis 0.04mm. changing this the system may follow any curve or area hence nonvarient **3. point E**: At this point phases SR,SM,SL are in equilibrium. The corresponding temp. is 160&Pis 1290 atm. changing this the system may follow any curve or area hence nonvarient
- Rapid cooling of SR allows existence of SR upto 114°C without forming SM & giving metastable curves BF. Similarly when SL is cooled suddenly, liquid phase exists up to 114°C without forming SM. It gives metastable curve CF.
 When curve BF & CF are obtained then existence of SM is totally vanished & point F will emerge as metastable triple point where SR,SL,SV are in equilibrium slight disturbance will vanishes point F & SR & SL converted to SM.

Phase equilibria of two component systems

- Applying the phase rule to two component systems we have the degrees of freedom, F=C- P+2=4-P. when a single phase is present in a two component system, the number of degrees of freedom, F=3, means that three variables must be specified to describe the phase and these are temperature, pressure and composition of the phase. When two phases are present, the number of degrees of freedom, 4-P, is reduced to 2, temperature and composition of the liquid phase. The values of the other variables get automatically fixed. If there are three phases present, then F=4-3=1 which means the value of only one variable needs to be stated to describe the phases
- The maximum number of degrees of freedom for a two component system we see from the preceding discussion is three.
- In order to represent the variation in three variables graphically, we require a three dimensional diagram, a space model, which is difficult to construct on paper.
- To overcome this difficulty, a common practice that is adopted is to keep one of the variables constant.
- There are various types of equilibria, that are generally studied at constant external pressure.
- Thus, out of the three variables (F=3), one is already stated and the variation in the other two can be represented on a two dimensional diagram.
- Equilibria such as solid-liquid equilibria are such systems in which the gas phase is absent and hence are hardly affected by small changes in pressure.
- Systems in which the gas phase is absent are called condensed systems. Measurements in these systems are generally carried out at atmospheric pressure.
- As these systems are relatively insensitive to small variation in pressure, the pressure may be considered constant.

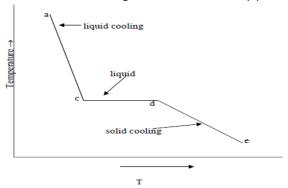
Reduced Phase rule

- · The phase rule takes the form
- P+F=C+1 One independent variable remain constant
- For such systems and in this form it is known as the reduced phase rule. For a two component system, this equation becomes F=3-P where the only remaining variables are temperature and composition. Hence solid-liquid equilibria are represented on temperature composition diagrams.
- · Determination of solid-liquid equilibria
- Many experimental methods are used for the determination of equilibrium conditions between solid and liquid phases. The two most widely used are the thermal analysis and saturation or solubility methods. Whenever required additional data are obtained by investigating the nature of the solid phases occurring in a system.
 Simple Eutectic & Solid Solution
- **Simple Eutectic:** If two substances are completely miscible in the liquid state, but completely immiscible in the solid state, form a simple eutectic. Of the various mixture, one mixture has the lowest melting point such a mixture is known as a eutectic mixture (eutectic means easy melting).

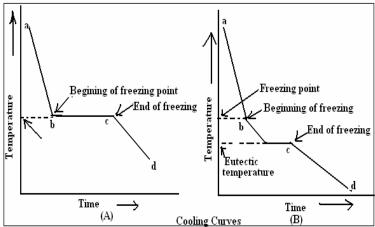
• **Solid Solution:** When two substances, especially metals, are completely miscible in both the solid and liquid states, they form solid solutions, where mixing takes place in the atomic levels. A condition for the formation of solid solution is, the two metals should not differ in atomic radius by more than 15%.

Cooling curve of a pure component

A pure component, say A, is taken and heated to get a melt. The liquid A is allowed to cool on its own and the temperature of the melt is noted at, say, every half a minute. A cooling curve is obtained by plotting temperature versus time



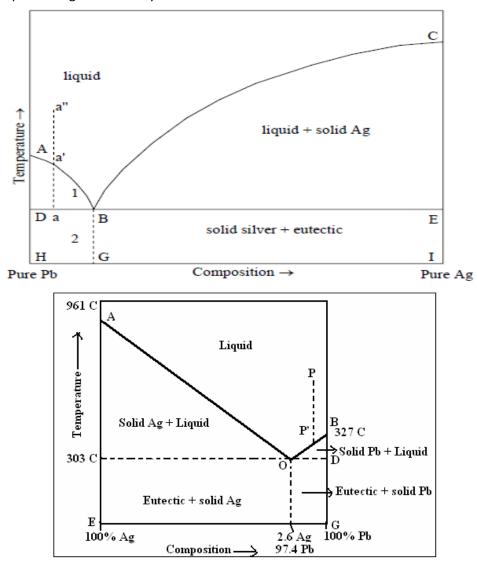
Cooling of liquid A takes place along ac, when at c solidification starts and the system has two phases in equilibrium becoming an invariant system (F=C+1-P=1+1-2=0). The temperature remains constant till the entire liquid A solidifies along cd. The system is cooling, losing heat to the surroundings, **yet the temperature remains constant during solidification. This is due to the fact that heat is released during solidification compensate for cooling.** Cooling of solid A takes place along de. The system represented by any point on either ac or de has only one phase and hence is univariant **Cooling curve of a mixture of two components with only pure components crystallizing on cooling the system.**Solid B is added to solid A to get a mixture of known composition. This mixture is heated to get it in the liquid phase.



- The liquid cools along ab and at b solid A starts solidifying. Temperature and composition of liquid phase have to be stated to define the liquid phase completely (P=1, F=3-P, F=2) when A starts solidifying, the system becomes univariant (P=2, F=3-P=1). Thus, the temperature at which solid A starts solidifying from the liquid mixture of known composition will have a definite
- value given by the point b. This temperature is expected to be a little lower than the freezing point of pure A as the
 addition of B to A lowers the freezing point of A. Solidification of a small quantity of A changes the composition of
 the liquid phase and hence the temperature at which A solidifies from this liquid will take place at another fixed
 value but lower than the previous temperature as the molality of B in the liquid increases with the solidification of
 A. Thus as more
- and more of A separates from the liquid, the temperature of the system falls along bc. The rate of cooling is affected by the heat evolved due to the solidification of A and hence a break is observed in the curve at b. The break point indicates the temperature at which A just starts solidifying. Along the curve bc, there are two phases, liquid and solid A, hence the system is univariant (P=2, F=3-P=1). As cooling continues along bc, more and more of solid A separates
- and the liquid gets richer in B. At the point C, the liquid becomes saturated in B and hence B starts separating along with A. Along cd both the solids A and B separate and the system becomes invariant (P=3, F=3-P=0). Solidification from a solution of fixed composition, one corresponding to the saturation solubility of B in A takes place at constant temperature. This results in a halt or complete arrest of the cooling curve (cd). As the saturation solubility of B in A has to be maintained at this temperature, the composition of the solid phase that separates will be the same as that of the liquid phase. The temperature of the systems will remain unchanged till the whole of the liquid phase solidifies. The cooling of the solid phase is represented by de and the system is univariant (P=2, F=3-P=1).
- Eutectic system: System in which definite proportion of component involved are simultaneously crystallized from melt at minimum possible temp.

- Eutectic Mixture: Definite composition of components from eutectic system, that solidifies at lowest possible temp.
- Eutectic point: Binary alloy system in which component involved are freezes/ crystallized simultaneously from melt at minimum possible temp
- Eutectic Temperature: Lowest possible temp. for eutectic mixure at which component involved are simultaneously crystallized or melt.

The Lead-Silver system \The metals lead and silver are completely miscible in the liquid state and do not form any compound. Hence the phase diagram of this system is



- Simple Eutectic (Pb-Ag system)
- It is a two-component system. The phase diagram of the Pb-Ag system is shown in the above fig
- Curve AO
- Point A is the *melting point of pure Silver*. Curve AO shows melting point depression of silver by the addition of lead. At any point in this curve there is equilibrium between solid Ag and liquids part. Hence curve AO called Freezing curve of pure Silver
- According to reduced phase rule equation. The system is univarient.
- F'=C-P+1; F'=2-2+1; F'=1
- Curve BO
- Point B is the melting point of pure lead, (327°C), curve BO shows the melting point depression of lead on gradual addition of silver to it. Along this curve solid lead and solution co exist and hence curve is called Freezing curve of Pure Pb & the system is univariant.
- Point O: The two curves AO & BO meet at point O, where three phases solid pb, solid Ag and their
- solution co-exist, according to condensed phase rule the system is invariant.
- F'=C-P+1; F'=2-1+1; F'=2
- The point 'O' is known as eutectic point, its composition (Ag=2.6%; Pb=97.4%) and temperature (303°C) is known as eutectic composition and eutectic temperature respectively. Further cooling below the eutectic temperature respectively. Further cooling below the eutectic temperature will cause simultaneous crystallization of a mixture of lead and silver
- Area AOB: Consists of only one phases namely pb-Ag solution. According to reduced phase rule equation. F'=C-P+1; F'=2-1+1; F'=2

- The system is bivarient i.e., both T & composition has to be specified to define the system.
- Below the eutectic point (O), area COEF consists of solid and eutectic compound, where
- crystalline silver and eutectic compounds are stable. Similarly the area ODFG consists of solid Pb and eutectic compound, where crystalline lead eutectic compounds are stable.

Pattinson process

• If a sample of argentiferrous lead, containing less than 2.6% Ag is allowed to cool gradually, lead will separate out and the solution will become progressively richer in Ag, till the percentage 2.6 of Ag is reached(Let us consider a point p, which represents a sample of lead containing less than 2.6% silver. On cooling the temperature falls gradually till point p'. On further cooling lead begins to separate and the concentration of Ag increase in the solution till the point O is reached, after that whole mass solidifies (2.6% Ag; 97.4% pb). This process is utilized in the pattinson's process of desilverization of lead.) and on further cooling, the whole mass will solidify as such. On the other hand, if lead-silver allow containing Ag greater than 2.6% is allowed to cool, and then pure silver separates along the curve AO, till the eutectic composition at O is reached

Phase diagram General Description

- Graphical representation of heterogeneous system and possible equilibrium states is phase diagram. It predicts effect of change in Temperature, pressure, composition on various possible equilibrium of system under study.
- Generally it is in the form of P-T,T-C,P-C diagram & the variables of least significance is neglected / kept constant where ever necessary
- In general as phase digram will consist Curves, Areas & points
- A)Curves: Region in phase diagram where two phases are in equilibrium along this region. The point on curves is defined by only one variable (univariant). Depending upon actual phase reaction curved are named like Liquid vapour (vaporization curve) Solid vapour (sublimation curve) Solid liquid (fusion/ freezing curve) Solid 1 solid 2 (transition curves) Metastable curves- extended stability of certain phase
- B) Area: Area is region of phase diagram where single phase exist. The point in area is defined with two variables (Bivarant)
- c) Points: There are various points in phase diagram like Freezing point, Boiling point, Critical Temp. critical pressure Triple point: This point where 3 curves meets. 3 phases are in equilibrium with definite sets of variables. Hence nonveriant
- Eutectic point: Binary alloy system in which component involved are freezes/ crystallized simultaneously from melt at minimum possible temp. Hence nonveriant
- It also help to show of polymorphism enantiotropy (Greek: opposite change) and monotropy (Greek: one change).
- E.g Water system

Applications of Eutectic system

- A mixture of 23.3% NaCl & ice by mass providing -21.2 °C eutectic temp. hence freezing mix is prepared by adding common salt to ice
- Eutectic alloy of Na& K (NaK) are liquid at RTP are acts as coolant in nuclear reactors
- Eutectic alloy of Pb & Sn and Ag & Au are used for soldering purpose
- Eutectic mixture are used as inks in inkjet printers which can operate at low temp.
- Eutectic alloy of low Melting point are used to prepare safety valve in pressure cookers, automobiles, boilers etc
- In semiconductor industry gold silver Eutectic is used.
- In brazing process one of the element from an alloy can be removed by diffusion of another element forming an eutectic that melts at a lower temp.
- In a rock, the mineral portion always contains both miscible (solid soln) & immisible (binery eutectic) phase & on heating it splite into two separate fractions
 - Temperature response i.e wood metal & field metals used for fire sprinklers

Uses (or) merits of phase rule

- 1. Applicable to both physical and chemical equilibria.
- 2.A convenient method to classify the equilibrium systems in terms of phases, components and degree of freedom.
- 3.Indicates that different systems having the same degrees of freedom behave similarly.
- 4. Decides whether the given number of substances remains in equilibrium or not.
- 5. Applicable to macroscopic systems without considering their molecular structures.
- 6. Does not consider the nature (or) amount of substances in the system

Limitations of phase rule

- 1. Phase rule can be applied only for the heterogeneous systems in equilibrium.
- 2. Only three variables like P, T & C are considered, but not electrical, magnetic and gravitational forces.
- 3. All the phases of the system must be present under the same conditions of pressure and temperature.
- 4. Solid and liquid phases must not be in finely divided state, otherwise deviations occur

Modified Adv/Disadv

Advantages/ Merits Phase rule

- 1 Simple approach to study equilibrium state of heterogeneous system
- 2 It confirmed that different system with same degree of freedom, behave similarly
- 3 It predicts behaviour of system towards change in T,P, Composition
- 4. Applicable to physical/chemical phase equilibria
- 5. Neglect nature of reactant and product
- 6. It predicts number of phases remains or not remaining in equilibrium after phase reaction

Disadvantages/Demerits Phase rule

- 1. Not applicable for system attain equilibrium slowly
- 2 Do not consider effect of electric charges, Magnetic forces, surface tension, gravitational forces
- 3. applicable to single equilibrium state at a time and not for other possible equilibriums
- 4. Phase in equilibrium must at same T,P and they should contain same chemical potential of component
- 5. two phase should not finely divided state.