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The Phase Rule

System – Part of the universe which is under consideration.

A system is a mass of material solid, liquid or gaseous or a combination of these three states. It consist of one or more constituents each of which is definite, distinct and homogenous substance.

A system may be homogenous or heterogenous

Homogenous. A system which is uniform throughout in physical and chemical properties is called homogenous system. eg – soln of NaCl in water.

Heterogenous : A system which consist of parts which have different physical or chemical properties is called heterogenous system.
eg – ice, water, vapour.

Phase – A phase is defined as a homogenous physically distinct and mechanically seperable portion of a system, which is seperated from other part of system by definate boundaries.

Mechanically seperable in the defination means that each phase can be seperated from every other phase by such operation as filteration, sedimentation, decantation or any other mechanical means of seperation as handpicking of crystals.

Does not include such seperation Method as evapouration, distillation, adsorption or extraction eg – Gas mixture – one phase
liquid – single phase – miscible
solid – invariably seperate phase

eg $CaCO_3(s) \rightleftharpoons \underset{(s)}{CaO} + CO_2(g)$

This is a three phase system.

Component – The smallest Number of independent variable constituent taking part in a state of equilibrium, by means of which the composition of each phase can be expressed in the form of chemical equation.

(1) eg Water system

$\underset{(s)}{Ice} \rightleftharpoons \underset{(l)}{water} \rightleftharpoons \underset{(g)}{Vapour}$

Phase
(1) Ice $= H_2O$
(2) Water $= H_2O$
(3) Vapour $= H_2O$

Chemical composition H_2O
∴ Num of component of the system is one.

(2) In the dissociation of calcium carbonate by heat, there are three different molecular species

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

Phase
$CaCO_3(s) = CaO + CO_2$
$CaO(s) = CaCO_3 - CO_2$
$CO_2(g) = CaCO_3 - CaO$

It is a two component system since each phase is represented by atleast any two of the independent variable constituents.

Degree of freedom — is meant by the minimum number of independently variable factors such as temp, pressure and composition of the phases which must be arbitrarily specified in order to represent prefectly the condition of system.

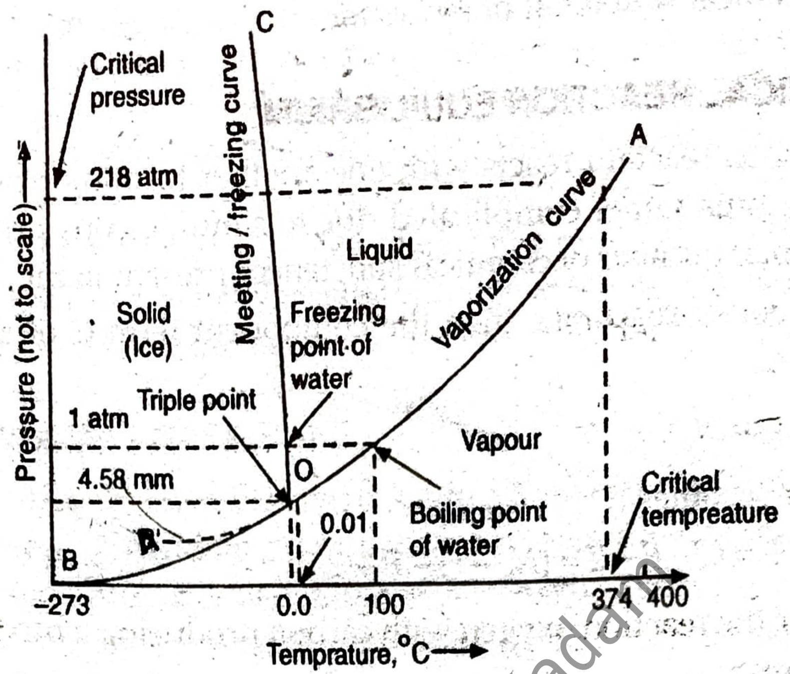
1. eg Ice ⇌ Water ⇌ Vapour
No need to specify any condition as this three phases will exist at only one particular temp and pressure. The system is invalent

2. Water ⇌ Vapour
either temp or pressure need to be specified.
The system is univarient.

3. Water or Vapour or ice (only)
Both temp and pressure need to be specified
The system is bivalent.

Phase Rule : Provided the equilibrium between any num of phase is not influenced by gravity, electrical or magnetic forces or by surface action and only by temperature, pressure and concentration then the number of degree of freedom (F) of the system is related to the Number of component (C) and of phases (P) by Phase Rule equation, $F = C - P + 2$. For any system at equilibrium at a definite temperature and pressure

WATER SYSTEM



The water system consist of three phases ice, water and water vapour

Ice (s) $\rightleftharpoons$ Water (l) $\rightleftharpoons$ water vapour (g)

Since H_2O is the only chemical compound involved therefore it is single or one component system.

From the phase Rule, when $C = 1$

$$F = C - P + 2$$

$$F = 1 - P + 2$$

$$= 3 - P$$

The degree of freedom depends on the Number of phases present at equilibrium.

Three different cases are present

1. $P = 1$ $F = 2$
2. $P = 2$ $F = 1$
3. $P = 3$ $F = 0$

For any one component system, the maximum number of degree of freedom is two. Hence the system is represented by two dimensional diagram.

(1) Area - AOB, AOC and BOC represent a single phase. on applying the phase Rule

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

The system is bivarient, In order to locate any point in these areas, temperature and pressure need to be specified.

(2). Curve - OA, OB and OC

OA - Vapourisation curve (water ⇌ Vapour)
OB - Sublimation curve (ice$_{(s)}$ ⇌ vapour)
OC - Melting / freezing curve (ice$_{(s)}$ ⇌ water)

On applying the phase Rule

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

The system is univarient. In order to locate any point on these curve (lines), temperature or pressure need to be specified.

curve OA has a natural upper limit at 374°c which is the critical point (critical temp)

curve OB - natural limit -273°c

curve OC - natural limit 218 atm (critical pressure)

The slope of OC is toward the pressure axis shows the melting pt of ice is decreased by increase in pressure.

(3) Point 'O' (also called Triple point)
At point 'O' $\underset{(s)}{\text{Ice}} \rightleftharpoons \underset{(l)}{\text{Water}} \rightleftharpoons \underset{(g)}{\text{Vapour}}$

On applying phase Rule

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

The system is invarient or zerovarient. In order to locate this point, Nothing has to be specified because this will occur at one particular temperature and pressure i.e 4.58 mm pressure 0.0098 or 0.01°c or 273.16°K temperature.

Curve OA' _ Metastable curve
(As water does not always freeze at 0°c, so if the vessel containing water and vapour is perfectly clean and free from dust, it is possible to supercool water several degrees below its freezing pt 'O')

Phase Rule for two component system

In a two component system, when P=1 degree of freedom (F) has the highest value

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

Since the maximum number of degree of freedom is three for a two component system.

So the phase behaviour for a two component system may be represented by three dimensional diagram which is not possible on the paper.

A solid liquid equilibrium of an alloy has practically no gas phase and the effect of pressure is negligible. Therefore the experiment are conducted at 1atm i.e. constant pressure, since in this system vapour phase is not considered ∴ it becomes a condense system

$$F = C - P + 1$$

This is known as the reduced (or condense) phase rule, having two variable, namely temperature and concentration (composition) of the constituents. Therefore solid-liquid equilibrium are represented on temperature - composition diagrams.

Some terms required to understand a two component alloy system.

Eutectic system. A binary system consisting of two substance which are miscible in all proportion in a liquid state, but which do not react chemically is known as the eutectic system

Eutectic mixture is a solid solution of two or more substance having the lowest freezing point of all the possible mixture of the components.

Eutectic point: Two or more solid substances capable of forming solid solution with each other having the property of lowering each others freezing pt and the minimum freezing pt attainable corresponding to the eutectic mixture is termed the eutectic point.

Thermal Analysis

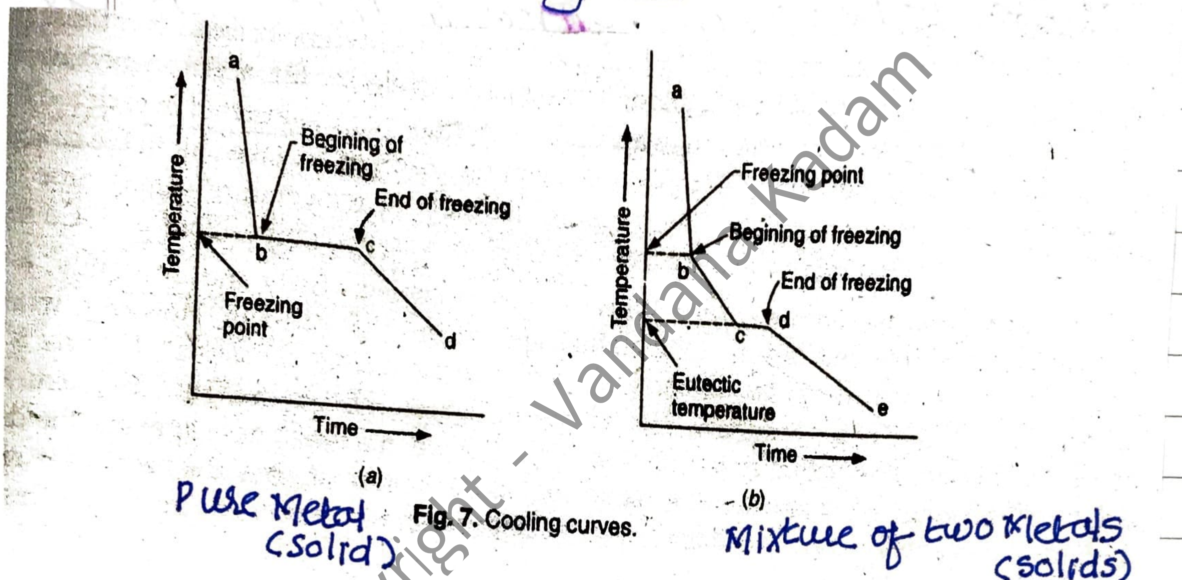


Fig. 7. Cooling curves.

If a mixture of two solids in the liquid state is cooled slowly we obtain a cooling curve. ~~We obtain a cooling curve~~ so long as the mixture is in a liquid state. when the solid phase emerges the rate of cooling abruptly changes the cooling curve exhibits a break. However, the temp does not remain constant, as in the previous case of cooling of a pure substance (Fig a). The temperature decreases continuosly, but at different rate and if the mixture form a eutectic the fall of temperature continues till the eutectic point is reached. The temp remains constant, util solidification is complete. Then again it fall at different rate.

LEAD AND SILVER SYSTEM

THE PHASE RULE

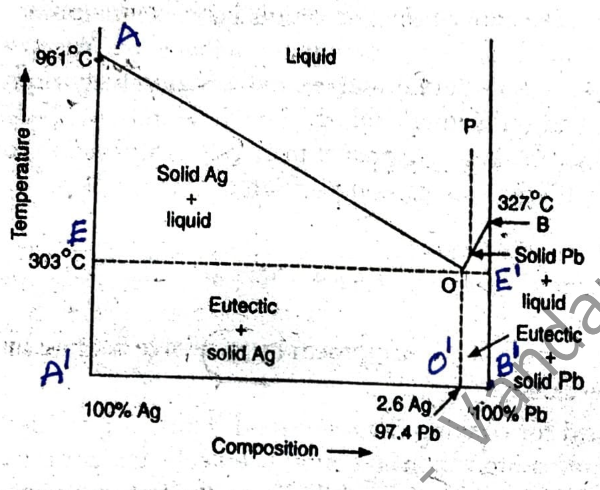


Fig. 10. T-C diagram of Pb-Ag sy

Simple Eutectic formation: Lead-silver system is two component system with four possible phases- ~~Solid~~ solid-Ag, solid Pb, solution Ag+Pb and vapour. (since the pressure has nearly no effect on equilibrium so that system can be conveniently represented by a temp-concn diagram at atomospheric pressure) As the gaseous phase is practically absent and one variable pressure is neglected the condensed phase Rule. $F = C - P + 1$ will be applicable.

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

In the diagram Point A represents the Melting point of pure Ag (961°C) and point B that is pure Pb (327°C)

Region AOB – Any component and temperature in this region forms a single homogenous stable liquid phase. Consisting of liquid alloy or melt of Ag and Pb. (Num phase = 1)

$F = C - P + 1$
$= 2 - 1 + 1$
$F = 2$ System is bivalient

Curve AO. Represents the melting point curve or freezing point curve of silver and shows the effect of addition of lead on the M.Pt of silver. The M.Pt decreases till it reaches Pt 'O'. Solid Ag and liquid (melt) co-exist along AO

Curve BO Repesents the M.Pt curve or freezing pt curve of lead and shows the effect of addition of silver on the M.Pt of lead. The m.pt decreases till it reaches point 'O'. Solid Pb and liquid (melt) co-exist along BO.

Number Phases = 2
$F = C - P + 1$
$= 2 - 2 + 1$
$F = 1$ system is univarient

Point O (eutectic point): The two curves AO and BO meet at point O, where three phases solid Ag, solid Pb and their solution (melt) co-exist. (Num phases = 3)

$F = C - P + 1$
$= 2 - 3 + 1$
$F = 0$ System is invarient

The point O (303 °C) represents a fixed

composition Ag = 2.6% , Pb = 97.4% and is called eutectic composition. No mixture of lead and silver has a melting point lower than the eutectic temperature.

Region AOE = solid crystalline Ag + liquid alloy
Region BOE' = solid crystalline Pb + liquid alloy
Region EOO'A' = Ag crystals + solid eutectic
Region EOO'B' = Pb crystals + solid eutectic

Limitation and Application of phase Rule

Application

1. It applies to physical as well as chemical phase reactions
2. We can classify equilibrium state of systems with the help of phases, components and degree of freedom.
3. Since it is applicable to macroscopic system information regarding molecular structure is not required
4. Phase rule does take into consideration the amount of substance present
5. Different system under same degree of freedom behave in a similar way. It helps in predicting behaviour of a system under different sets of conditions of the governing variables.
6. It helps in deciding whether under given set of conditions

a) Various substance would exist together in $\rightleftharpoons^m$

or b) some substance may be interconverted

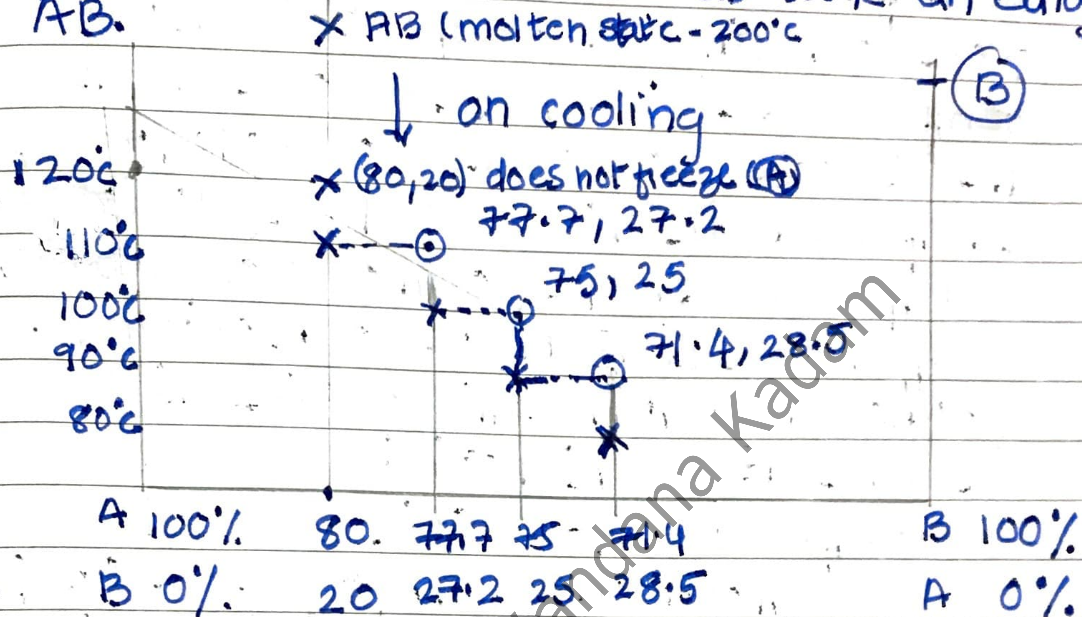
or c) Some substance may be eliminated.

Limitation of phase Rule.

1. Applied only to system which are in equilibrium. (Not applicable to slow equilibrium system)
2. All the phases of system must be present under the same conditions of temperature, pressure and gravitional force
3. Applies only to a single equilibrium state
4. It considers only num of phases and not quantities.
5. The solid and liquid should not be finely sub divided as to bring about deviation from their normal values of vapour pressure.

Numericals on Phase Rule.

In order to solve the Numericals certain facts about the two component system need to be known. Let us take an alloy say AB.



Amount - 80gm A 20% B

Alloy composition taken - 80% A and 20% B

The Alloy AB is heated to the temp of 200°c. So now it is above the freezing temp of both the constituent of Alloy, hence exist in the liquid state (melt). Now ~~coo~~ on cooling it reaches the temperature of 120°c. At this temperature (A) should freeze, but this does not happen. when it reaches a temperature of 110°c (A) starts freezing i.e solidification of (A) starts. suppose 10 gm of (A) has solidified, the amount (A) decreases i.e Now it becomes 70 gm. (This happen's because A in this case is acting like a solvent and B is acting like solute hence there depression in freezing point due to presence of impurity.) The amount of B

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remains the same. The percentage composition of A is 77.7% and B is 22.2%. The percent composition of B increases, solute ~~impu~~ impurity further increases causing a depression in freezing point, this goes on till we keep decreasing the temperature further. At one temperature i.e at 80°c B starts to solidify that temperature is called as Eutectic temperature, the composition at that temperature is Eutectic composition. The point at which this occurs is called as the Eutectic point.

temperature - 80°c
composition 71.4% (A) : 28.5% (B)

* (solute's mass does not change till Eutectic
* solute goes into the eutectic at Eutectic composition ∴ we get Eutectic + solvent mass)

Numericals

(1) An alloy of tin and lead contains 73% Sn. Find the mass of eutectic in 1kg of solid alloy, if the eutectic contains 64% Sn

%Alloy	%Sn	% Pb
100%	73%	27%
1000gm	730gm	270gm.

At Eutectic

100%	64%	36%
	?	270gm

Since the mass of Pb which is the solute in this case remains constant at Eutectic i.e 270gm. Hence the mass of Sn

Mass of Pb - 270gm
∴ Mass of Sn = ?

$$\frac{\text{Mass Sn}}{64} = \frac{\text{Mass Pb}}{36}$$

$$\text{Mass Sn} = \frac{270 \times 64}{36}$$

$$= 480 \text{ gm.}$$

Eutectic - Mass Sn + Mass of Pb
480 + 270
= 750 gm.

2. 1000kg of sample of argentiferrous lead containing 0.1% silver is melted and then allowed to cool. If the eutectic contains 2.6% silver. What mass of (i) eutectic will be formed (ii) lead will seperate out?

Alloy	Ag	Pb
100%	0.1%	99.99%
1000kg	1kg	999 kg

Silver is the solute, hence its mass remains the same at Eutectic.

Eutectic	Ag	Pb
100%	2.6%	97.4%
y kg	1 kg	x kg

100% Eutectic contains 2.6% Ag

y kg of eutectic contain 1 kg Ag

$$\therefore y = \frac{1 \times 100}{2.6} = 38.46 \text{ kg}.$$

Mass of eutectic formed is 38.46 kg

(since the mass of silver does not change ie 1 kg this goes in the eutectic — ie the solute mass goes into the eutectic) so what remains is the mass of solvent)

$\therefore$ Mass of Pb seperated = Total − Mass Eutectic

$= 1000 \text{ kg} - 38.46 \text{ kg}$

$= 961.54 \text{ kg}$

Other Method

At Eutectic

$$\frac{\text{Mass of Ag}}{\text{\% of Ag}} = \frac{\text{Mass of Pb}}{\text{\% of lead}}$$

$$\frac{1}{2.6} = \frac{x}{97.4}$$

$x = 37.46$ kg Pb at Eutectic

∴ Mass of Pb seperated out

Original Mass of Pb - Mass at Eutectic Pb
999 kg - 37.46 kg
= 961.54 kg

(3) An alloy AB of 10gm weight contained A at 25%. The molten AB on cooling gave out B and an eutectic alloy with A and B at equal percentage. what is the amount of B that is formed.

Alloy(AB)	A	B.
100%	25%	75%
10 gm	2.5gm	7.5gm.

(since here A is the solute whose mass remains same ~~up~~ up to Eutectic)

Eutectic	A	B
100%	50%	50%
	2.5gm	x gm.

$$\frac{\text{Mass of A}}{\text{\% of A}} = \frac{\text{Mass of B}}{\text{\% of B}}$$

$$\frac{2.5}{50} = \frac{x}{50}$$

$$\therefore x = 2.5 \text{ gm.}$$

Amount of B formed

original mass of B - Mass of B at eutectic
7.5 - 2.5 = 5 gm.

Assignment 7

1. An alloy AB in 20 gm weight contains A at 20%. The molten AB on cooling gave out B and an eutectic alloy with A and B at equal percentage. What is the amount of B that is formed

Alloy	A	B
100%	20%	80%
20 gm	4 gm	16 gm

(Mass of A does not change at Eutectic)

Eutectic	A	B
100%	50%	50%
	4 gm	x gm

$$\therefore \frac{\text{Mass A}}{\text{\% of A}} = \frac{\text{Mass B}}{\text{\% of B}}$$

$$\frac{4}{50} = \frac{x}{50} \quad \therefore x = 4\,gm$$

$\therefore$ Amount of B formed (seperated out)

Original amount of B − Amt of B at Eutectic

16 gm − 4 gm = 12 gm of B.

2. An alloy of cd and Bi contains 25% of cd. find the mass of eutectic in 1kg of alloy, if the eutectic system contains 40% cd.

Alloy	cd	Bi
100%	25%	75%
1000 gm	250 gm.	750 gm

(Mass of cd - remains same)

Eutectic	cd	Bi
100%	40%	60%
x gm.	250 gm.	

$$\frac{\text{Mass of Eutectic}}{\text{\% of Eutectic}} = \frac{\text{Mass of cd}}{\text{\% of cd at Eutectic}}$$

$$\frac{x}{100} = \frac{250}{40}$$

$$x = 625 \text{ gm}$$

625gm is mass of Eutectic.