Phase Rule:–Terminology, One component system (H_2O system and CO_2 – system), two components system, Simple eutectic system (Pb–Ag), system with congruent melting point (Zn – Mg), system with incongruent melting point (Na_2SO_4 – H_2O),Cooling curves.

PHASE RULE

Given by Willard Gibb's in 1876

It deals with the behaviour of the heterogenous system and it tells us about qualitative prediction of effect of changing pressure temperature and concentration on heterogenous system in equilibrium

It states that

$F = C - P + 2$

Where F is degree of freedom
C is No. of components and
P Is No. of Phases

Conditions necessary

1. System should not be affected by external electrical or magnetic fields
2. System must be in equilibrium
3. System may or may not be heterogenous

Phase:

Any homogenous or uniform part of the system having all physical and chemical properties same through out

Examples

$H_2O(l)$: P=1

$H_2O(l) \longleftrightarrow H_2O(g)$ P=2

Mixture of gases

e.g. $H_2(g) + N_2(g)$ P=1

Two or more completely miscible liquids P=1

Two immiscible liquids P=2

Mixture of allotropes

e.g. $S_R \longleftrightarrow S_M \longleftrightarrow S(v)$ P=3

$CaCO_3(s) \longleftrightarrow CaO(s) + CO_2(g)$ P=3

Components:

The least No. of independent chemical constituents in terms of which every phase is expressed by means of a chemical equation

When all the phases of system can be expressed in terms of one chemical individual it is designated as one component system

e.g. $H_2O(s) \leftrightarrow H_2O(l) \leftrightarrow H_2O(v)$

Mixture of gases $O_2 + N_2$

Phases — Chemical constituents

One (gaseous phase) — O_2 and N_2 So C=2

NaCl sol^n (*aq*)

Phases — Chemical constituents

One (Solution Phase) — NaCl and H_2O So C=2

Mixture of allotropes

$S_R \longleftrightarrow S_M \longleftrightarrow S(v)$

Phases — Chemical constituents

3 — S So C=1

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

Phases — Chemical constituents

3 — 2

$NH_4Cl(s) \longleftrightarrow NH_4Cl(g) \longleftrightarrow NH_3(g)$ and $HCl(g)$

C=1

Degree of freedom

It is the least no. of variable factors which must be specified so that remaining variables (c, T and P) are fixed automatically and the system is completely defined

A system with F=0 Non-variant or invariant system

F=1	Univariant
F=2	Bivariant
F>2	Multivariant

e.g.

For Pure gas F=2

Mixtures of two gases F=3

Water(*l*) $\longleftrightarrow$ Water(*v*) F=1

$CaCO_3(s) \longleftrightarrow CaO(s) + CO_2(g)$ F=1

True equilibrium:

- Is said to exist in a system under a given set of conditions when the same state can be realised from either direction by following any procedure.
- Ice(s)
- Water(l).
- At a pressure of 1atm.,the temp. of the system will be 0^oC irrespective of the fact whether the eqbm. Is attained by partial melting of ice or by freezing of water.

Meta stable equilibrium

- It is possible to cool water slowly and carefully to a temp. of -1^{o}C without appearance of ice. Thus water is not in stable eqbm. With ice. It is said to be in **metastable equilibrium.**

Find out the values of P, C, F for the following systems

N_2O_4 (*g*) ⟷ $2NO_2$ (*g*)

NH_4Cl (*s*) ⟷ NH_4Cl(*g*) ⟷ NH_3(*g*) and HCl(*g*) when *P*(NH_3) = *P*(HCl)

H_2O (*s*) ⟷ H_2O(*l*)

NH_4Cl (*s*) ⟷ NH_4Cl(*g*) ⟷ NH_3(*g*) and HCl(*g*) when *P*(NH_3) # *P*(HCl)

Ag-Pb Soln (*l*) ⟷ Pb(*s*) ⟷ Ag(*s*)

An emulsion of Oil in water at 2atm and 70° C

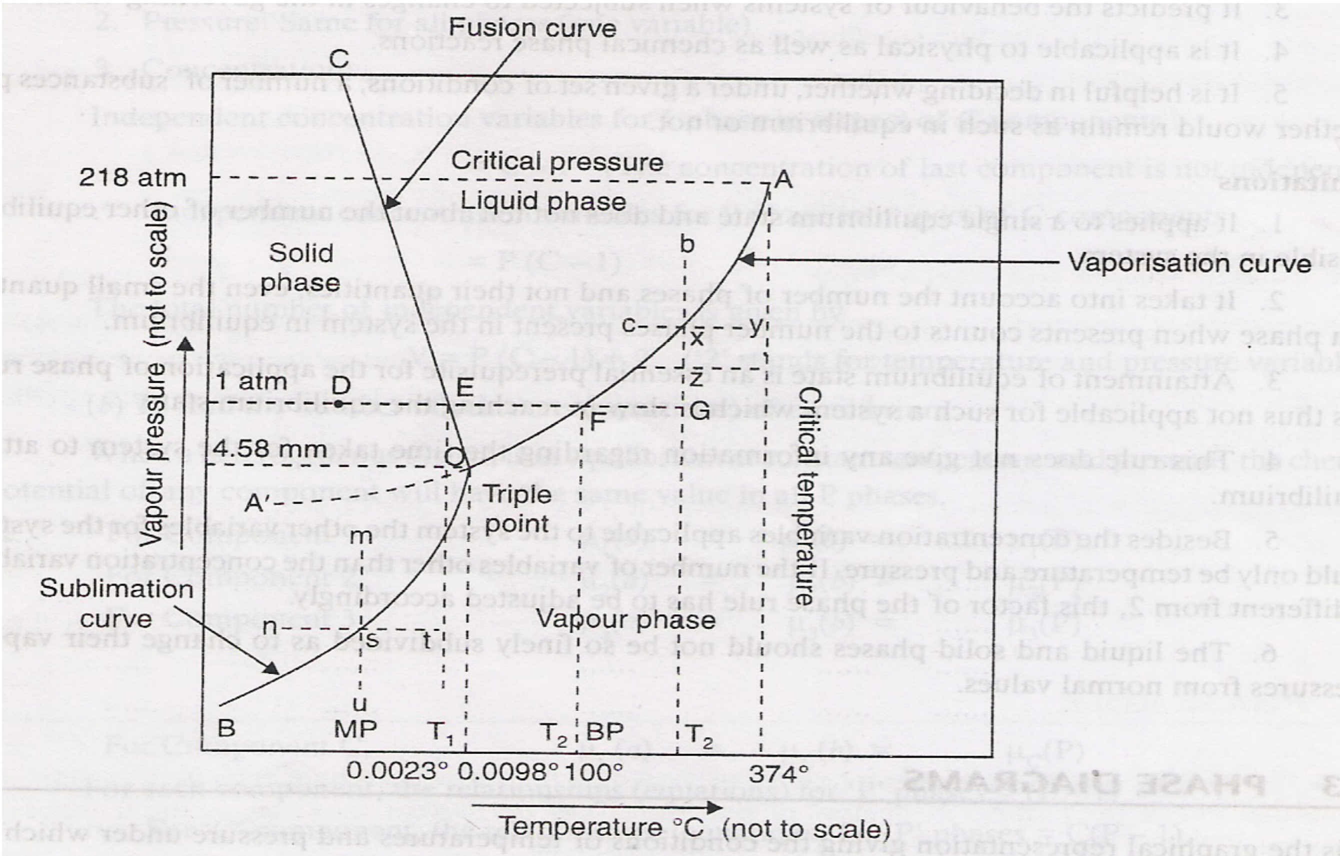
Water system at 4.578 mm of Hg and at 0.0098° C

PCl_5 (*g*) ⟷ PCl_3 (*g*) + Cl_2(*g*) *P*(PCl_3) # *P*(Cl_2)

$2KClO_3$(*s*) ⟷ 2KCl (s) + $3O_2$ (*g*)

Phase Diagram

H_2O



One Component System

- This system consists of three curves OA,OB and OC, three areas AOC, BOC and AOB, a triple point O and only one metastable curve OA'
- *Curve OA :* It represents following equilibrium

$$liquid \leftrightarrow vapour$$

Curve start from O and extends up to critical temperature (374^0 C) at critical pressure (218)

Here P= 2 and C= 1

Applying Phase Rule

$$F = C - P + 2$$

$$= 1 - 2 + 2 = 1$$

Hence the system is univariant

- ***Curve OB:***

It represents the following equilibrium

Solid ↔ Vapour

- Curve starts from O (FP) and extends up to absolute zero.

  Here $P = 2, \; C = 1$

  Therefore,

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

Since the degree of freedom is one, hence the system is univariant.

- *Curve OC:* It represents solid liquid equilibrium

Solid ↔ Liquid

Here P= 2, C= 1

Therefore, F= C– P+ 2= 1

Hence the system is univariant.

- *Curve OA':* It represents the liquid water–water vapour in metastable equilibrium.

POINTS

- *Triple point O:* It is the point at which all the three phases, ice, water and vapor coexist in equilibrium. The three curves OA, OB and OC intersect each other at point 'O'. This is called triple point.
- Here $P = 3, \quad C = 1$

$$F = C - P + 2$$

$= 1 - 3 + 2$

$= 0$

since the degree of freedom is zero, hence the system is invariant.

AREAS,between the lines:

(i) Area AOC: The area abov the curve OA i.e., consists of liquid phase only.

$P = 1, \; C = 1$

$F = C - P + 2$

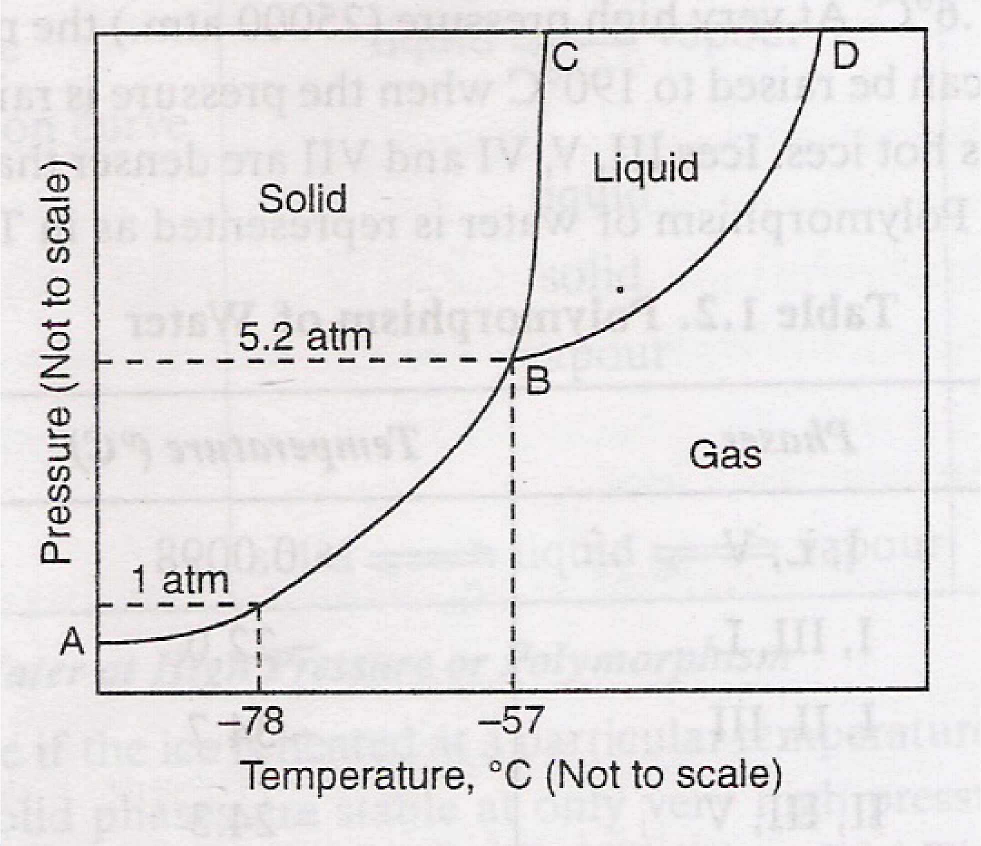
$= 1 - 1 + 2 = 2$

- (ii) Area AOB: This area represents only vapor phase. Hence the degree of freedom is two i.e., the system is bivariant.

  (iii)Area BOC: It represents only solid phase. Degree of freedom is two, so it is also a bivariant system.

Phase Diagram

CO_2



Assignment

- Define phase rule and its limitations.
- Explain application of phase rule to one–component system
- Compare water system with carbon di– oxide system.

Eutectic system (easy to melt)

A binary system in which two components are miscible in all proportions in the liquid state. They do not react chemically and each component has property of lowering others freezing point. Such system is called a system with eutectic point

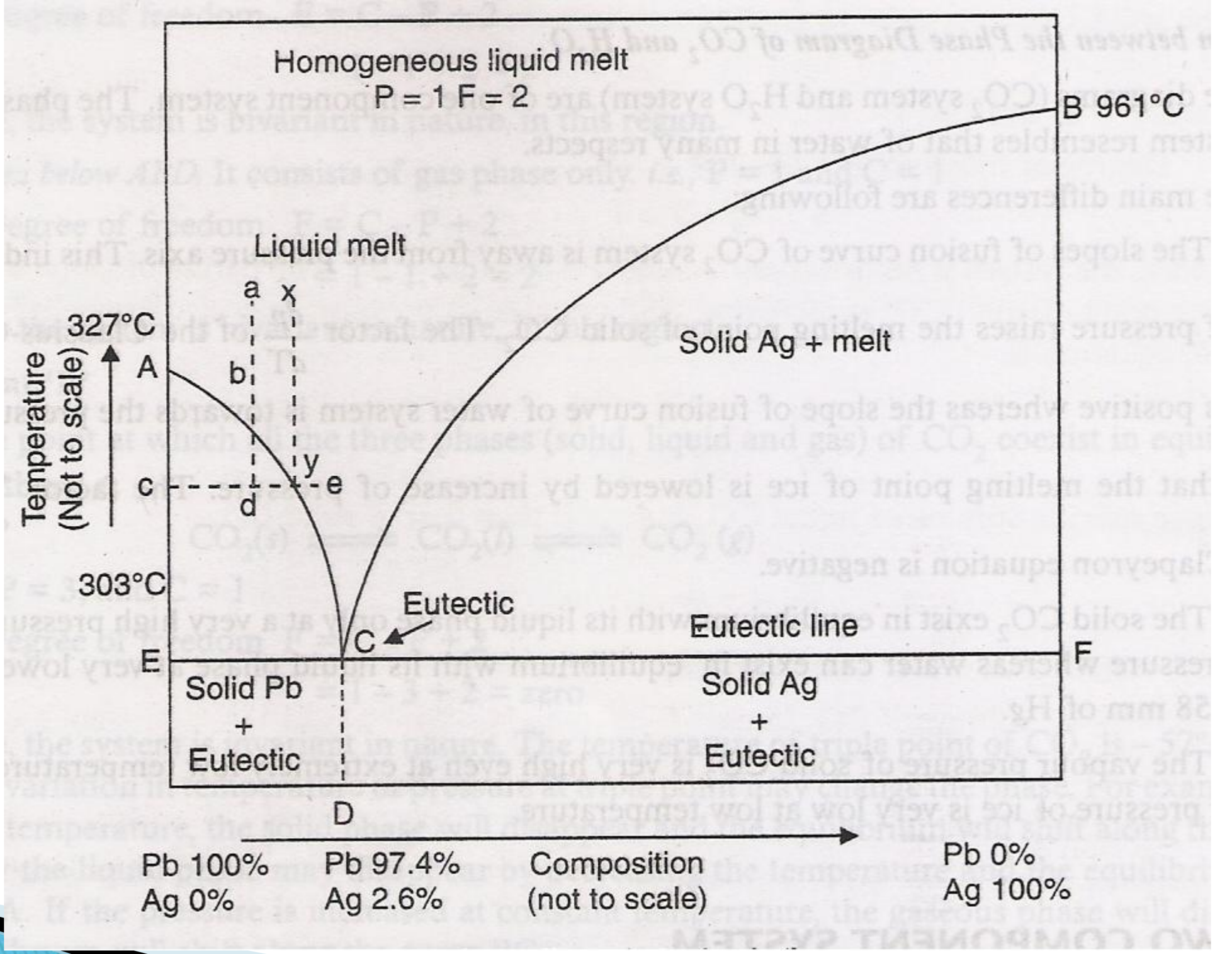
e.g. Ag-Pb system

Although Eutectic mixture has definite M. P But not regarded as compound because

1. Components are not in stoichiometric proportion
2. Separate crystals of components were seen under electronic microscope
3. Physical properties of individual components persists even in the mixture

Two component eutectic system

Pb – Ag System



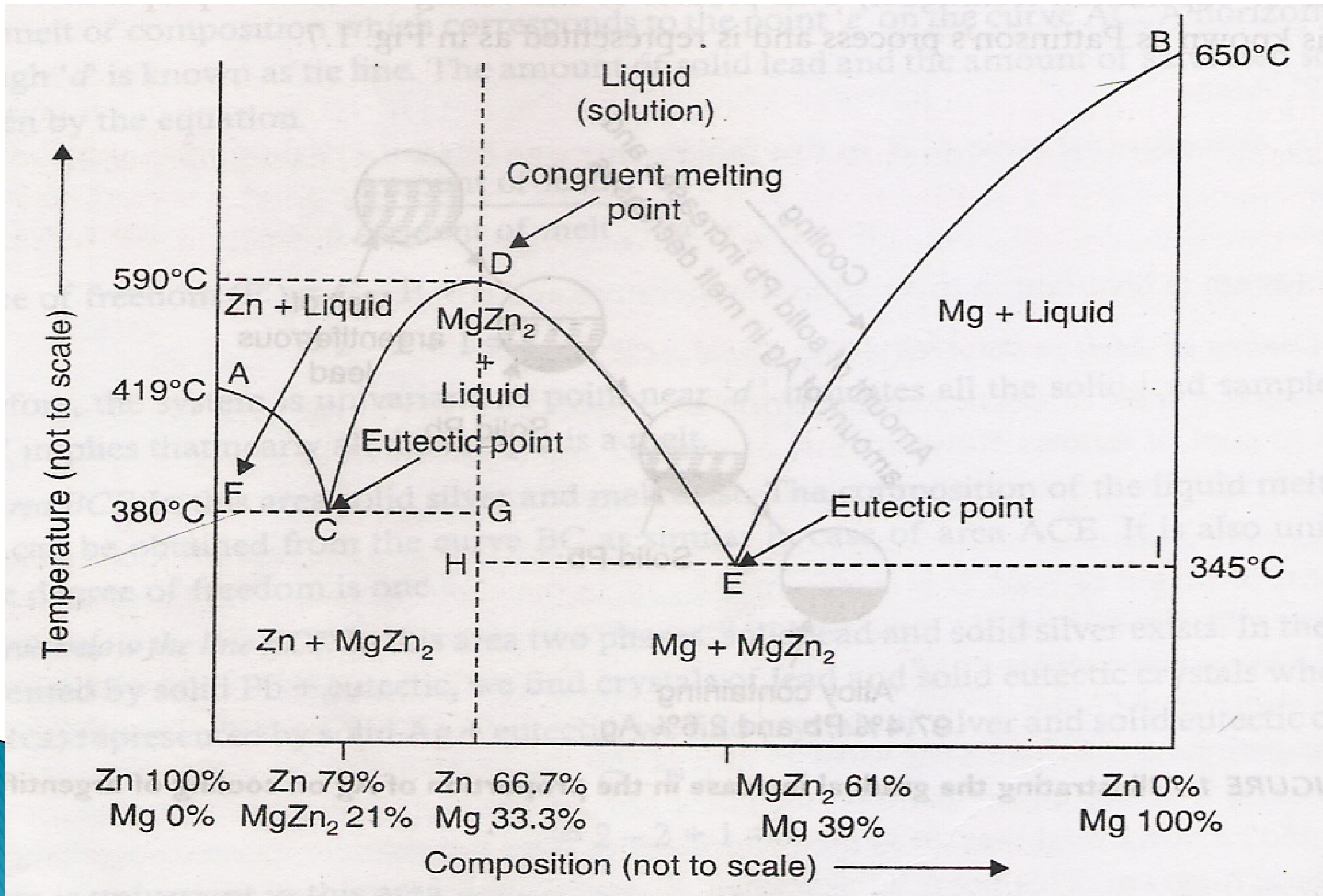
Congruent M. P

A binary system is said to possess congruent M. P. when its components at a certain state form a compound which melt at a sharp temperature to give liquid of the same composition as that of the solid and the temperature at which this compound melt is called Congruent M.P.

e.g.
Zn-Mg system form a compound $MgZn_2$ having congruent M.P i.e 575^{o} C

Two component congruent m.p. system

Zn – Mg System



Assignment

- Define simple eutectic system and name such a system.
- Apply phase rule to a two-component system.
- Define the term congruent melting point. Explain Zn- Mg system with well labelled phase diagram.

Incongruent M.P.

It is a temperature below M.P. at which compound starts decomposing to give a new solid phase and a solution with different composition from that of the solid phase

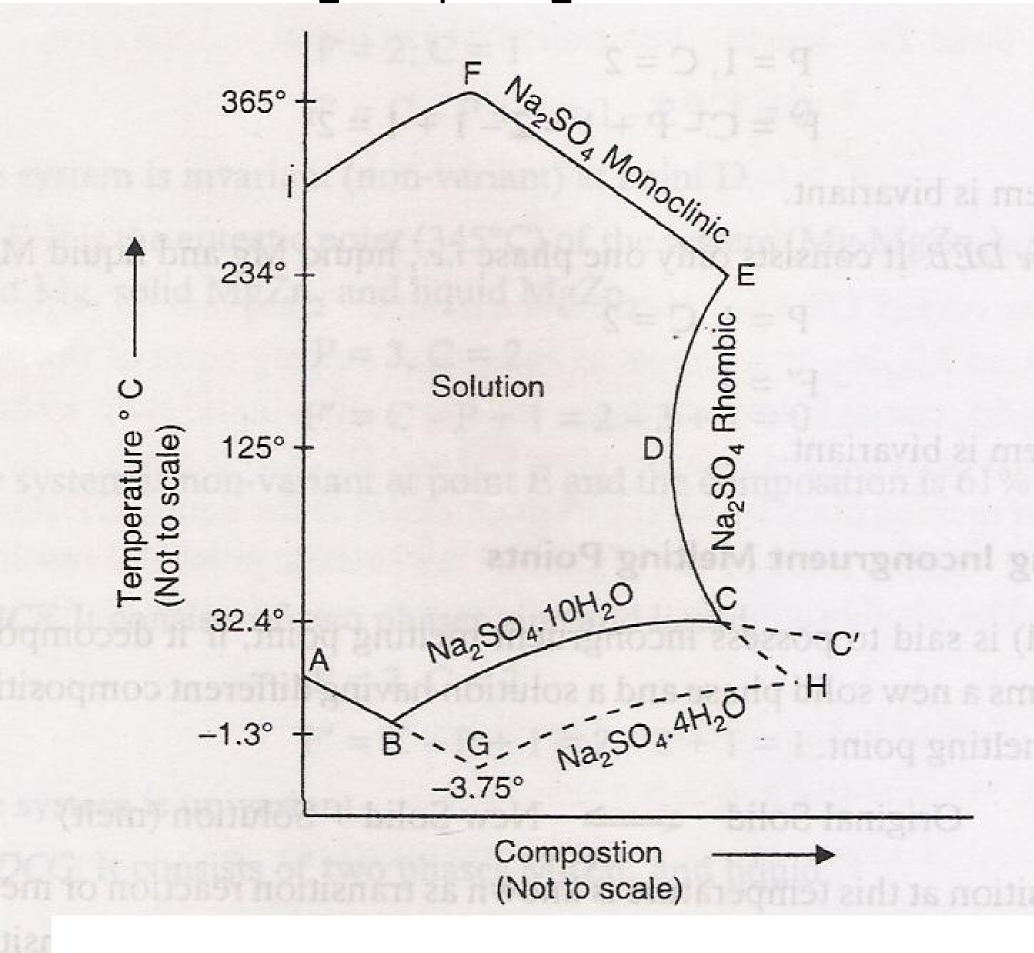
Compound(s) $\xrightleftharpoons{\text{temp} < \text{Incongruent M.P.}}$ New solid phase + Solution (diff. composition)

e.g.

1. Na–K system
2. Au–Sb system
3. KCl–$CuCl_2$ system
4. Picric acid –Benzene system

Phase Diagram

Na_2SO_4 - H_2O



Sodium Sulphate- Water System

- Sodium sulphate forms following phases:
- 1. decahydrate
- 2. heptahydrate
- 3. anhydrous sodium sulphate rhombic
- 4. monoclinic form
- 5. ice
- 6. Liquid phase
- 7. Vapour phase

- The vapour phase can be ignored.
- The Sodium-Sulphate Water system is a six phase condensed system.
- The system consists of four curves and three points.

1. **The curve RS** (*The melting point curve of ice*)

R is the melting point of ice, curve RS shows the lowering of melting point of ice on the addition of anhydrous sodium-sulphate.

- Applying the reduced phase rule

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

Thus the system is univariant.

2. **The curve ST**(*The solubility curve of sodium sulphate decahydrate)* : Along this curve, saturated solution of sodium sulphate and sodium sulphate decahydrate are in equilibrium. Curve ST shows the solubility of sodium sulphate decahydrate increases with temp. until the point T is reached.

. Applying the reduced Phase Rule

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

Thus the system is univariant along the curve ST

3.The curve TV (*The solubility curve of rhombic sodium sulphate*):

If heating is continued at point T, all the sodium sulphate decahydrate will disappear and only two phases i.e., anhydrous sodium sulphate and solution will be left. Applying the reduced phase rule:

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

1.The point S (*Eutectic point*) :

- At this point S, three phases (ice, sodium sulphate deca hydrate and solution) coexist in equilibrium. Applying reduced phase rule :

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

- Thus the system is nonvariant at this point.

2. The point T (*The Transition point*):

At point T, the sodium sulphate decahydrate decomposes into the anhydrous rhombic sodium sulphate. So the temp. corresponding to this point "T" represents the transition temperature (32.4). This temp. may also be regarded as the incongruent melting point of sodium sulphate decahydrate.

- .Applying the reduced phase rule

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

- Thus the system is invariant.

3. The point V (*The transition point*):

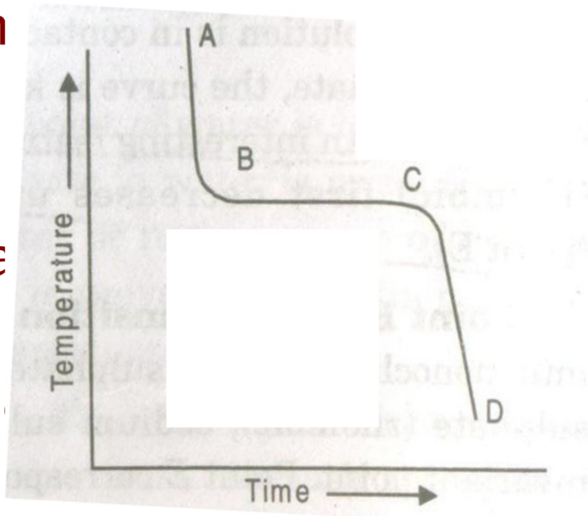
At this point , the anhydrous sodium sulphate exist in rhombic, monoclinic and solution form. So applying the reduced phase rule.

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

- Thus point “V” is also invariant point.

Cooling curves

- Cooling curve of a substance is defined as a graph obtained by plotting of time of cooling against temperature.
- For a pure substance
- At point A-Whole mass is in liquid form
- Along curve AB-Rate of cooling is rapid
- At B-liquid begins to solidify.
- From BtoC-Due to phase transition ,hea
- librated and temp.remains constant.
- At C-liquid is completely converted int
- solid.



Phenomena of super cooling

In case of careful cooling the solid phase may not appear at its freezing point but may be cooled below it, without the separation of solid phase .Such a process is called super cooling and liquid is known as supercooled liquid.When the separation of solid starts from the supercooled liquid,there is slight rise in temp.upto B,instead of fall.Therefore cooling continue as such along the freezing pt. Curve.

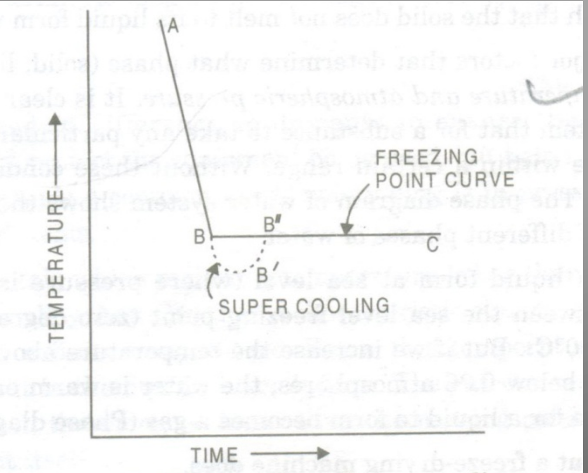


Fig. 1.12. Phenomenon of supercooling.

Cooling curve of two component system forming a eutectic

With the passage of time the temp. of the system Falls along AB. the cooling is quite rapid along curve AB since The separation of solid has not started so far.
At B-one of the solid has started solidifying. And as heat is liberated
So temp.falls more slowly along BC.
Here at B temp. does not remain constant as composition of the mixture is changing continuously whereby the temperature of solidification is correspondingly changed.