ENGINEERING CHEMISTRY

Department of Science and Humanities

Class content:

- ***Reduced phase rule for a 2-component system***
- ***Phase diagram of a 2-component system***
  - ***Phase diagram of Pb-Ag system***
- ***Determination of solid-liquid equilibria***
- ***Pattinson's process***

PES UNIVERSITY

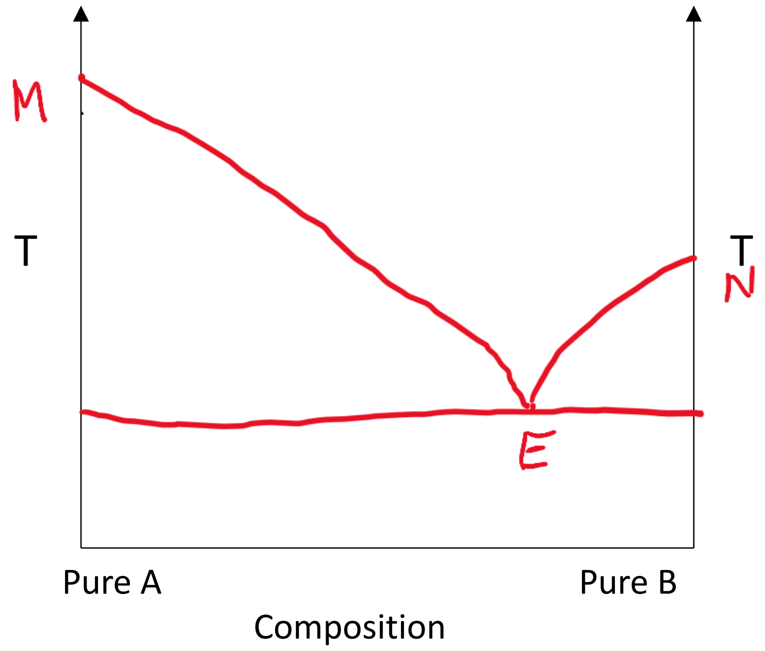
Phase diagram of a two component system

- The phase rule equation is **$F = C - P + 2$**
- For a 2 component system the ordinary phase rule cannot be used
- For a two component system, $C = 2$ then $F = 2 - P + 2 = 4 - P$
- The minimum number of phase is 1; $F = 4 - 1 = 3$
- This requires **3 dimensional space** which cannot be explained on the plane of paper
- **One of the three variables is kept constant**
- Measurements in these systems are generally carried out **at atmospheric pressure**
- Pressure may be considered constant ; degrees of freedom is reduced by 1,
- **$F = C - P + 2 - 1$**

- **The phase rule takes the form F = C – P + 1 and is known as the reduced phase rule**
- 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**
- **F = C – P + 1 is also known as condensed phase rule**

Phase diagram of a 2-component system

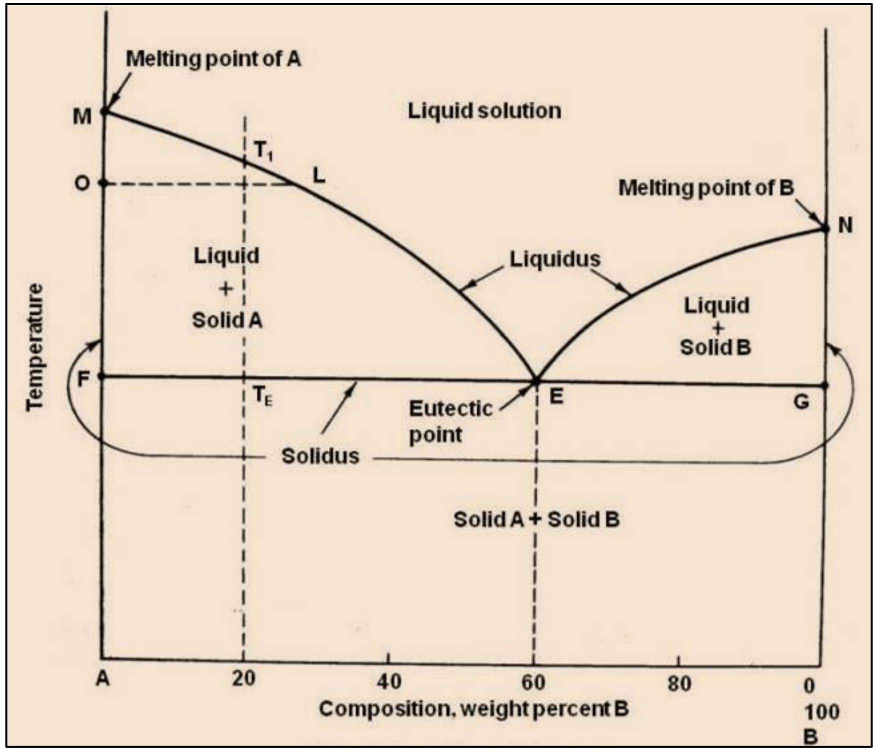
- Phase rule for a 2- component system : **F = C-P+1**
- **Pressure is constant**
- Plot is between **Temperature and Composition**
- A and B are miscible in all proportions in the liquid (molten) state
- In solid state they are completely immiscible



ENGINEERING CHEMISTRY

Module 2- Phase equilibria

Simple eutectic system



Source:https://in.pinterest.com/pin/818107088531422918/

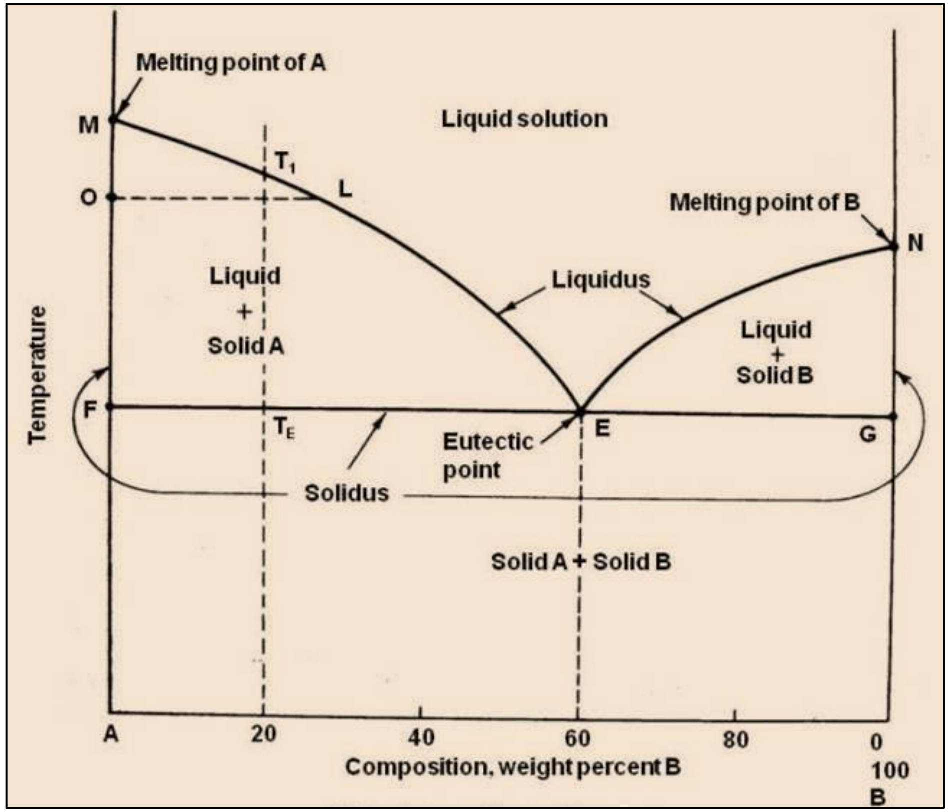
When a mixture of the 2 components is heated till the mixture melts and then cooled:

- First crystal of A if formed when **f.pt. of A in the mixture** is reached
- On further cooling more solid A precipitates and **liquid melt becomes richer in B**
- With decrease in temperature more and more solid A separates and the liquid melt moves along curve ME
- Finally when temperature reaches F, **solid B also starts precipitating**
- Three phases are present at E: **solid A, solid B and the liquid melt**
- Further cooling will just result in cooling of solid A & B

ENGINEERING CHEMISTRY

Module 2- Phase equilibria

Simple eutectic : Pb-Ag system



A-B system

- A : 100% A
- B : 100% B

- Area above MEN: Liquid melt
- Area MEF : Solid A + Liquid melt
- Area NEG : Solid B + Liquid melt
- Below FEG : Solid A + Solid B

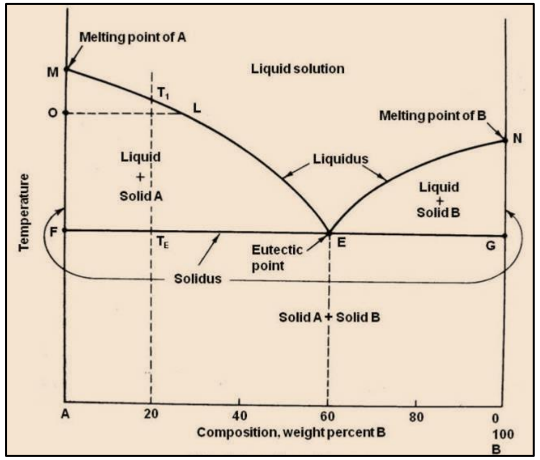
- Eutectic point – “E”
- Curves : ME and NE

ENGINEERING CHEMISTRY

Module 2- Phase equilibria

Eutectic point

- **Eutectic mixture:** A mixture of two components which has the lowest freezing point of all the possible mixtures of the components
- Number of phases at eutectic point = **3**
- F = C-P+1; C =2, P = 3,so **F = 0**; invariant point
- It has a **definite composition** and a **sharp melting point**



For Pb-Ag system:

Melting point –

Ag : 961^{o}C , Pb : 327^{o}C

Eutectic temperature: **303^{o}C**

Eutectic composition:

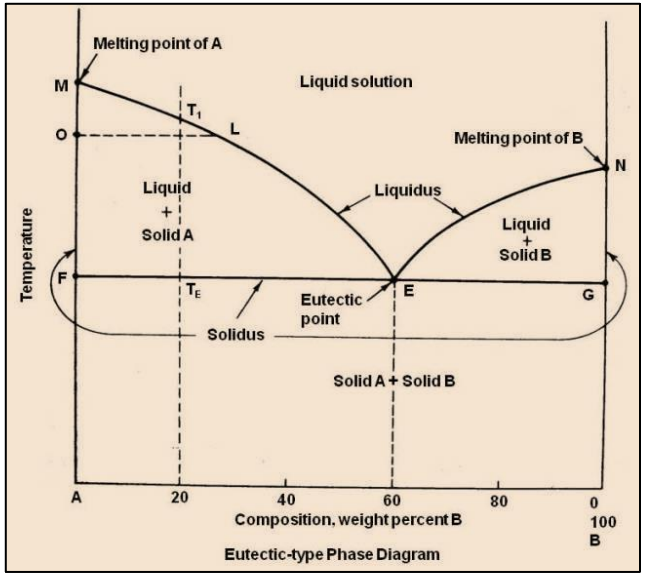
97.4 % Pb and 2.6 % Ag

CURVE ME : **freezing point curve of A**

- It shows decrease in freezing point / melting point of A due to the addition of B to A
- Solid A is in equilibrium with liquid melt of B in A
- Here C = 2 and P = 2, then the reduced phase rule is F = C – P + 1 = 2 – 2 +1 = 1
- Hence the system is **univariant**

CURVE NE: freezing point curve of B

- It shows decrease in freezing point of B due to the addition of A to B
- Solid B is in equilibrium with liquid melt of A in B
- Here C = 2 and P = 2, then the reduced phase rule is F = C – P + 1 = 2 – 2 +1 = 1
- Hence the system is **univariant**



Determination of solid-liquid equilibria

- For the determination of equilibrium conditions between solid and liquid phases – **Thermal Analysis**

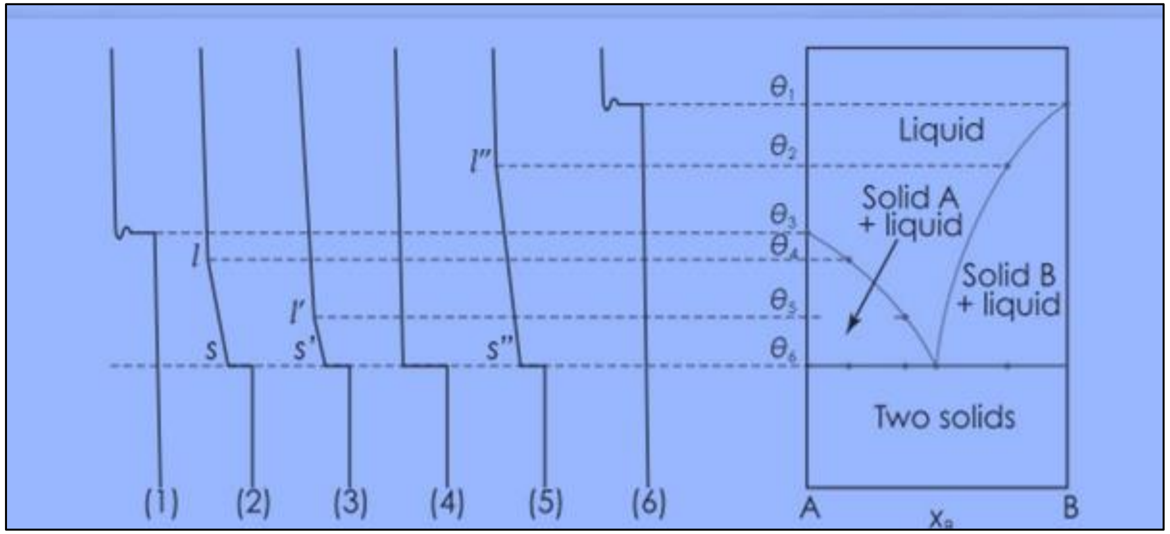
Thermal analysis:

The study of the **cooling curves** of various compositions of a system during solidification

Cooling curves:

- Temperature versus time
- **Freezing point** and **eutectic point** can be determined from the cooling curves

Construction of phase diagram using cooling curves



Source:http://www.mchmultimedia.com/PhysicalChemistry-help/clientstories/study-tips/digging-into-phase-diagrams-cooling-curves.html

For pure solid: Initially the rate of cooling is continuous from 'a' till the point 'b' where solid is begins to appear. Then the temperature remains constant until the liquid is fully solidified and solidification completes at the point 'c'.

For a mixture of solids: When crystallisation of one of the components starts ,cooling curve exhibits a break. The temperature decreases continuously until the eutectic point is reached. Now the temperature remains constant, till the completion of solidification.

THANK YOU

Department of Science and Humanities