APPLIED CHEMISTRY

Phase Rule

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(Deemed to be University)

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LEARNING OUTCOMES

By the end of this session participants should be able to:

Understand and Interpret

- ✓ The reduced phase rule.
- ✓ Two component system
- ✓ Simple Eutectic systems

Outline : Lecture 3

- Reduced / Condensed Phase Rule
- Two component system
- Simple Eutectic system

Phase Rule

Reduced Phase Rule

For a two-component system, C = 2, therefore according to phase rule the degree of freedom of a two-component system is given by: F = C – P + 2

$$F = 2 - P + 2 = 4 - P$$

When P = 1, F = 3 (highest value) i.e three variables (temperature, pressure and composition) are required to explain the system completely.

Since, three dimensional diagram cannot be represented on paper, therefore to construct a single-phase diagram for a two-component system, any two of the three variables can be chosen for graphic representation, assuming the third to be constant.

The cases may be:

(i) Pressure–temperature diagram (P–T) when composition is constant

(ii) Temperature–composition diagram (T–C) when pressure is constant

(iii) Pressure–composition diagram (P–C) when temperature is constant

Experiments are generally conducted at room temperature. Hence in most cases, pressure is kept constant at 1 atmosphere and the phase diagram is constructed using the variables, temperature and concentration.

Phase Rule

In the solid–liquid equilibrium:

- **The gas phase is generally absent**
- **The effect of pressure on the system is hence negligible.**

Such a solid–liquid equilibrium with the gas phase absent is termed as the condensed system.

Keeping the pressure constant, reduces the degree of freedom by one and for such a system, the phase rule becomes: $\mathbf{F = C - P + 1}$ **or** $\mathbf{F' = 3 - P}$

This is known as reduced or condensed phase rule applicable to solid-liquid two component systems

The solid–liquid equilibria are represented on temperature–composition diagrams.

Phase Rule

Simple Eutectic systems

The term Eutectic means easy to melt

A binary system having two substances, completely miscible all proportions in the liquid state but immiscible in the solid state, is known as Eutectic system. For example, a mixture of lead–silver comprises such a system

They do not react chemically and have tendency to lower each other's freezing point .

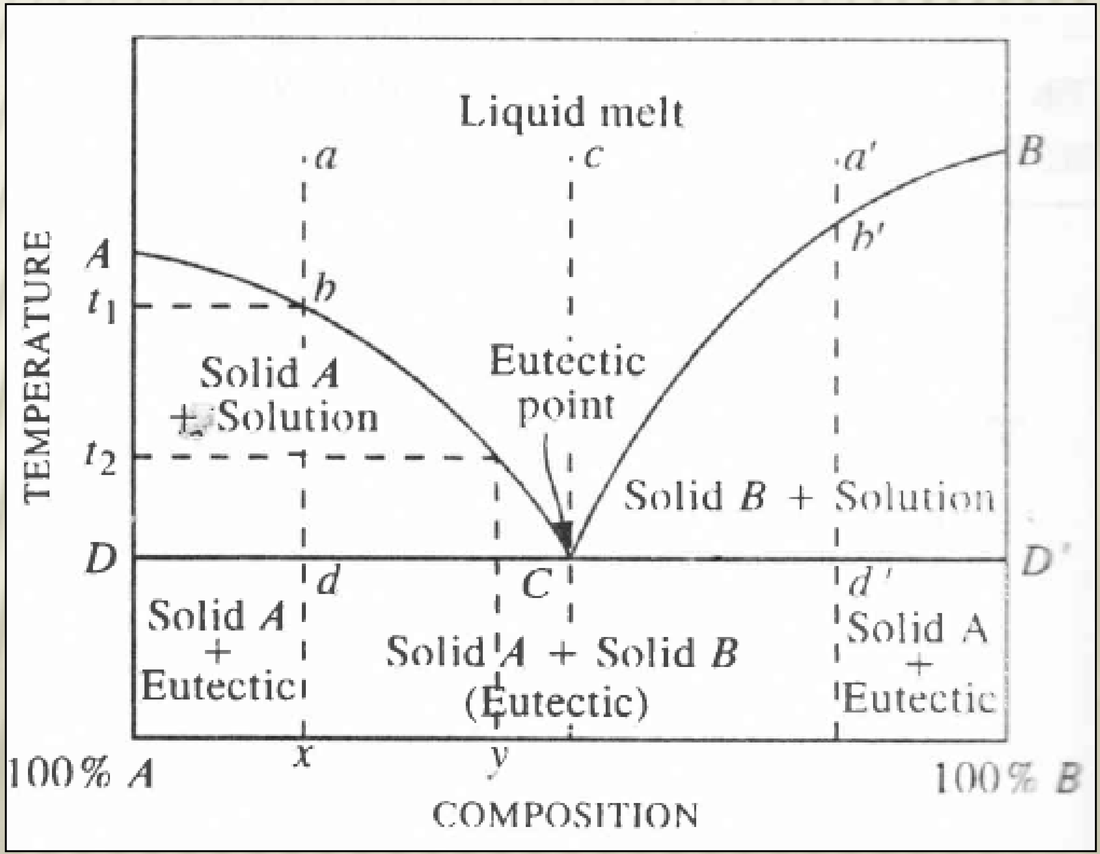
Eutectic point - Two or more solid substances capable of forming solid solutions with each other have the property of lowering each other's freezing point and the minimum melting point attainable by the eutectic mixture is termed as the eutectic point (lowest melting point)

Eutectic mixture - It is a solid solution of two or more substances having the lowest freezing point of all possible mixtures of the components.

Phase Rule

Simple Eutectic systems

Characteristics: **The eutectic mixture has a definite composition and a sharp melting point, that is, it melts to a liquid of the same composition. Hence, it resembles a compound. However, it is not a compound as the components are not present in stoichiometric proportions.**



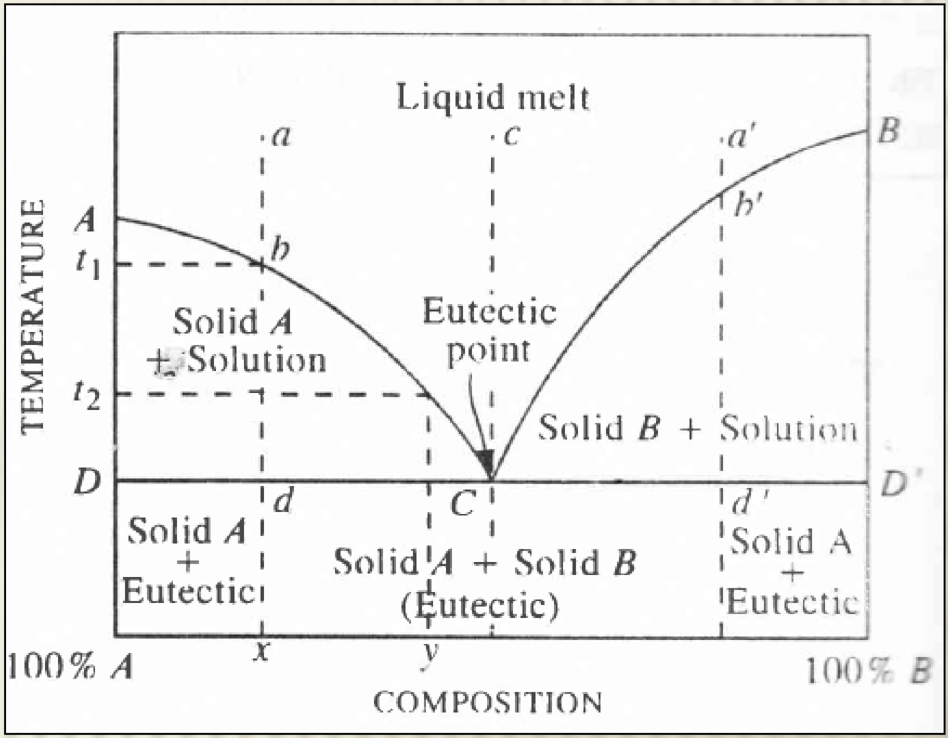
Principles of physical chemistry by Puri Sharma Pathania

Phase Rule

a, b, d case

❑The points A and B represent the melting points of the components A and B

If a liquid mixture of composition "a" is cooled at constant pressure;



Observations:

❑ Temperature will fall without any change in composition upto the point b on the freezing point curve AC

❑ At this temperature t_1, solid A separates out – two phases – Monovariant

❑ Temperature will fall only with change in composition of liquid phase

❑ As cooling continues, component A keeps on separating out and the solution becomes relatively richer in B

❑ The temperature and the solution composition, both change along the curve bC

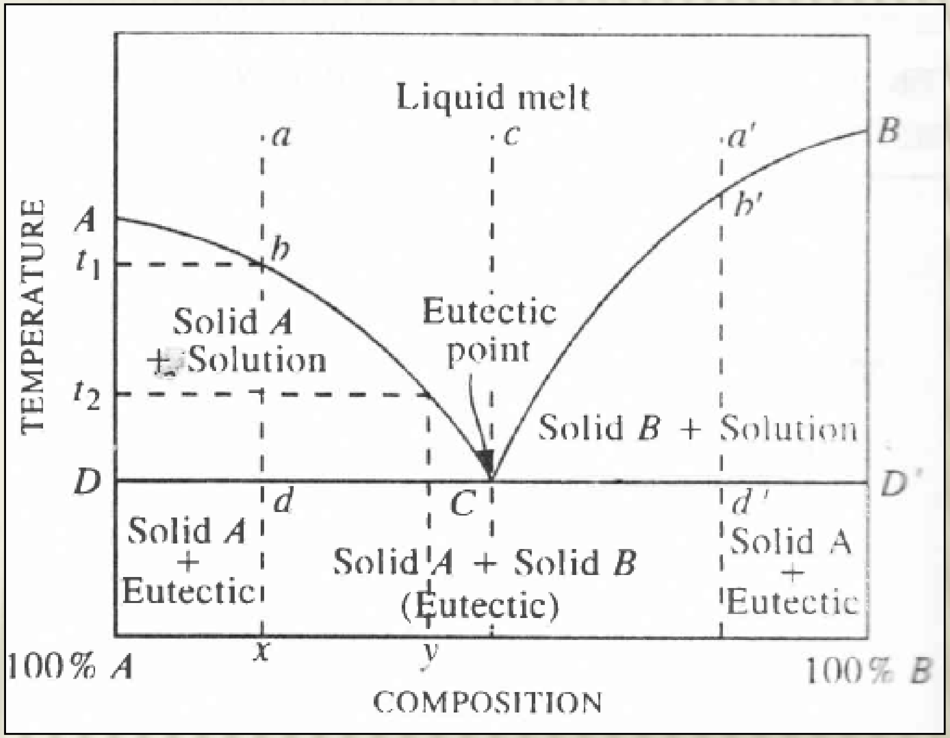
Phase Rule

•**At $t_{1:}$**

Solid A $\rightleftharpoons$ Solution of composition x

•**At $t_{2:}$**

Solid A $\rightleftharpoons$ Solution of composition y



•**Area ACD – solid A in equilibrium with solution of varying composition given by curve AC depending on temperature**

• **At Eutectic temperature (point d)-the second solid B also begins to crystallize -3 phases (Invariant)**

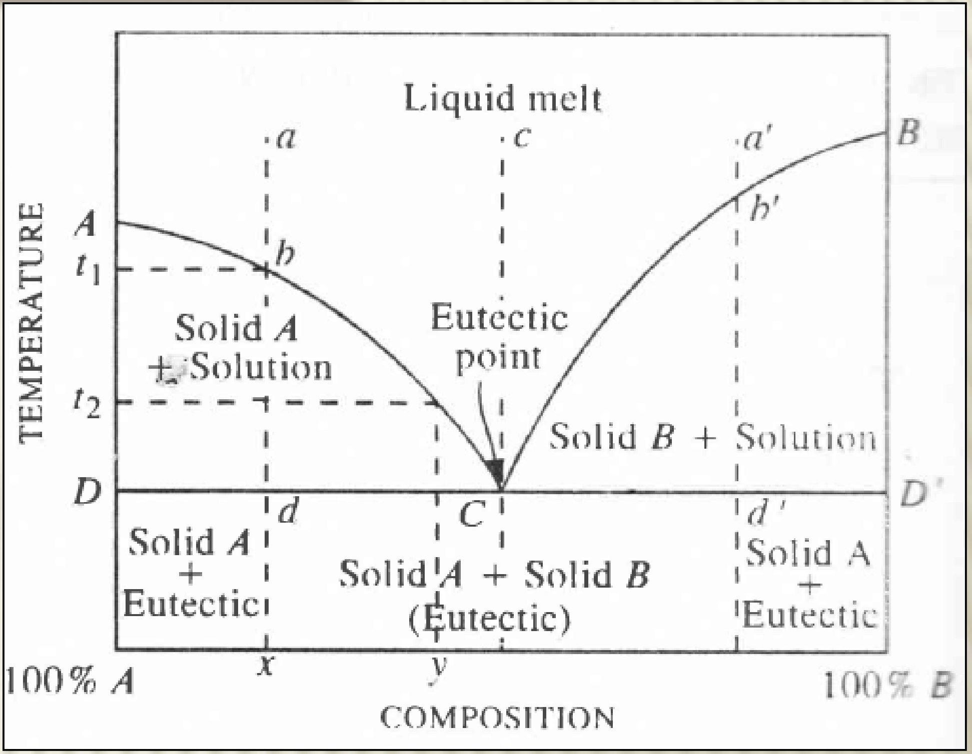
• **On further cooling the system, A and B separate out together in a fixed ratio – composition of solution remains constant – indicated point C – temperature remains constant**

Phase Rule

- The points A and B represent the melting points of the components A and B

- As increasing quantities of B are added to A, the freezing point of A falls along the curve AC.

- Similarly, as increasing quantities of A are added to B, the freezing point of B falls along the curve BC.



- ♣ **Curve AC** – Solid A is in equilibrium with solution of component B in A
- ♣ **Curve AC** – Freezing point curve of component A
- ♣ **Curve BC** – Solid B is in equilibrium with solution of component A in B
- ♣ **Curve BC** – Freezing point curve of component B
- ♣ **Number of phases along AC and BC – 2**

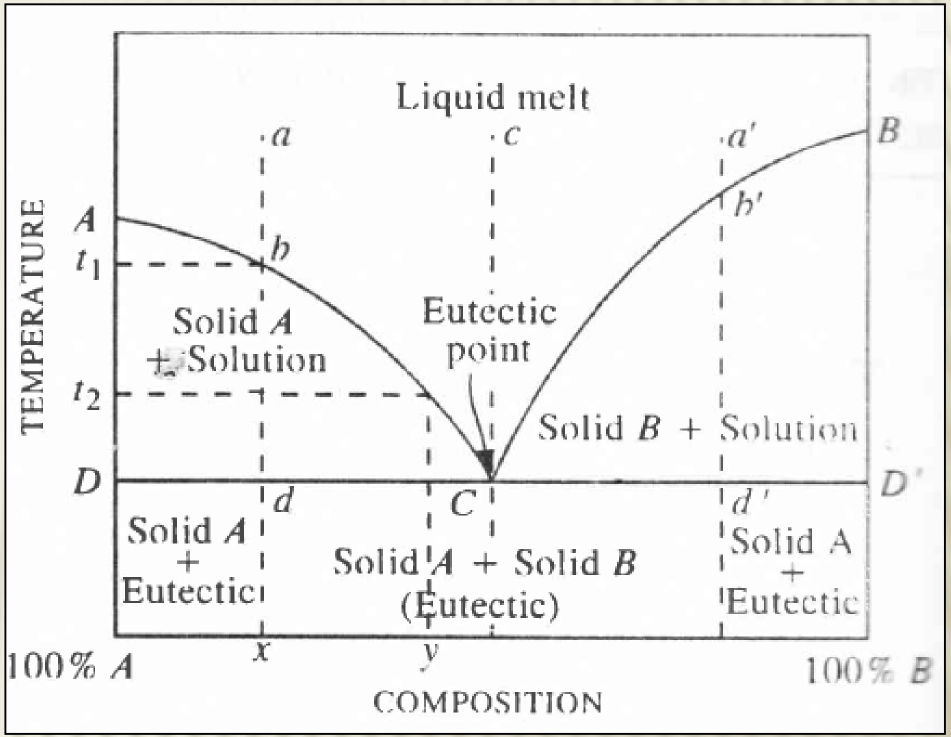
Phase Rule

- Applying reduced phase equation for curves AC and BC: **F = C – P + 1**

  i.e F = 2- 2 + 1 = 1 (monovariant

- The composition varies with temperature along AC or BC

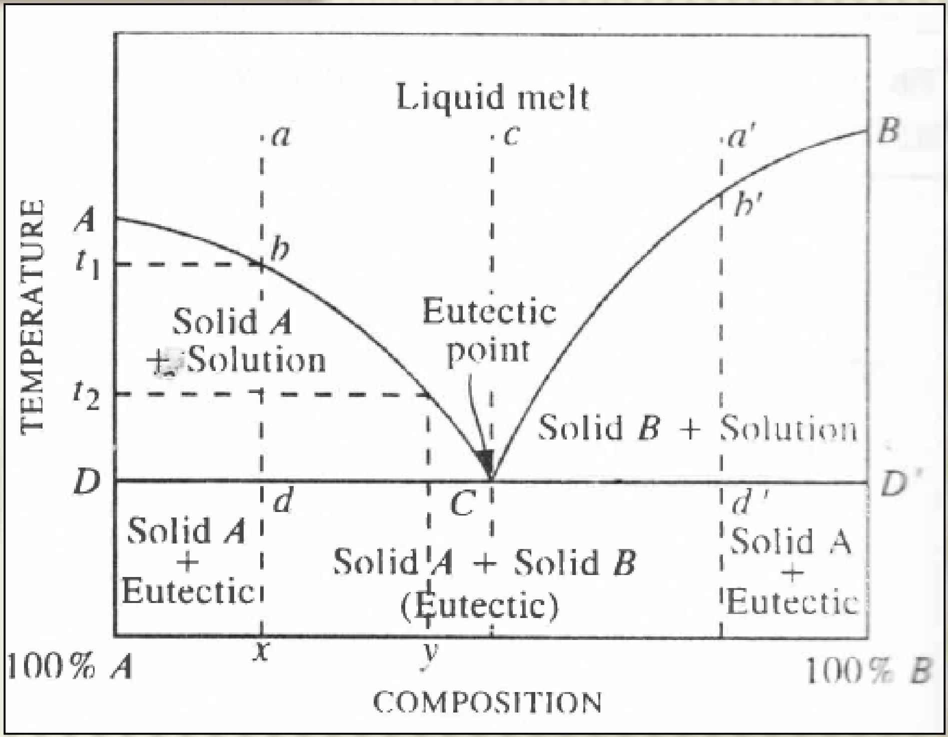
- The two curves intersect at point C – Both the solids are in equilibrium with solution i.e., the liquid solution of the two components



At C, number of phases = 3, F` = 0, hence system at C has no degree of freedom (Invariant)

Phase Rule

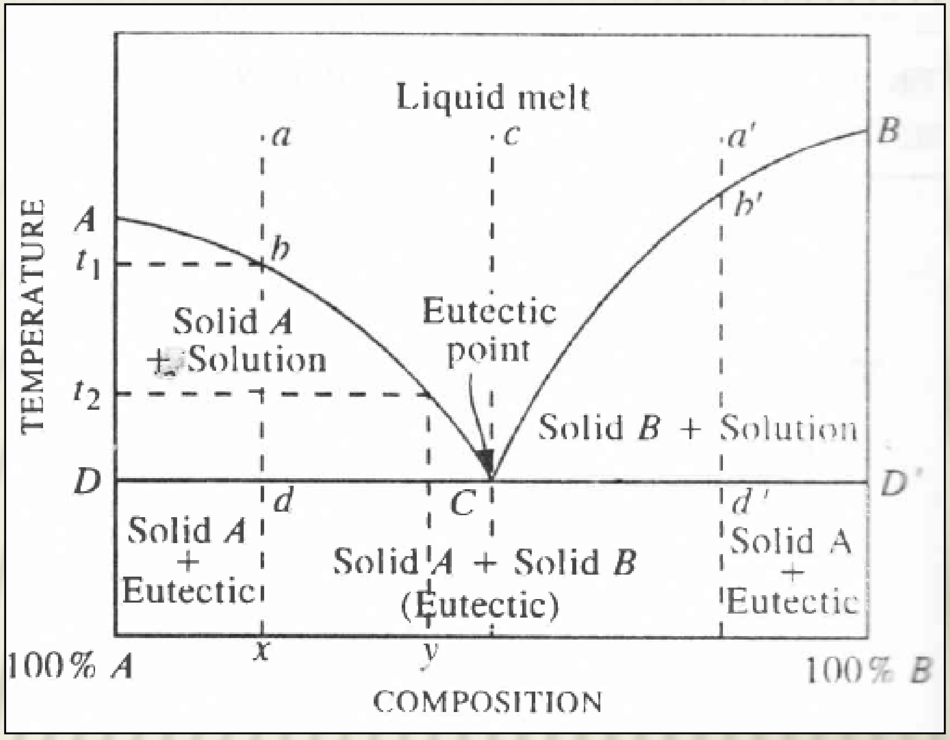
- Under a given pressure, the system consisting of two solids and their solution, A-B-L, can exist only at a definite temperature and composition of solution is also definite.



- **Point C-** Lowest temp. at which liquid (solution) can exist in equilibrium with solids A and B
- **Eutectic Point** - The mixture of A & B of composition corresponding to the point C has the lowest melting point.

- In the area above the line AC and BC, the two components are present as homogenous liquid solution – one phase – bivariant
- In order to define any point in this area, it is necessary to specify temperature and composition

Phase Rule



- **After complete solidification of solution phase, system consists of mixture of solid A and B – Monovariant – <u>cooling results in fall of temperature</u>**

- **Below the line D–D` - only two solids exist**

THANK YOU