Two Component Systems

Two components system

➤ *Here, two components constitute the smallest number by means of which the composition of each phase can be expressed. This means, C = 2*

➤ *F = C - P + 2 → → F = 2 – P + 2 = 4 – P*

➤ *Maximum Number of Phases:*
- *When F is minimum, P becomes maximum*
- *The minimum no. of degree of freedom possible In any system is zero.*

$$F_{min} = 4 - P_{max}$$
$$0 = 4 - P_{max}$$
$$P_{max} = 4$$

➤ *Maximum Number of F:*
- *F is maximum, when P becomes minimum.*
- *As the minimum no. of phases in any system is one.*

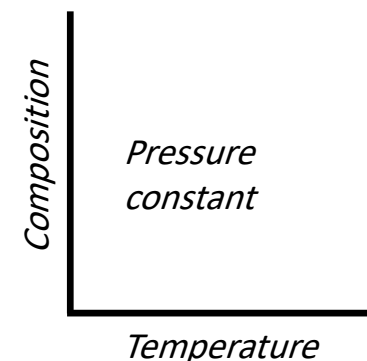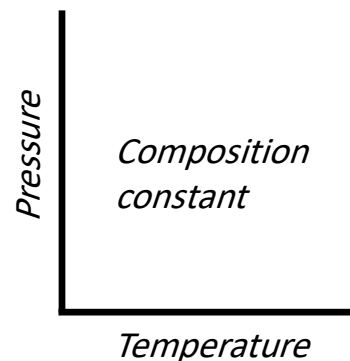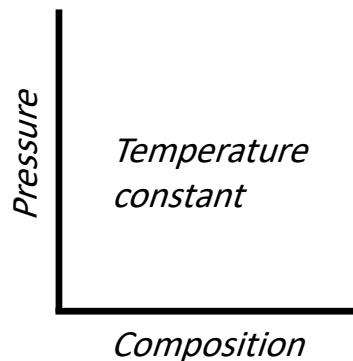$$F_{max} = 4 - P_{min}$$
$$F_{max} = 4 - 1$$
$$F_{max} = 3$$

✓ **This means, <u>to define completely two components system</u>, we have to mention <u>three variables, i.e., pressure, temperature, and composition</u>.**

Phase diagram for two components system

❑ *In order to present three variables (pressure, temperature and composition) by three co-ordinate axes at right angles, one needs space models.*

❑ *The space models cannot represented on paper.*

❑ *To simplify this phase diagram, it is a usual practice to choose any two of three variables, assuming the third to be constant.*

❑ *So, we can have the following three types of curves:*

     i.   *Pressure – temperature diagram (P – T).*

    ii.   *Temperature – composition diagram (T – C).*

   iii. *Composition – pressure diagram (C – P).*

Pressure (y)		Pressure (y)		Composition (y)	
Temperature constant		*Composition constant*		*Pressure constant*	
Composition		*Temperature*		*Temperature*	

It is a usual practice to keep the pressure constant and thus, an T – C diagram is the one which is most often met.

Reduced Phase Rule (Solid/liquid systems)

- *In the aforementionned curves $P - T$, $T - C$, and $C - P$ diagrams, one of the variables is fixed.*
- *Thus, the degree of freedom of the system is reduced by one.*
- *Therefore, $F - 1 = C - P + 1$, $F` = C - P + 1$, $F`$ gives the remaining degrees of freedom of the system.*

Reduced Phase Rule

Types of two components systems

- *Upon the nature of the phases, two component systems can be classified as follow:*
    - i. *Solid – gas system (constant temperature).*
    - ii. *Solid – liquid system.*
    - iii. *Solid – water system.*
    - iv. *Liquid – liquid system.*

    constant pressure

Gas– Solid Systems Examples: pressure is a variable

1. Dissociation of salts and salt hydrates (copper sulphate & $CaCO_3$).
2. Dissociation of amino compounds and formation of amino compounds.
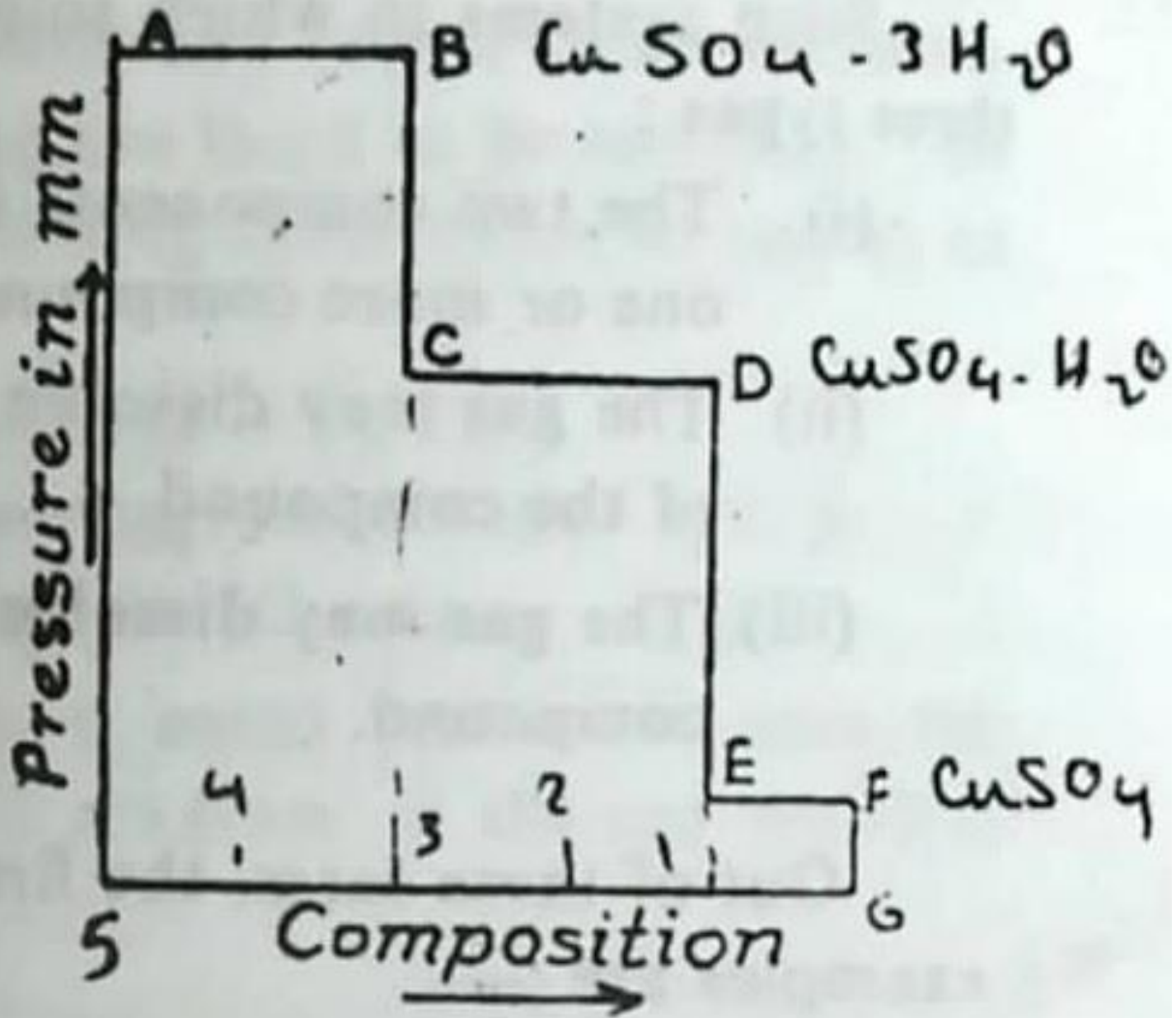
EX1. $CuSO_4 – H_2O$ system
It is a two component system consisting of five phases:

Phase	Composition
CuSO4.5H2O	CuSO4 + 5H2O
CuSO4.3H2O	CuSO4 + 3H2O
CuSO4.H2O	CuSO4 + H2O
Anhydrous CuSO4	CuSO4 + 0H2O
Water Vapour	0CuSO4 + xH2O

EX2. Formation of amino compounds
There is five phases as well:

Phase	Composition
Pure AgCl	AgCl + 0NH3
Pure NH3	0AgCl + NH3
AgCl.NH3	AgCl + NH3
2AgCl.3NH3	2AgCl + 3NH3
AgCl.3NH3	AgCl + 3NH3

Pressure in mm (vertical axis)

Composition (horizontal axis)

B CuSO$_4$ - 3H$_2$O

D CuSO$_4$·H$_2$O

F CuSO$_4$

A

C

E

4   3   2   1

5   G

Solid-Liquid Systems:

1. Here, the effect of pressure is disregarded.
2. Such a system, in which only solid and liquid phases are considered and the experiments are carried out under atmospheric pressure, is known as a condensed system.
3. There are three categories within this solid-liquid equilibria: category one, category two, and category three.

Category one; type I. Formation of Simple Eutectic
- In this type, the two components are completely miscible in liquid state.
- The word eutectic has been derived from the Greek word, eutectic which means easy melting.
- Easy melting refers to the lowest temperature of melting.
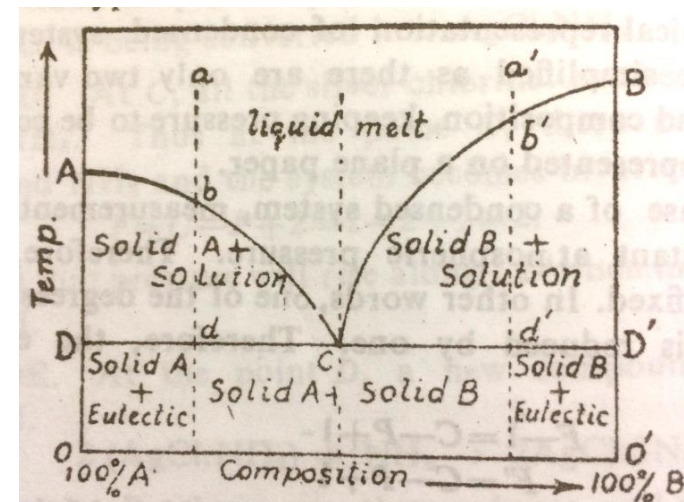
Two–Component Systems
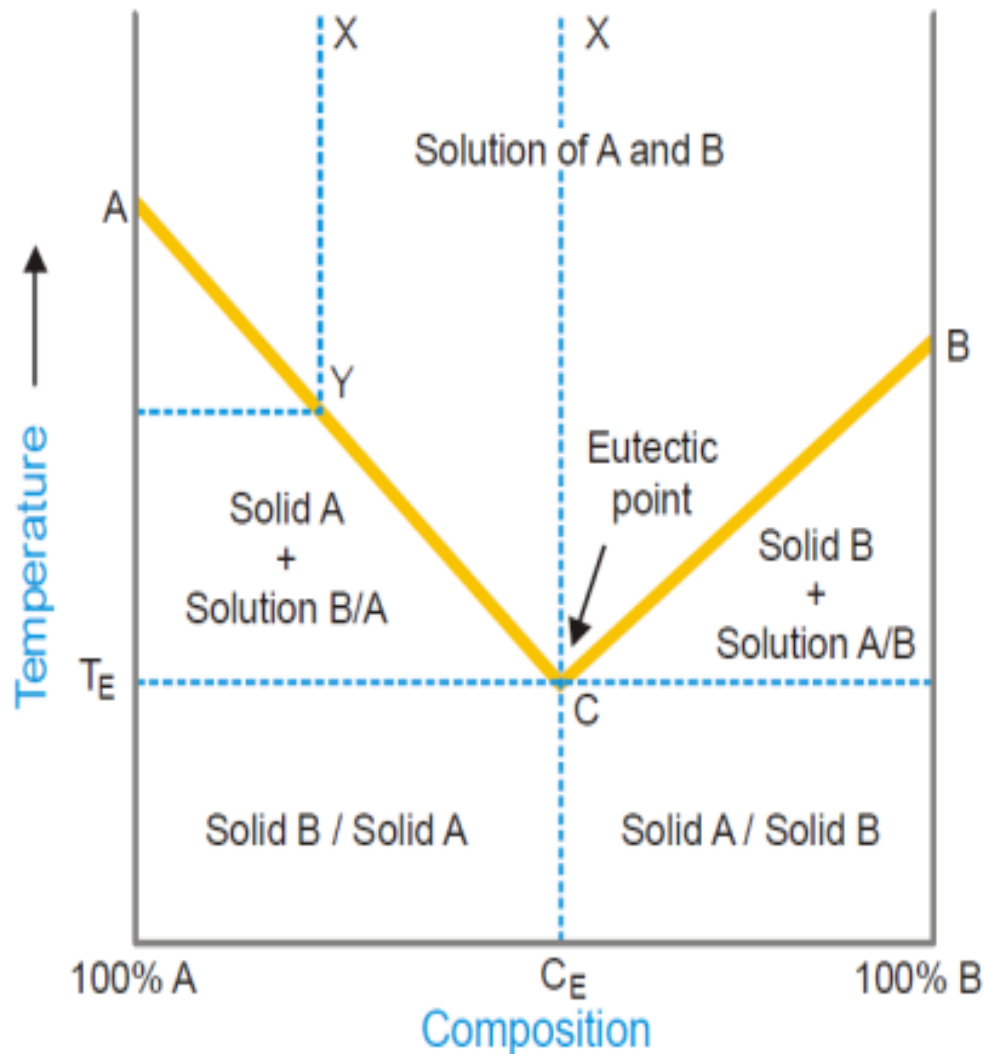
When a single phase is present in a two-component system, the degree of freedom is three,

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

This means that three variables must be specified in order to describe the condition of the phase.

Thus in such a system, in addition to pressure and temperature the concentration of one of the components has also to be given.

For graphic representation of these variables, three coordinate axes at right angles to each other would be required. Therefore the phase diagram obtained would be a solid model.
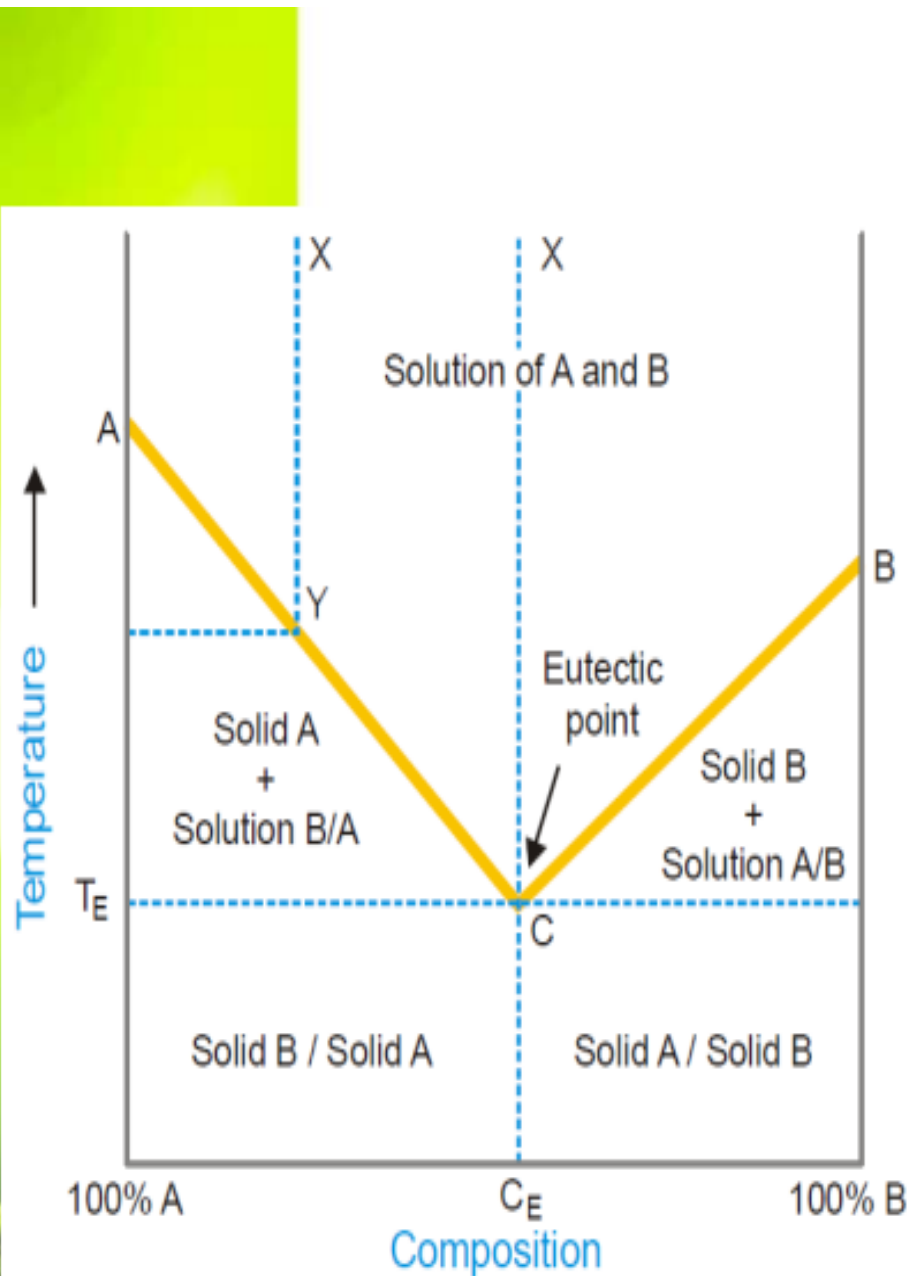
For the sake of having simple plane diagrams we generally consider only two variables, the third one being a constant. For example, for a solid-liquid equilibrium, the gas phase is usually absent and the effect of pressure on the equilibrium is very small.

Thus, when a two-component system consists of solid and liquid phases only, the effect of pressure may be disregarded. Then it is necessary to take into account the remaining variables *viz.*, temperature and concentration.

Such a solid/liquid system with the gas phase absent is called a condensed system.

Since the degree of freedom in such a case is reduced by one, we may write the **Reduced Phase rule** as

$$F' = C - P + 1$$
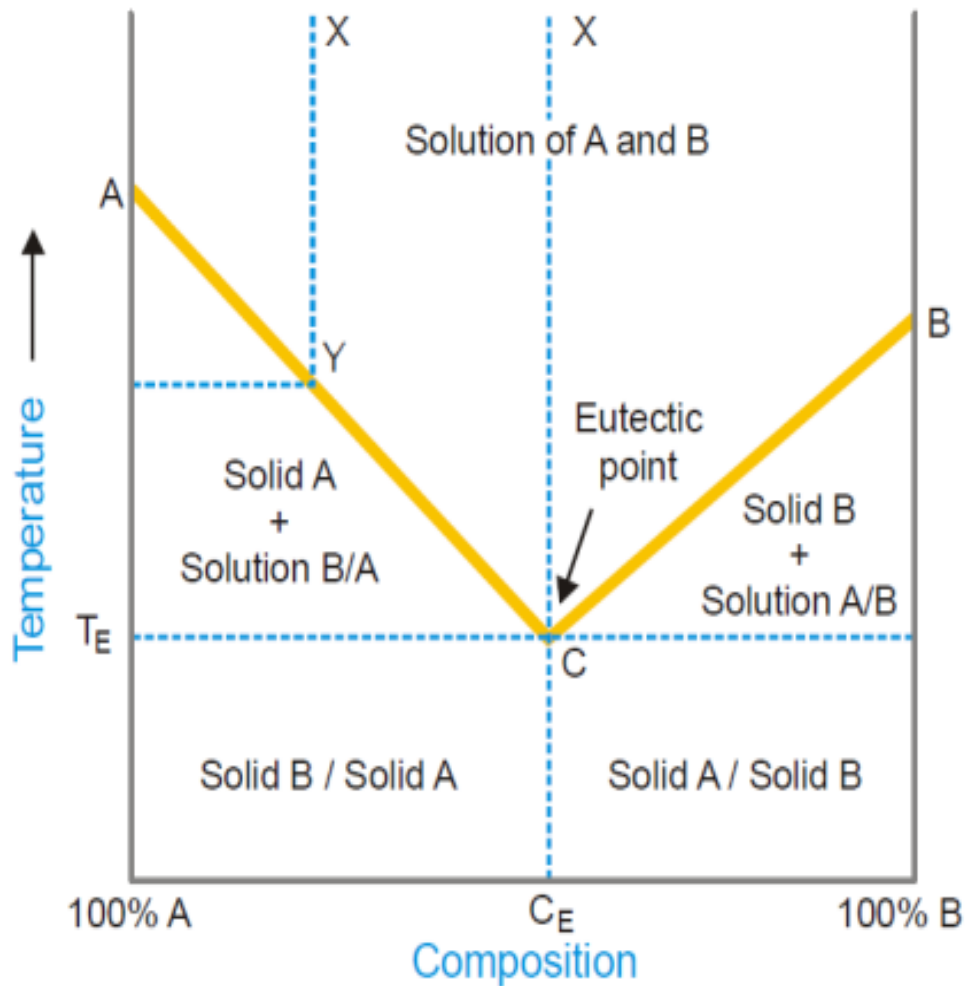
Where, F' gives the remaining degrees of freedom of the system. The reduced phase rule is more convenient to apply to solid/liquid two-component condensed system. Since the only variables for two-component solid/liquid systems are temperature and composition, the phase diagrams for such systems consist of Temperature-Concentration graphs (*TC graphs*).

Simple Eutectic Systems

The general form of the phase diagram of such a 2-component condensed system is shown in Figure. Here the two components A and B are completely miscible in the liquid state, and these solutions on cooling yield only pure A or pure B as solid phases.
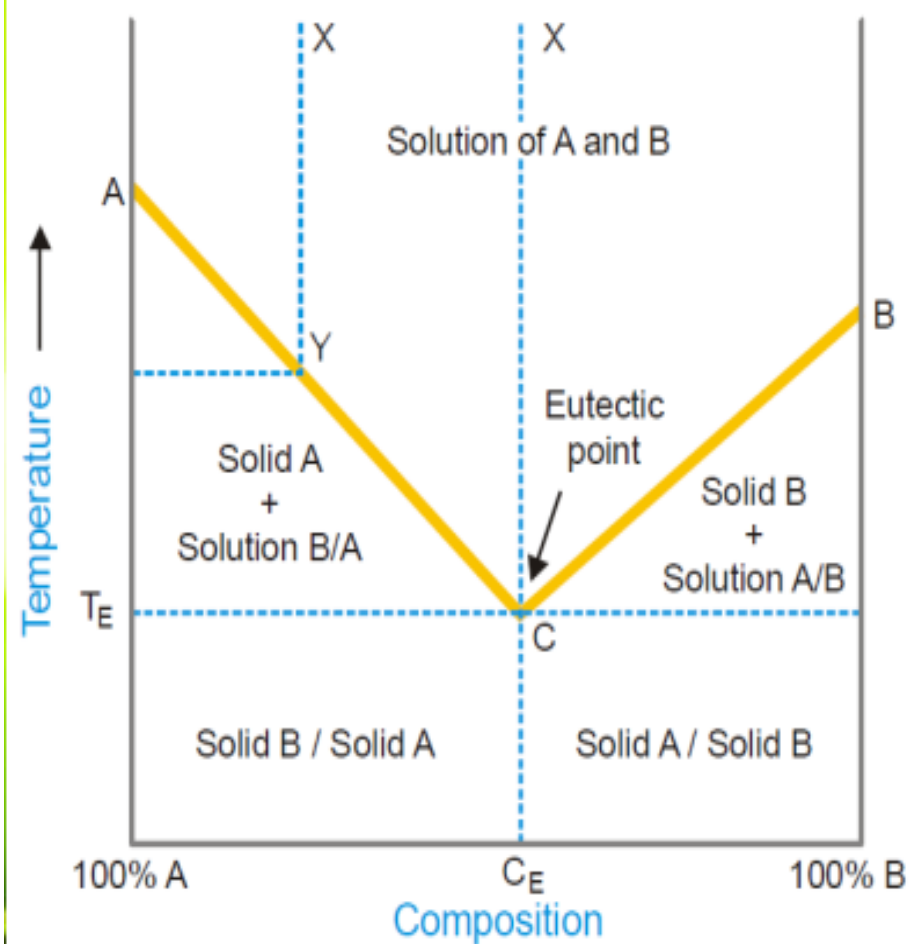
The diagram consists of:

Curve AC; the Freezing point curve of A. The point A represents the freezing point of A. The curve AC shows that the freezing point of A falls by the addition of B to A. Thus along this curve, the solid A is in equilibrium with the liquid solution of B in A.

Curve BC; the Freezing point curve of B. The point B shows the freezing point of B. The curve BC exhibits the fall of freezing point by the addition of A to B. Along this curve, the solid B is in equilibrium with the liquid solution of A in B.

Applying the reduced phase rule equation to the equilibria represented by the curve AC and CB i.e., solid A/solution and solid B/solution respectively, we have
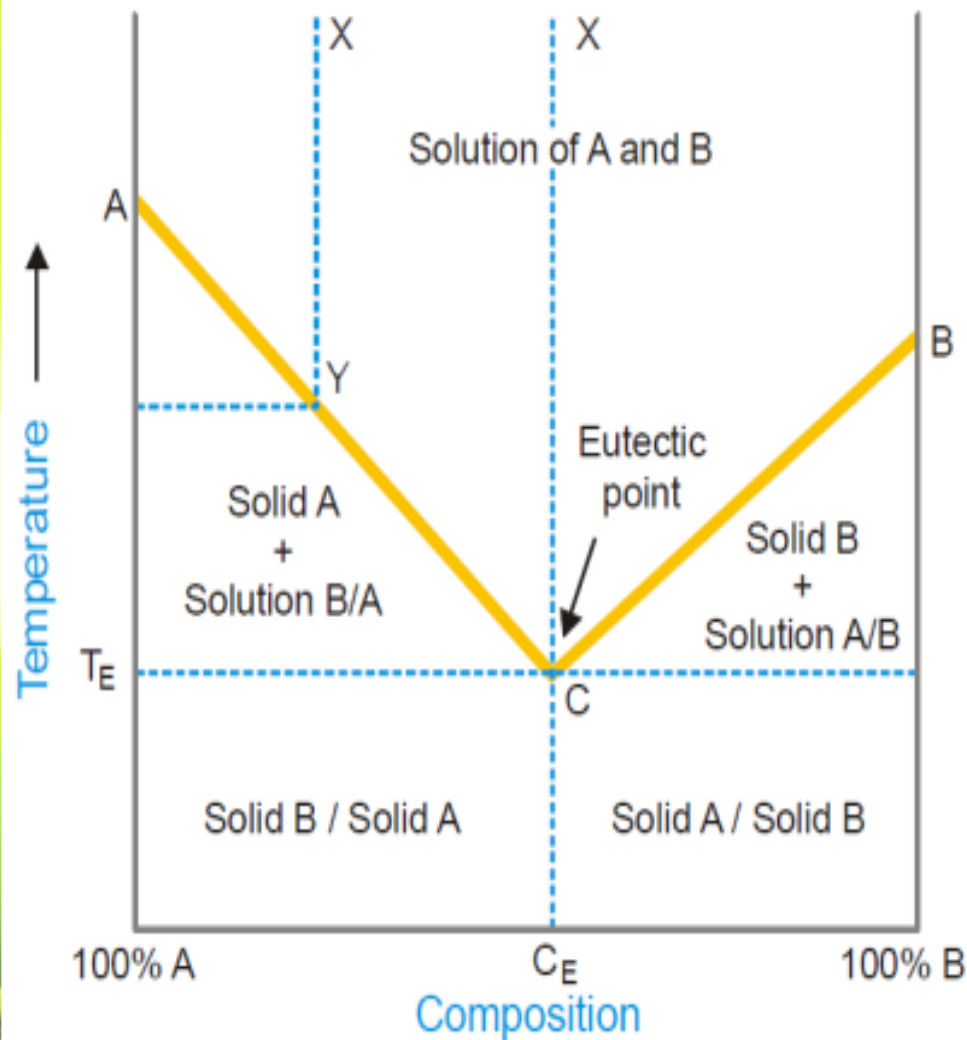
$$F = C - P + 1 = 2 - 2 + 1 = 1$$

The degree of freedom is one i.e., both equilibria are monovariant.
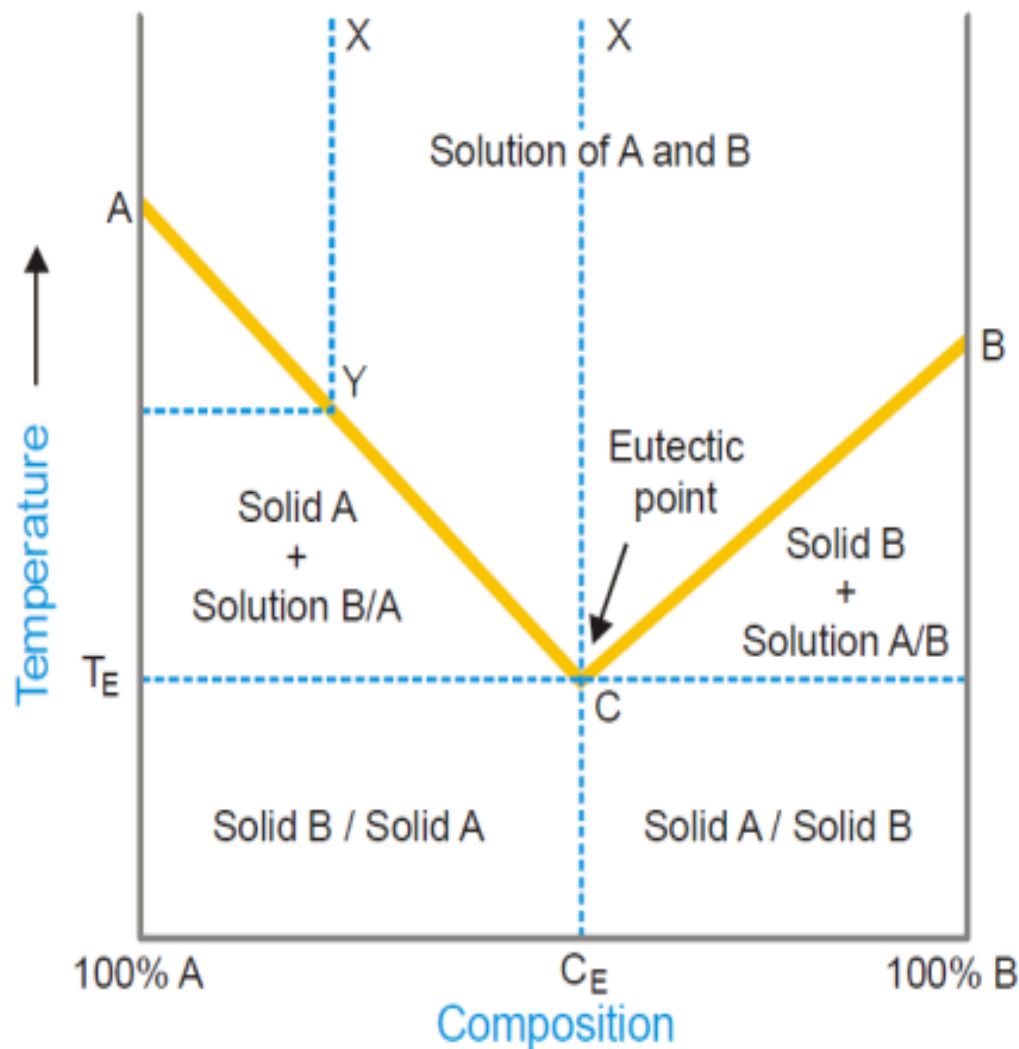
The Eutectic point C. The two curves AC and BC meet at the point C. Here both the solids A and B must be in equilibrium with the solution phase (solution of A and B). The number of phases is 3. By applying the reduced phase rule equation , we have

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

Thus, the system represented by the point C is *nonvariant*. In other words, both temperature and composition of the system solid A-solid B-solution are fixed. The mixture of components A and B as at point C melts at the lowest temperature T_E indicated on the graph. The *point C is t* herefore, called **the Eutectic point** (Greek *eutectos* = easy melting). The corresponding composition (C_E) and temperature (T_E) are known as the **eutectic composition** and the **eutectic temperature** respectively of the system.

X | X

Solution of A and B

A

Y

Solid A
+
Solution B/A

Eutectic
point

Solid B
+
Solution A/B

T_E

C

Solid B / Solid A | Solid A / Solid B

100% A

C_E
Composition

100% B

B

Temperature

The **eutectic mixture, although it has a definite melting point, is not to be regarded as a compound.**

The reasons are: (*i*) the components are not in stoichiometric proportions; and

(*ii*) on examination under a microscope these reveal the existence of separate crystals of the components.

The Area above the curves *AC* and *BC*. Here the two components *A* and *B* are present as *liquid solutions* of varying compositions. As a homogeneous solution of *A* and *B* constitutes one phase only, this system is *bivariant*.

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

Therefore, to define the system at any point in this area, both temperature and composition have to be specified.
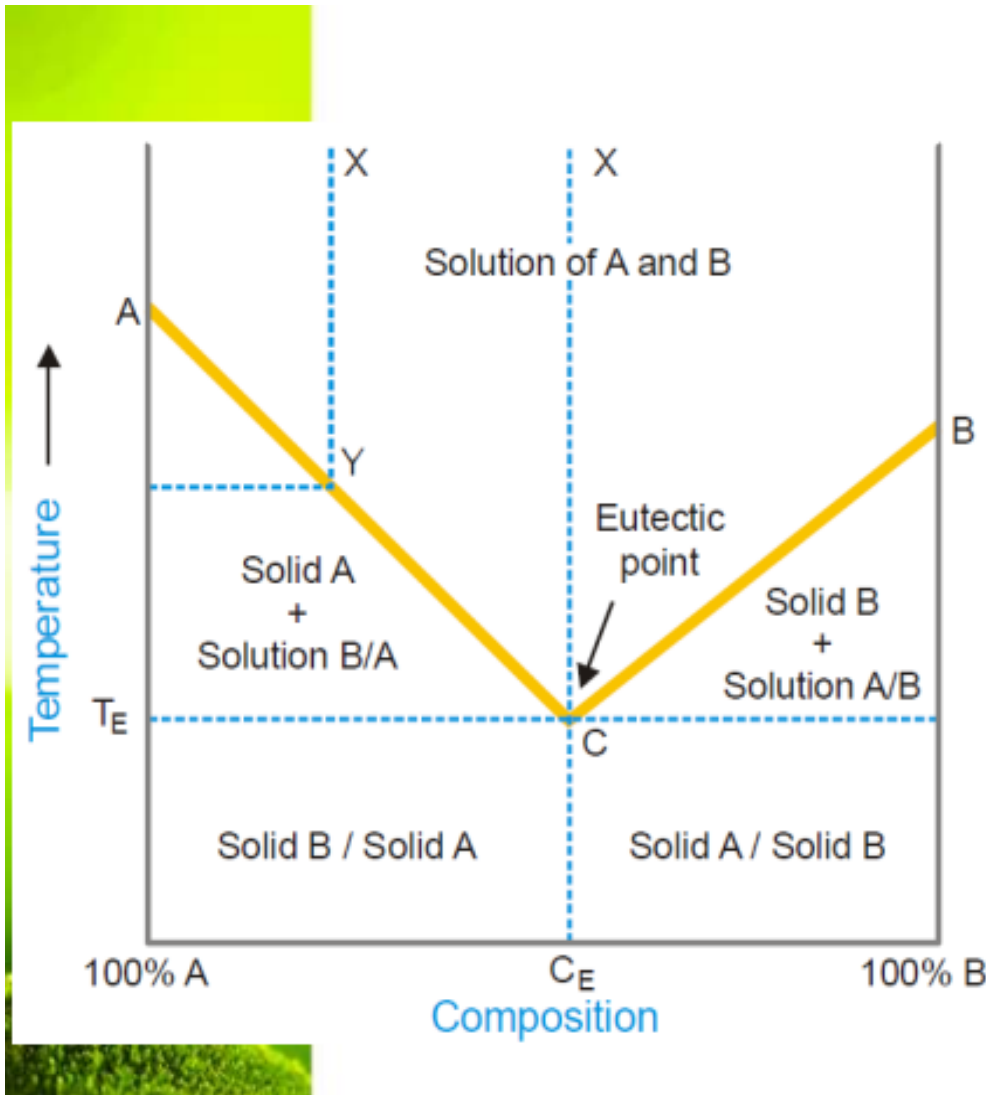
Effect of Cooling

When the A/B solution at any point in the area above ACB is cooled, the cooling dashed line meets the curve AC, say at Y. Here solid A separates and the equilibrium shifts down along the curve AC. The change of composition and temperature continues till the eutectic point C is reached when solid B also separates.

Thus in the area below AC and above T_E line, there exist two phases $viz.$, solid A and solution A/B, and the system is $bivariant$. Similarly, cooling of solution B/A on the other side of eutectic, on reaching the curve BC would yield solid B/solution system.

Thus, the area below BC up to T_E line would represent solid B and solution.

If the solution just above the eutectic point is cooled, a solid mixture (*eutectic mixture*) of eutectic composition C_E, will be obtained straightaway.

Category one; type I. Formation of Simple Eutectic
- The phase diagram consists of:
  - ➢ Curves AC and CB
  - ➢ Points A, B, and C
  - ➢ Areas ADC, D`CB, OO`DD`, and area above the curve ACB
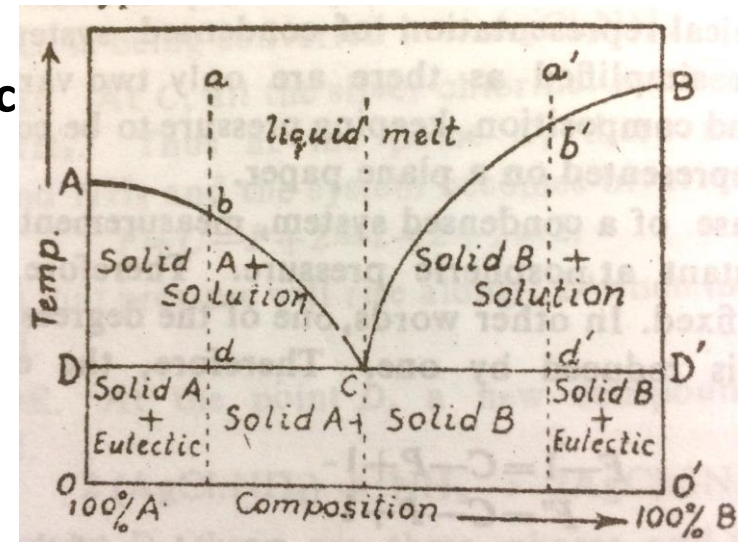

Description
- ✓ **Point A.** It represents the melting point of the pure component A.
- ✓ **Point B.** It represents the melting point of the pure component B.
- ✓ **Point C.** It is known as the eutectic point. It is the lowest temperature at which the liquid can exist. The eutectic point has been derived from the Greek word eutectic which means easy melting. Herein this point represents the lowest melting point of any mixture of solids A and B. at point C, there is an equilibrium between three phases (solid A, solid B, and liquid A&B). F`= 2 -3 + 1 = 0. So, the system at this point is non-variant. This means that, there is only one temperature at which the liquid phase can be equilibrium with both solids A and B, and that the composition of the liquid phase must also be definite.

Description

✓ **Curve AC.** It is known as the freezing point curve of the component A. Along this curve AC, the solid A is in equilibrium with the solution of the component B in A (liquid) at different temperatures. P = 2, along the curve. So, F`= 2- 2+1 = 1. Thus, any point on the curve AC is univariant. It means that only composition varies along the curve AC.
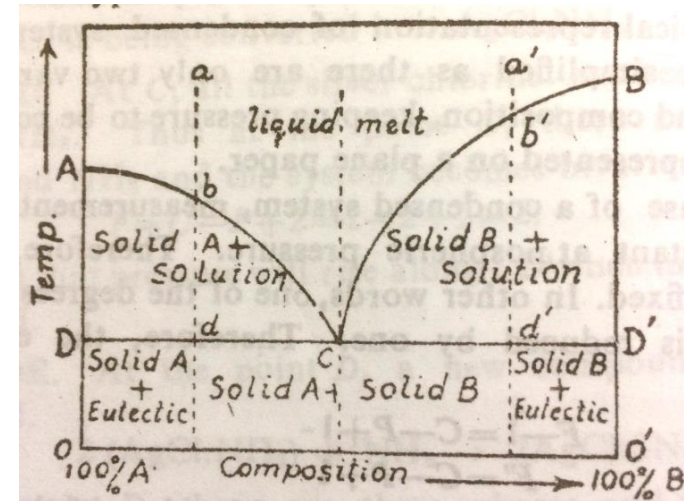
✓ **Curve CB.** It is known as the freezing point curve of the component B. Along this curve CB, the solid B is in equilibrium with the solution of the component A in B (liquid) at different temperatures. P = 2, along the curve. So, F`= 2 – 2 + 1 = 1. Thus, any point on the curve CB is univariant. It means that only composition varies along the curve CB.

Description

✓ **Area ACB.** In this area, the two components A and B exist in a homogeneous liquid solution. This means that, there is only one phase in the area (P = 1). F` = 2 − 1 + 1 = 2. Thus, the system is bi-variant. It means that temperature and composition are required to define any point in the area above the curve ACB.
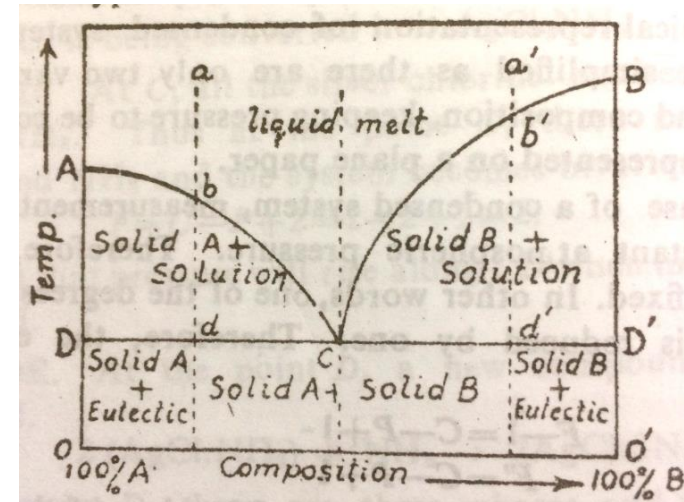
✓ **Area OO`DD`.** In this area only solid can exist because the liquid phase can not exist below the eutectic temperature. Here, P = 2, F`= 2 − 2 + 1 = 1, and the system is uni-variant.

From the phase diagram, it is possible to predict the behavior of any system on heating or cooling by using equilibrium diagram. This type of study is of of special importance in the study of alloys in metallurgy.

Examples:

- ✓ **Antimony – lead system**
- ✓ **Silicon – aluminium system**
- ✓ **Bismuth – cadmium system.**
- ✓ **KCl – CaCl$_2$ system.**
- ✓ **Benzene - methyl chloride system**
- ✓ **KI – H2O system.**
- ✓ **Lead – silver system.**

Lead – silver system.

- o It is an example for two components system.
- o Its phase diagram forms a simple eutectic point.
- o The eutectic point can be represented by point C in the above figure.
- o This point C lies at temperature (300°C) which is lower than the melting point of silver and lead metals.
- o The composition of eutectic point (point C) is corresponding to an alloy of lead 97.6% and silver 2.4%.
- o This phase diagram is utilised in the separation of silver from lead in Pattinson's process for desilvarisation of lead.
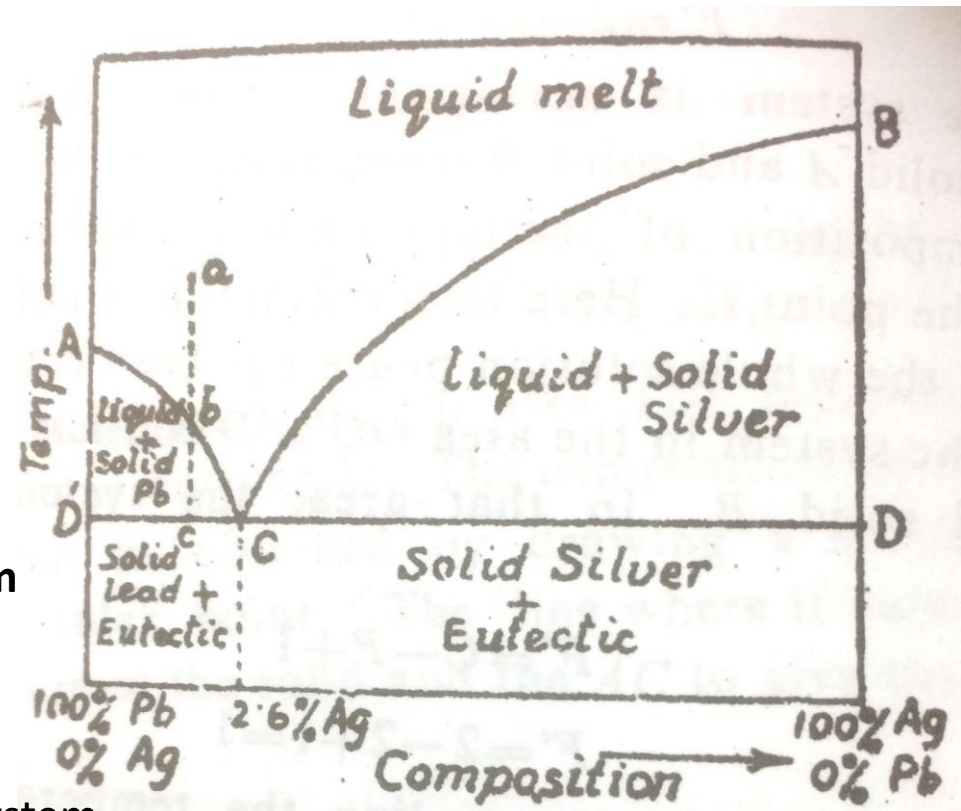
THE SILVER–LEAD SYSTEM

This system has **two components** and **four phases.** The phases are : (*i*) solid silver; (*ii*) solid lead; (*iii*) solution of molten silver and lead; and (*iv*) vapour.

The boiling points of silver and lead being considerably high, the vapour phase is practically absent. Thus Ag/Pb is a condensed system with three phases. In such a case, pressure can have no effect on the system. Therefore we need consider only the two remaining variables, namely the temperature (*T*) and concentration (*C*). The complete *TC diagram* of the system Ag/Pb is shown in Fig.

■ Figure 19.6
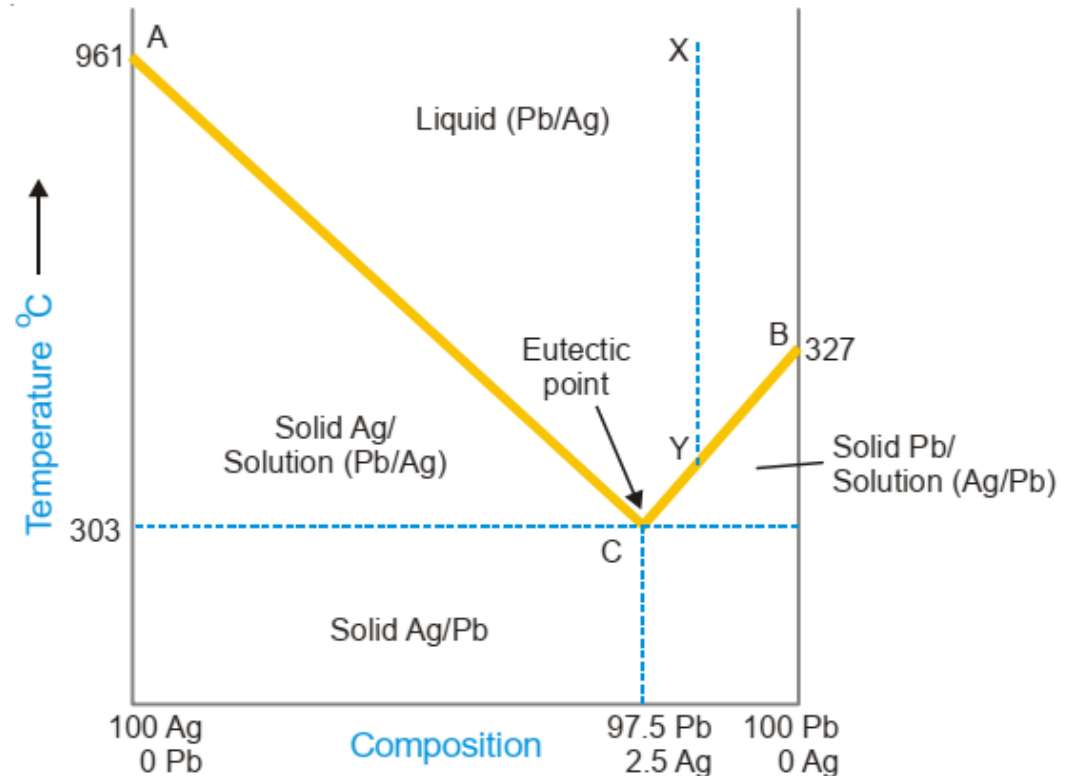
The salient features of the diagram are :

(*a*) Two curves, *AC* and *BC*
(*b*) Eutectic point, *C*
(*c*) Three areas : (*i*) *above ACB*; (*ii*) *below AC;* (*iii*) *below BC*
Curve AC; the Freezing point curve of Ag. *A* represents the freezing point or melting point of
solid silver (961ºC) and the curve *AC* shows that the addition of lead lowers the melting point along it. The phases in equilibrium along *AC* are solid silver and solution of silver and lead. Applying the reduced phase rule equation

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

Thus the system Ag/solution is *monovariant.*

Curve *B*; the Freezing point curve of Pb. *B* represents the melting point of solid lead (327ºC) and the curve *BC* shows that the melting point is lowered by addition of silver. The phases in equilibrium along *BC* are solid lead and solution. The system is *monovariant.*
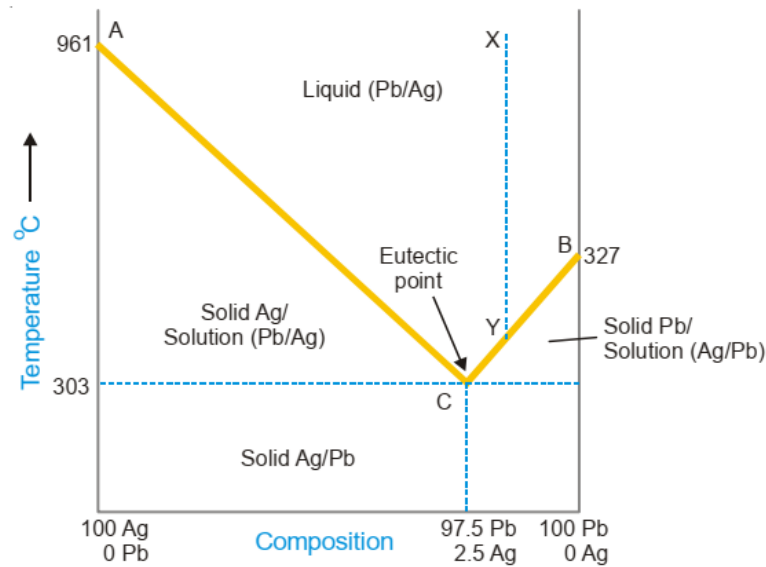
Figure 19.6

The Eutectic point C. The curves AC and BC intersect at C, which is called the *eutectic point.* Here three phases solid Ag, solid Pb, and solution are in equilibrium. Applying the reduced phase rule equation $F' = C - P + 1 = 2 - 3 + 1 = 0$

Thus the system Ag/Pb/solution at C is *nonvariant.* Both the variables, temperature (303ºC) and composition (97.5% Pb, 2.5% Ag) are fixed. If you raise the temperature above the eutectic temperature, the solid phases Ag and Pb disappear and if you cool below it, you will land in the solid Ag/Pb area where solution phase is nonexistent.

The Area above AOC. This region represents the single phase system, the solution of molten Ag and Pb. Applying the reduced phase rule equation, we have

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

Thus the system solution Ag/Pb is *bivariant.* The area below AC represents the phases Ag + solution, while that below BC the phases Pb + solution. The area below the temperature 303º, represents solid Ag + solid Pb. All these areas have two phases and one degree of freedom,

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

Pattinson's Process for the Desilverisation of Argentiferous Lead

This process of recovery of silver from argentiferous lead is based on the facts contained in the diagram (Fig. 19.6). The argentiferous lead containing small amount of silver (less than 0.1%) is melted well above the melting temperature of pure lead (327ºC). Let the point X represent the system 'molten lead' on the diagram. It is then allowed to cool when the temperature of the melt falls along the dashed line XY.

As the temperature corresponding to Y on the curve BC is reached solid lead begins to separate and the solution would contain relatively larger amount of silver. On further cooling, more of lead separates and we travel along the curve BC until the eutectic point C is reached. Lead is continuously removed by means of ladles and the percentage of silver in the melt goes on increasing. At C, an alloy containing 2.5% Ag and 97.5% Pb is obtained. This is treated for the recovery of silver profitably (cost-effective).

ALLOYS
INTRODUCTION

Generally metals are insoluble in ordinary solvents like water, alcohol but a metal can dissolve in another metal in molten state forming a homogeneous liquid mixture. This on cooling solidifies to a solid mixture called an alloy. Most of the metals can mix up in all proportions forming alloys, e.g. tin and lead. Alloys are formed not only by metals among themselves, but also by metal and non-metal. From the above explanation, it is clear that an alloy contains atleast one metal.

DEFINITION

An alloy is defined as *"homogeneous solid solution of two or more different elements, one of which at least is essentially a metal"*. *Alloys containing Hg as a constituent element are called amalgams.*
The metals in excess amount are known as base metal and other elements in lesser amounts are known as alloying elements.

PROPERTIES OF ALLOY

➢ Alloys are harder, good strength less malleable (soft) and ductile (elastic).
➢ Alloys have low electrical conductivity and low melting point than pure metals.
➢ Alloys resist corrosion and the action of acids.

MPORTANCE (OR) NEED (OR) PURPOSE OF MAKING ALLOYS

➤ Generally pure metals possess some useful properties like high melting point, high densities, malleability, ductility, good thermal and electrical conductivity.

➤ As said above, the properties of a given metal can be improved by alloying it with some other metal (or) non-metal. The purpose of making alloys are as follows:

1. To increase the hardness of metals
Generally pure metals are soft, but their alloys are hard.
Examples
(i) Gold and silver are soft metals; they are alloyed with copper to make them hard.
(ii) Addition of 0.5% arsenic makes lead so hard and used for making bullets.

2. To increase the strength of metals
Pure metals have less strength than their alloys.
Examples: *Pure iron metal has less strength but when alloyed with carbon has more strength.*

3. To lower the melting points of metals
Alloying makes the metal easily fusible.
Examples
Wood's metal (an alloy of lead, bismuth, tin and cadmium) melts at 60.5° C, which is far below the melting points of any of these constituent metals.

4. To resist the corrosion of metals
Metals, in pure form, are quite reactive and easily corroded by surroundings, thereby their life is reduced. If a metal is alloyed, it resist corrosion.
Examples: *Pure iron gets rusted, but when it is alloyed with carbon(or) chromium (stainless steel), resists corrosion.*