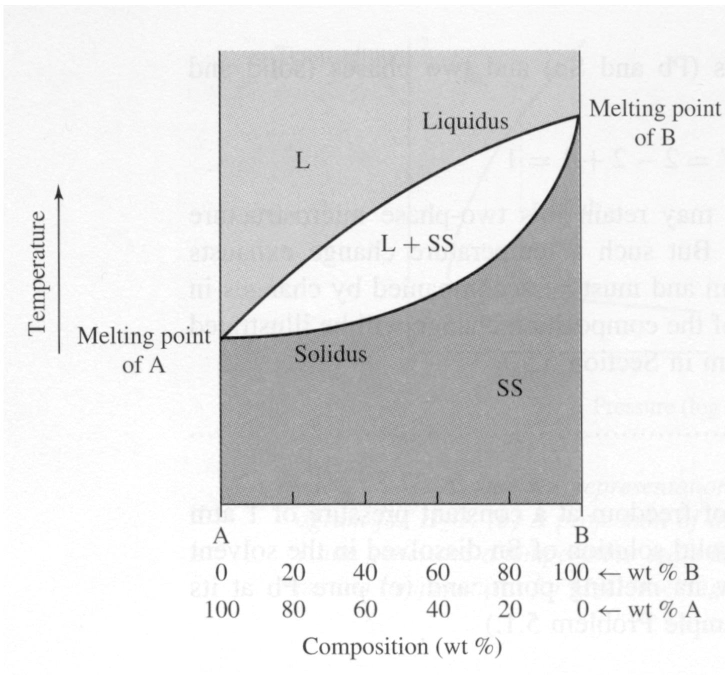
1.6 Liquid-Solid Systems

The phase diagrams of solid-liquid systems look similar to the liquid-vapour phase diagrams, except that in place of liquid you have solid and in place of vapour you have liquid and the phase change involved is melting or freezing instead of boiling or condensation. Once again we will examine these at a constant pressure, i.e. by T-X diagrams.

4.7.1 Completely Miscible Solids

Such systems are common in metallurgical systems dealing with metal alloys. Let us look at a generic case first.



- The figure looks very much like the vapour-liquid phase diagram of two fully miscible liquids. The two-phase region is sandwiched by two single phase zones, one representing solid phase and the other representing liquid phase.
- The line between the liquid region and the two-phase region is called liquidus. It is similar to the dew point line.
- The line at the bottom of the two-phase region is called solidus and is similar to the bubble point line.

Let us now examine a real system, the one shown in Figure 4-9.

Antimony and Bismuth mix in all proportions in solid phase. The T-X is similar to the generic case, showing a two-phase region bounded by two single phase regions.

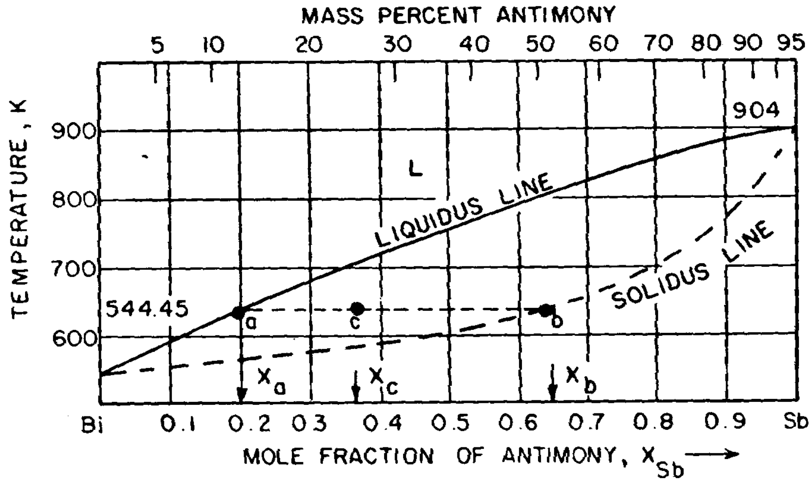


Figure 4-9 Temperature-Composition Diagram for Bismuth-Antimony

All of the techniques that you learned for the vapour-liquid systems can be applied to the solid-liquid system also. This includes the Lever-Rule for determining the relative amounts of the two phases present.

Figure 4-10 shows a minimum melting azeotropic system comprising Cesium-Potassium.

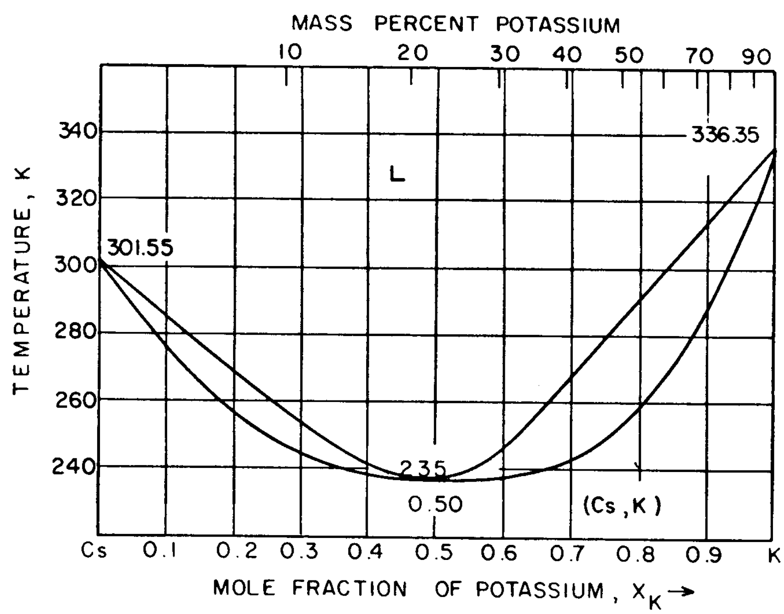


Figure 4-10 Temperature-Composition Diagram for Cesium-Potassium

At about 0.49 mole fraction of potassium, the mixture melts at about 235 ^{o}C, that is lower than the melting point of the pure metals. Also note that the two-phase region shrinks to nothing at the azeotropic point. The composition of liquid and solid phases would be identical for the azeotropic mixture.

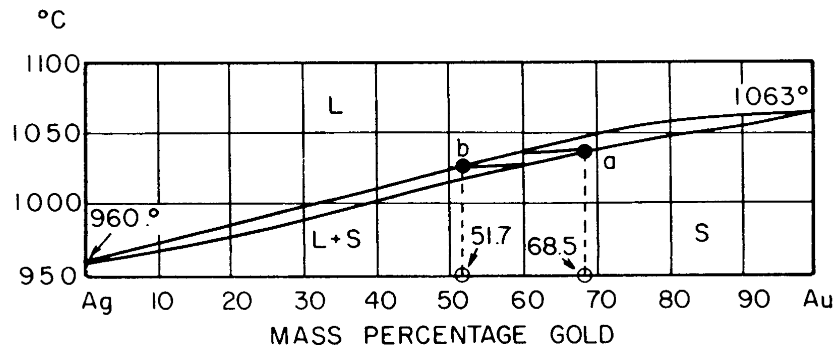


Figure 4-11 Temperature-Composition Diagram for Silver-Gold
(Diagram for Example Problem 4-9)

A third miscible solid system shown in the text is that of silver and gold.

In this case the two-phase region is the narrow zone between the two curves.

4.7.2 Immiscible Solids

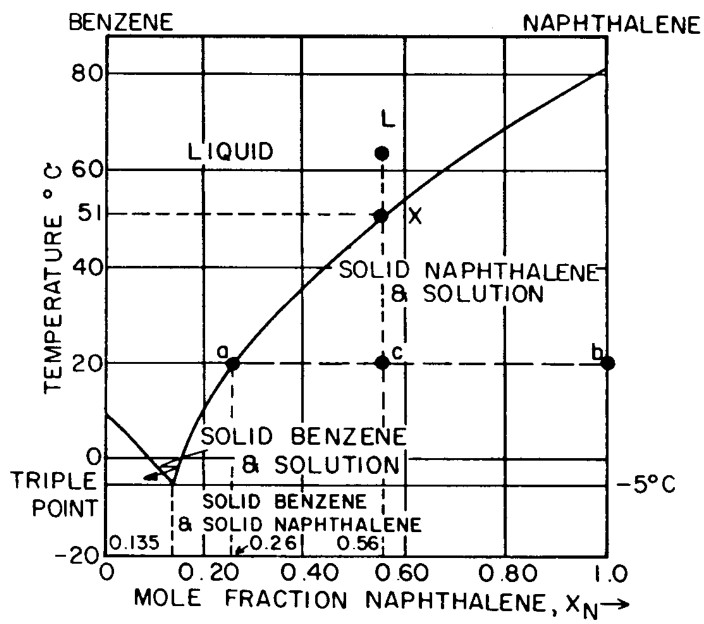


Figure 4-12 Temperature-Composition Diagram for Benzene-Naphthalene

To be miscible in the solid phase the two components must be similar in crystalline structure and molecular sizes. When different sizes and crystal structures are involved, the tow components could be totally immiscible in the solid phase. Yet, they may be completely miscible in the liquid phase. We will examine one such system, that of benzene (single-ring molecule) and naphthalene (two-ring molecule).

In the solid phase the two components crystallise in separate phases, but in the liquid phase there is complete miscibility. There are several noteworthy features of this phase diagram.

⇒ There are two two-phase regions, one representing pure benzene solid in equilibrium with a solution containing dissolved naphthalene in benzene, the other representing pure naphthalene solid in equilibrium with a solution of benzene in naphthalene.
⇒ There is a triple point at which the liquid is in equilibrium with both pure solids. This point happens to be at a temperature lower than the freezing point of both pure components.
⇒ A mixture with the lowest freezing point is called a "Eutectic Mixture."
⇒ The phenomenon of a mixture having a lower freezing point than the individual components is quite common. Any time you dissolve a different component in a pure liquid, you will lower the freezing point of the liquid. If you dissolve salt in water, the freezing point of water becomes lower. The process is called freezing point depression. This is the reason for using road salt to melt ice.

4.7.3 Partially Miscible Solids.

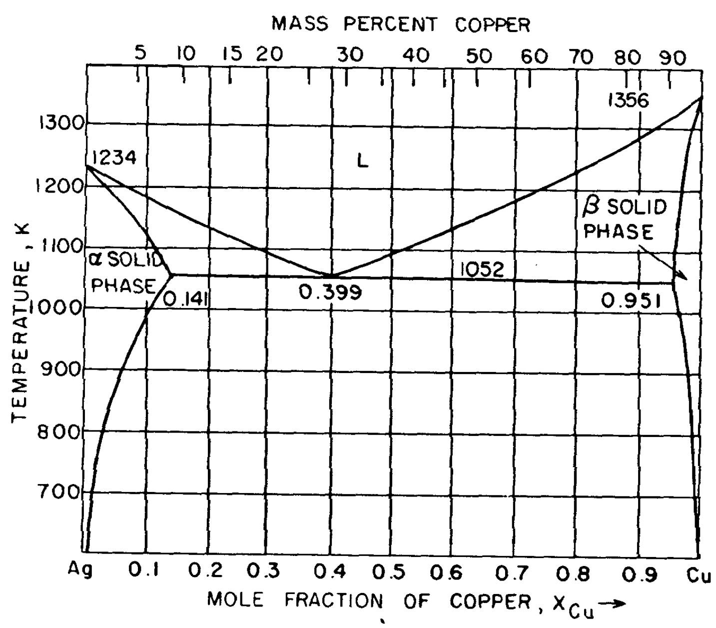


Figure 4-14 Temperature-Composition Diagram for Silver-Copper

Often you may find that there is partial miscibility in the solid phase. This is equivalent to the partially miscible liquid systems, where some mutual solubility exists in the liquids. Solids solutions may also show similar behaviour, i.e. one solid dissolves to a limited extent in the other solid. The text book presents two examples of partial miscibility in solids, in Figures 4-14 and 4-15.

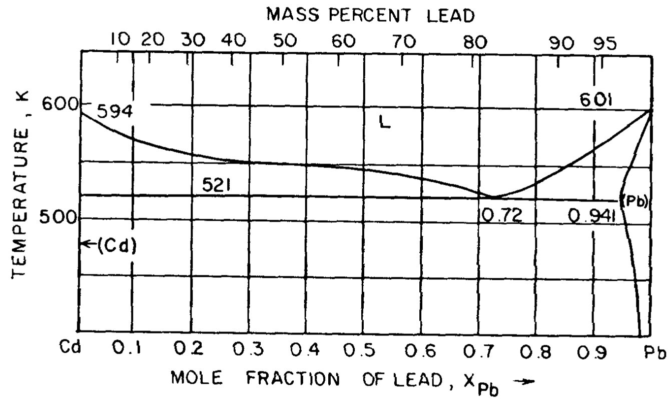


Figure 4-15 Temperature-Composition Diagram for Cadmium-Lead

Figure 14 shows the phase diagram for Silver Copper system. The two single solid phase regions, marked α solid phase and β solid phase represent solid solutions. The big region in the bottom half of the figure represents two-phase conditions where the two solid phases coexist.

The system shown in Figure 4-15 is that of Cadmium and Lead. In this case the single-phase region to on the left-hand side is very small, practically indistinguishable from pure cadmium line at this scale of drawing. It means that lead is practically insoluble in cadmium.

The single-phase region on the right hand side is relatively larger, reflecting the fact that cadmium is more soluble in lead.

4.7.4 Invariant Reactions

For a binary system, the phase rule tells us that,

$F = 4 - P$

If P = 3, F = 1. If we fix P or T, then all other intensive variables of the three-phase system are automatically fixed. If you fix P, equilibrium T for three-phases to coexist is automatically fixed. If you fix T, the equilibrium pressure at which three-phases will coexist is automatically fixed. Thus when three phases coexist, fixing one intensive variable makes all other intensive variables invariant.

The eutectic point in Figure 4-12 or 4-13 is such an invariant point. It is only one of the four different classes of invariant points in solid-liquid systems.

The term "invariant reaction" is used to describe the behaviour of three-phase systems. The use of word reaction in this case does not mean a chemical reaction. It is referring only to phase transformations.

Depending on what type of three-phase system is involved, we have several different types of invariant reactions.

Vapour-Liquid Systems can have only one type of three-phase system, L_1-L_2-V, i.e. two liquids in equilibrium with a vapour phase. The azeotropic points are the invariant points in such systems.

Liquid-Solid Systems can have four different types of invariant reactions.

i. **Eutectic:** meaning transformation of a homogeneous liquid to a mixture of two solid phases by cooling.

   L (eutectic) ----> $\alpha + \beta$

ii. **Monotectic:** means that the cooling of a homogeneous liquid produces a solid phase and a different liquid phase. The three-phase system of this type will have two immiscible liquids in equilibrium with a solid.

   L_1 -----> $L_2 + \alpha$

iii. **Peritectic:** It involves a situation in which a two-phase solid-liquid system, upon cooling solidifies to a different solid phase.

   $L_1 + \alpha$ ----> γ

iv. **Syntectic**: Here two immiscible liquids, upon cooling solidify to a single solid phase.

   $L_1 + L_2$ ----> γ

Solid-Solid Systems: There can also be situation in which three solid phases are in equilibrium with each other. Such systems can have three different invariant reactions.

i. **Eutectoid:** A single-phase solid, upon cooling produces two distinct solid phases.

   γ ----> $\alpha + \beta$

ii. **Peritectoid:** Here two immiscible solid phases become a single phase as a result of cooling.

$$\alpha + \gamma \text{ ----> } \beta$$

iii. **Monotectoid**: It is similar to the eutectoid in the sense that one solid phase transforms to two different solid phases as a result of cooling. The difference is that α and γ become structurally identical above certain temperature. We will examine a system of this type in the next section.