

4.6.1 Two Completely Miscible Liquids

An example of such a system is acetone and ethanol. A T-X diagram for this system at the atmospheric pressure is given in the text as Figure 4.6.

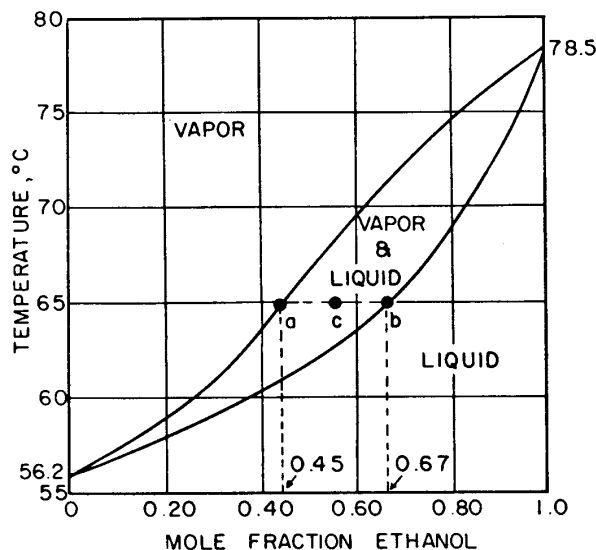


Figure 4-6 Temperature-Composition Diagram for the System Acetone-Ethyl Alcohol at One Atmosphere

Note that the x-axis represents mole fraction of ethanol. We could have selected mole fraction of acetone instead. Keep in mind that the two mole fractions must add to one, hence specifying one automatically fixes the other.

The top boundary of the two-phase region is called the dew-point curve. When the system's state is on this curve, the mixture would be almost all vapour in equilibrium with a tiny amount of liquid. The formation of condensation, or dew, starts when the vapour temperature cools down to this curve.

The bottom curve is called the bubble point curve. It represents the temperature at which the liquid mixture starts to boil to form the first bubble of vapour phase.

- Coming back to our system represented by point c, we can read the compositions of the gas and liquid phases directly from the diagram by reading the x-axis at point a and point b.
- What about the number of moles in each phase? That requires an application of the Lever Rule.

$$M_a = \frac{X_b - X_c}{X_b - X_a} M_c$$

and

$$M_b = \frac{X_c - X_a}{X_b - X_a} M_c$$

where:

M_c = Total number of moles in the mixture
 M_a = Total number of moles in vapour phase
 M_b = Total number of moles in liquid phase
 X_a = Mole fraction of ethanol in vapour phase
 X_c = Mole fraction of ethanol in the mixture
 X_b = Mole fraction of ethanol in liquid phase

These relationships can be derived by using conservation of mass principles.

$$M_a + M_b = M_c$$

$$X_a \cdot M_a + X_b \cdot M_b = X_c \cdot M_c$$

Multiply the first equation by X_b and subtract the second equation.

$$M_a \cdot X_b + M_b \cdot X_b = M_c \cdot X_b$$

$$X_a \cdot M_a + X_b \cdot M_b = X_c \cdot M_c$$

$$(X_b - X_a)M_a = (X_b - X_c)M_c$$

or

$$M_a = \frac{X_b - X_c}{X_b - X_a} M_c$$

To summarise, the binary P-X diagram can be used to obtain the following information:

1. Boiling point of pure components.
2. How many phases and what types of phases are present in a specified composition at given temperature.
3. Composition of all phases present.
4. Amount of material present in each phase, given the total amount present.
5. Bubble point and dew point of the mixture, given the mixture composition.

Let us see how this is done by an example, using Figure 4-6.

Boiling point of Acetone.

Boiling Point of Ethanol.

Consider 5 total mole of a mixture containing 70 % ethanol at 70 °C.

How many phase are present?

What is mole fraction of ethanol in vapour phase?

What is mole fraction of ethanol in liquid phase?

What is the bubble point temperature of the mixture?

What is the dew point temperature of the mixture?

How many moles of material are present in the liquid phase?

Two Completely Miscible Liquids with Azeotropic Point

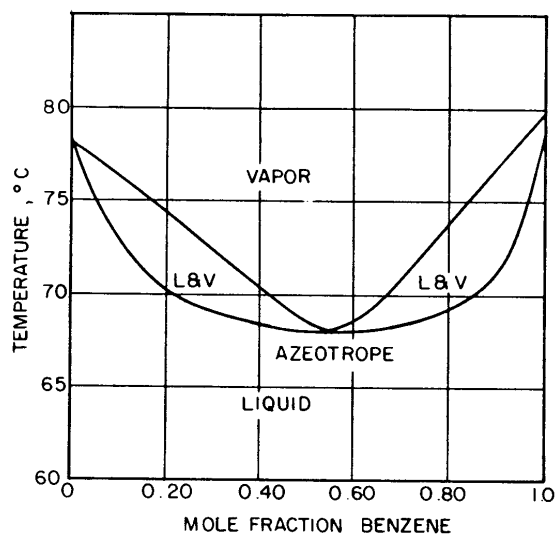


Figure 4-7 Temperature-Composition Diagram for the System Benzene-Ethanol at One Atmosphere

- A mixture in which the liquid and vapour have the same composition at equilibrium is called an "Azeotrope."
- The mixture is called "azeotropic mixture."
- On T-X and P-X diagrams, the two curves for bubble-point and dew point touch each other at the azeotropic point.
- Figure 4-7 in the text is an example of an azeotropic system. It shows behaviour of Benzene-Ethanol system.
- Both, pure benzene and pure ethanol boil at temperature around 78 - 79 °C. Note that the bubble point curve drops down from the pure component boiling points. The mixtures of these two components boil at lower temperatures than the pure components.
- The dew-point curve (the upper curve) touches the bubble point curve (the lower curve) at about 0.57 mole fraction of benzene. *If you draw a vertical line at this composition and consider the increase of temperature along this line starting from 60 °C. As you heat the liquid you will come to the bubble point of the mixture at about 68 °C. The entire mixture will boil off to a vapour phase at this temperature, because there is no vertical separation between the bubble point curve and the dew point curve. The composition of the first bubble formed in the system will be identical to the liquid composition.*
- Now consider a composition to the left of the azeotropic point, say at 20% benzene. As you heat this liquid and come to the bubble point curve, the composition of the first bubble formed is given by the intersection of a horizontal line at the bubble point and the dew point curve. Note that it will have more than 40% benzene. Thus boiling off a part of the mixture and condensing the vapours separately will give you a liquid richer in benzene. In the distillation process, we use repeated boiling and condensation of a binary

mixture to separate the two components. Note that an azeotropic mixture can not be separated by distillation. However, there are other separation techniques available.

- If the mixture composition was to the right of the azeotropic point, the first bubble formed will be richer in ethanol, since the dew point curve is now to the left of the bubble point curve.
- The system shown in Figure 4-7 is a minimum boiling azeotrope, since it boils at a temperature lower than the boiling point of the pure components and other mixtures.
- There are other binary systems that show a maximum boiling azeotrope, where the boiling point of azeotrope is higher than the boiling point of pure components and other mixtures.

Two Partially Miscible Liquids

In many cases the two liquids are not miscible in all proportions but show some mutual solubility. In such systems you can have two liquid phases in equilibrium with a common vapour phase. Figure 4-8 shows the T-X diagram for one such system comprising isobutyl alcohol and water.

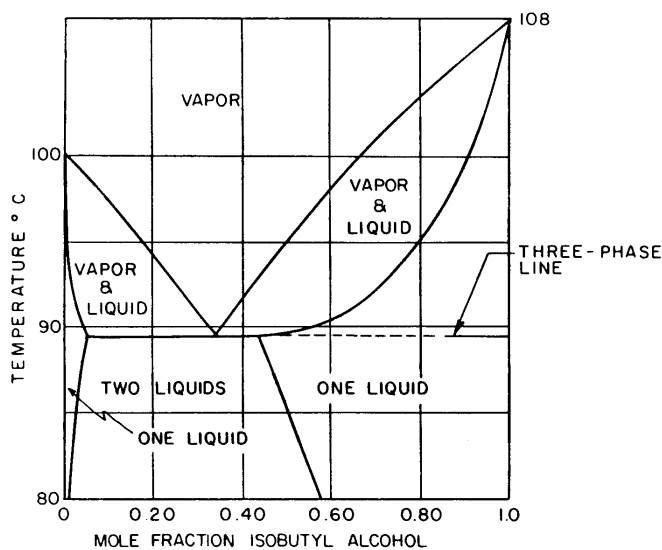


Figure 4-8 Temperature-Composition Diagram for Isobutyl Alcohol-Water at One Atmosphere

Recall that for a two component system,
 $F = 4 - P$

- When P is equal to three, $F = 1$. This degree of freedom is used up in fixing the temp at 1 atm. Hence the three-phase region on this curve will be a fixed point.
- There are two single-phase liquid regions on the two sides, in this system one small and one fairly large. These represent solutions of one component in the other. The small region on the left represents solutions of isopropyl alcohol in water. IPA has only a limited solubility in water that varies with temperature reaching a maximum at around 88

°C. The large one liquid region on the right hand side of the picture represents solutions of water in isopropyl alcohol. Water is much more soluble in IPA. The solubility varies from about 42 percent at 80 °C to 55% at 88 °C .

- The two-liquid region represents conditions under which the liquid phase splits into two immiscible liquids. The composition of these two liquids is given by the lines bounding this two-phase region. You can use the Lever-Rule in this area to determine the relative amounts of the two phases.
- The two areas labelled vapour and liquid, represent conditions under which a liquid exists in equilibrium with a vapour. In the vapour liquid zone on the left, you have a water-rich liquid in equilibrium with a vapour. The composition of this liquid is represented by the two-phase boundary line on the left. In the two-phase region on the right, you will have a vapour in equilibrium with an IPA rich liquid. The liquid composition is now given by the two-phase boundary line to the right.
- There is a point where the two vapour-liquid regions meet. This is the three-phase point where the vapour will be in equilibrium with both liquids.

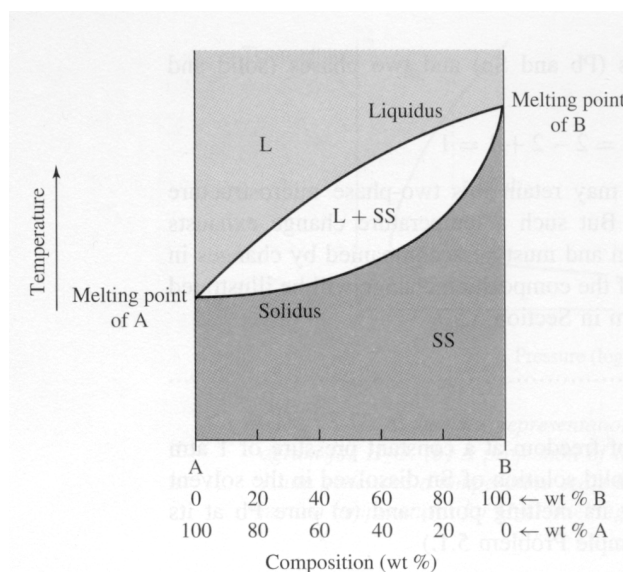
Completely Immiscible Liquids

This is a special case of the partially miscible system in which the single phase liquid regions shrink to infinitesimally small area and are represented by the vertical lines. The T-X diagram for such a system will look something like this.

5.6 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.

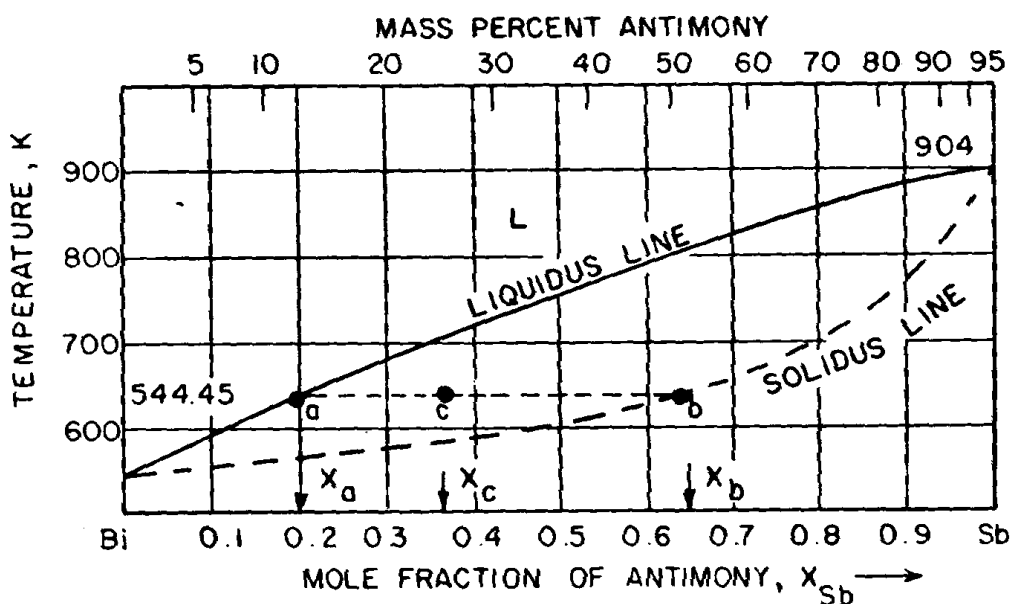


Figure 4-9 Temperature-Composition Diagram for Bismuth-Antimony

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.

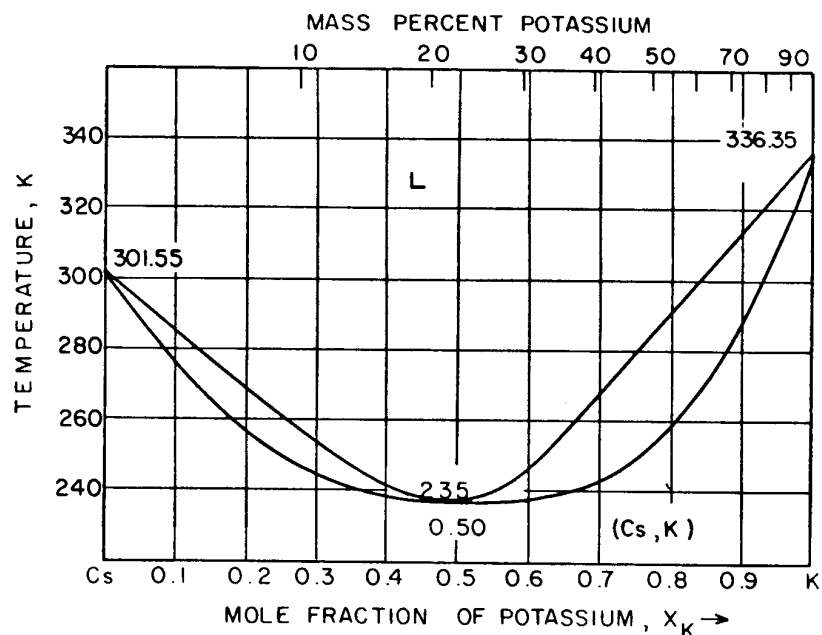


Figure 4-10 Temperature-Composition Diagram for Cesium-Potassium

At about 0.49 mole fraction of potassium the mixture melts at about 235 °C, which 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.

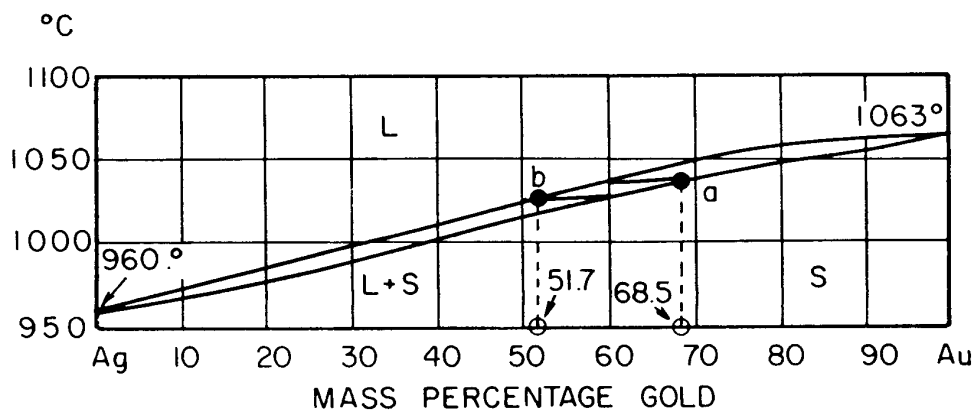


Figure 4-11 Temperature-Composition Diagram for Silver-Gold
(Diagram for Example Problem 4-9)

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.