Binary Solid-Liquid Phase Diagram

In this lab, the heterogeneous equilibrium between solid and liquid phases of a two-component naphthalene-diphenylamine system is investigated. The binary phase diagram is constructed by measuring the cooling curves of the mixture at different overall compositions. From the phase diagram, the eutectic temperature and composition of the mixture, as well as the melting points and heats of fusion for both naphthalene and diphenylamine, are determined.

For a pure substance, phase transitions occur at a characteristic temperature for a given pressure. At this transition temperature, the two phases are in equilibrium. A phase diagram shows the thermodynamically allowed regions of pressure and temperature for which a given phase can exist. The phase boundaries, designated by lines on the phase diagram, are pressure-temperature points where the two phases are in equilibrium. The triple point of a substance (point A in Figure 1) is the temperature and corresponding pressure coordinate for which all three phases are in equilibrium. The critical point (point B in Figure 1) is the point at which a supercritical fluid forms. A supercritical fluid is a state in which gas and liquid cannot be distinguished from one another.

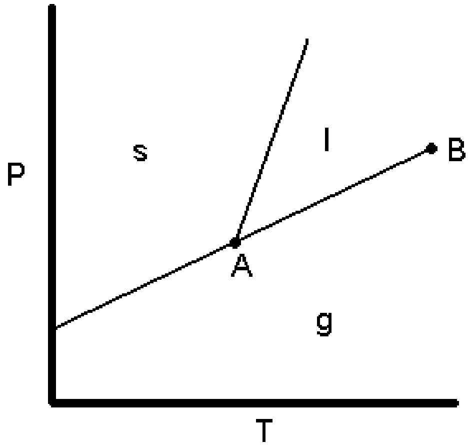

Figure 1. General phase diagram for a pure substance. Solid, liquid, and gas phases are separated by phase boundaries (lines). Point A designates the triple point. Point B designates the critical point.

A two-component system can have a much more complex phase diagram. In this case the stability of a certain phase depends on the pressure, temperature, and the composition of the solution.

The binary solid-liquid phase diagram in Figure 2 shows the stability of different phases as a function of temperature and composition at a given pressure. This particular example shows a case where the solid components are partially miscible. In this figure, α(s) represents a solid state mixture predominantly composed of substance A, with B present as an impurity, and β(s) represents the opposite case where A is an impurity. When a substance is dissolved in a liquid and the freezing point of the liquid is lowered, this is called freezing point depression. The shape of the phase boundaries between the α + liquid region and β + liquid region (the liquidus curves) describes the freezing point depression for this mixture. The equation for the liquidus curves can be derived from the Clausius-Claperyon equation under the assumption that the solution behaves ideally:

$$T(X_A) \approx T_{f,A} + \ln(X_A)\, RT_{f,A}^2/\Delta H_A = T_A - ((1-X_A) + (1-X_A)^2/2 + \ldots)\, RT_{f,A}^2/\Delta H_A \quad \textbf{(2)}$$

$T_{f,A}$ is the freezing point of compound A, and is also shown in Figure 2. ΔH_A is the heat of fusion for compound A and X_A is the mole fraction of compound A. An analogous equation can be written for compound B. The two liquidus curves intersect at the eutectic point, C.

Below the liquidus curves are two regions, α + liquid and β + liquid. The “α + liquid” region represents a mixture of α dissolved in liquid A and B, while the “β + liquid” region is a mixture of solid β dissolved in liquid A and B. The bottom-most region “α (s) + β (s)” is a solid solution of α and β. The regions at the edges of the phase diagram denoted α (s) and β (s) are present because the solids are partly miscible. For compounds that are less miscible, these regions are smaller, whereas for solids that are completely immiscible these regions would not exist. In the latter case, the regions of the phase diagram corresponding to the solid states α and β would be replaced by regions corresponding to pure A and pure B.

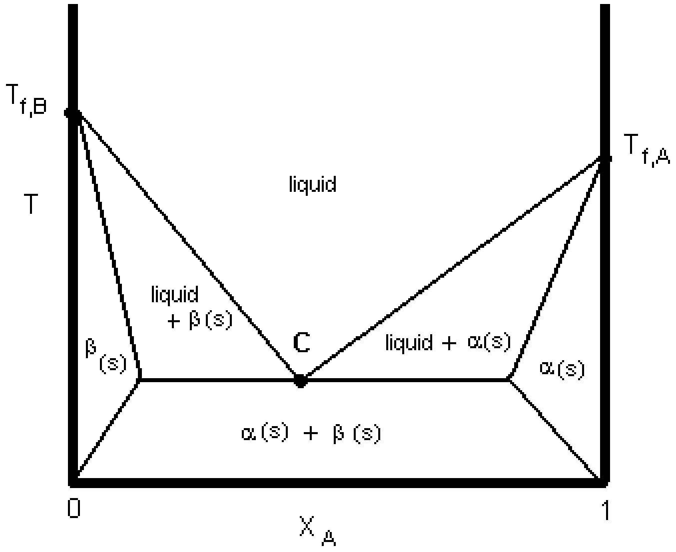

Figure 2. A general phase diagram for a two-component system in which the solids are partially miscible as a function of mole fraction of A (X_A) and temperature. Point C represents the eutectic point. $T_{f,A}$ represents the freezing point of pure A, while $T_{f,B}$ represents the freezing point of pure B. α(s) represents a solid state composed predominantly of A, with B present as an impurity; β(s) represents a solid state composed predominantly of B, with A present as an impurity.

The phase diagram can be constructed from observed changes in slope of the temperature versus time profile, or a cooling curve. In the absence of a phase change, the rate of change of the temperature obeys Newton's Law of cooling, which predicts an exponential approach to the ambient temperature. When a solid is formed, the rate of cooling is changed because part of the heat exchanged with the surroundings contributes to the phase transition. During the freezing process of a pure substance, the temperature remains constant, which is called a thermal arrest. In a two-component system, as the temperature is lowered, one component begins to freeze while the other component remains in the liquid state. During this type of freezing process, the concentration of the liquid mixture changes as more and more solid forms, which consequently changes the freezing point. For this reason, the rate of cooling is not constant, but is different from the rate of cooling of the original liquid mixture. This change in the rate of cooling is known as a thermal break. When the remaining liquid reaches a certain ratio of the two components, a thermal arrest is observed. This temperature and concentration point is known as the eutectic point. A common example of a eutectic mixture is solder, which is the eutectic mixture of tin (67%) and lead (33%) which melts at 183 ^{o}C.

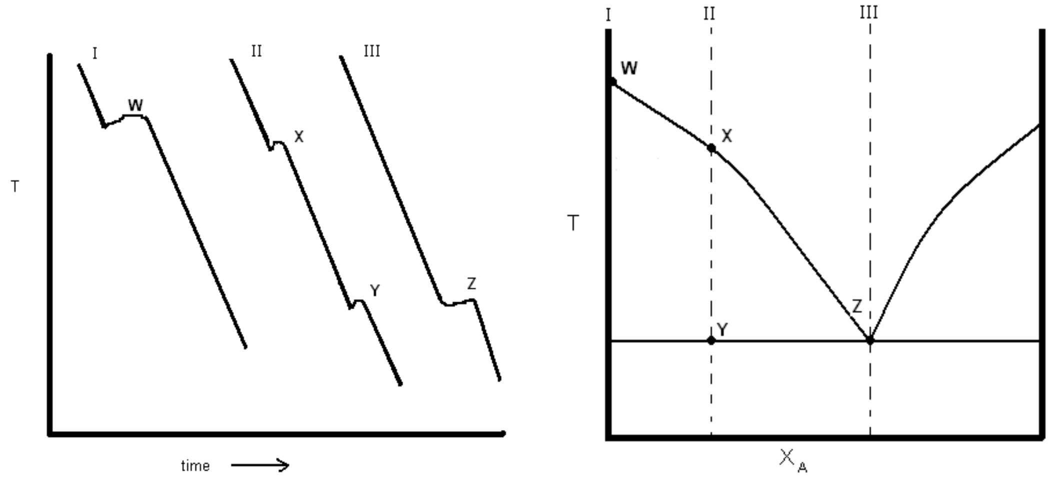

Figure 3. Example cooling curves and a corresponding phase diagram. W, Y and Z denote thermal arrests, and X denotes a thermal break.

EXPERIMENTAL

The binary system will be naphthalene-diphenylamine. The temperature measurements will be made with a thermocouple system. A thermocouple system produces a voltage proportional to the temperature difference between the two junctions. One junction is kept at 0°C by immersing it in a slushy mixture of distilled water and ice. The thermocouple system is attached to a chart recorder to plot voltage as a function of time to see the thermal arrests and breaks. Charts will be available in the lab to convert the voltage reading to temperature. A diagram of the apparatus is attached to the end of this document.

Make up the first mixture in as specified in Table 1 in a small test tube. Make sure to record exactly how much of each compound you add to the tube.

First Run

% Wt. N	Add to tube
100	0.50g N
90.9	0.05 g D
83.3	0.05 g D
76.9	0.05 g D
66.7	0.10 g D
58.8	0.10 g D
50.0	0.15 g D
40.0	0.25 g D
33.0	0.25 g D

Second Run

% Wt. N	Add to tube
0	0.50 g D
9.0	0.05 g N
16.7	0.05 g N
20.6	0.03 g N
25.0	0.037g N
28.0	0.03 g N
31.0	0.03 g N
34.0	0.03 g N

Table 1. Mixture details**.** Here, N stands for naphthalene and D stands for diphenylamine.

Next, it is necessary to obtain a cooling curve. To do this, one must first heat the mixture in a beaker of water until it is completely liquified. Remove the test tube from the hot water bath and insert a thermocouple. It is possible that some of the liquid mixture may have solidified on the tip of the thermocouple upon its insertion. If this is the case, return the test tube to the hot water bath until the solid mixture is completely remelted. Turn the chart recorder on. The small test tube can then be transferred to rest inside a beaker and allowed to slowly cool. While it is cooling, the mixture must be agitated.

When the mixture has completely solidified, the chart recorder can be turned off. You should see at the least a single arrest on the chart. Continue to add to the mixture as specified in Table 1. After adding a large amount of "impurity" to your original sample, it may be necessary to have an ice bath to cool the mixture.

CALCULATIONS

- On each cooling curve, determine the break and/or arrest temperatures using the thermocouple chart.
- Calculate mole fractions.
- Plot break/arrest temperatures vs. mole fraction. Find the liquidus curves by fitting with a polynomial fit trendline.

- Calculate the melting points of both naphthalene and diphenylamine from the phase diagram.
- Find the eutectic mixture and eutectic temperature from the intersection of the trendlines for the liquidus curves. Estimate the error.

References

Atkins, P. Physical Chemistry, 5th edition. New York: W.H Freeman and Company, 1994.

Levine, I. N. Physical Chemistry, 5th edition. New York: McGraw-Hill, 2002.

Shoemaker, D.P, Garland C.W., Nibler, J.W., Experiments in Physical Chemistry 7th edition. New York: McGraw-Hill, 2003.

White, M.A. Properties of Materials. New York: Oxford UP, 1999.

PHASE DIAGRAM APPARATUS