

Experiment 6

Phase Diagram of a Binary Solid-Liquid System

Purpose :

This experiment illustrates the use of cooling curves to establish the phase diagram for a binary system.

Principle :

The equilibrium or phase diagram which is obtained when two components are soluble in the liquid state, but insoluble in the solid state, is of the simple type shown in **Fig. 6-1**. In this diagram, curve *AE* represents the lowering of the freezing point of solvent *A* by solute *B*; it may also be considered to represent the solubility of *A* in solution. Similarly, curve *BE* may be designated either as the freezing point lowering curve of pure *B* or the solubility curve of *B* in solution.

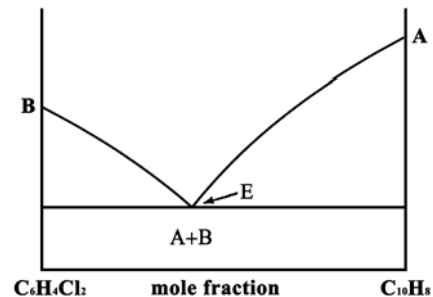


Fig. 6-1

The relationship between solubility and freezing point of a component in an ideal binary solution is given by the ideal solubility or freezing point equation.

$$Rd \ln x = \frac{\Delta H}{T^2} dT \quad (1)$$

Eq. (1) may refer to either component.

In the thermal analysis of a binary system, a selected number of mixtures of the two components are melted and allowed to cool. The cooling curves are made by recording the temperature at regular time intervals. **Fig. 6-2** show the cooling curves for two component system at various compositions. A thermal "arrest" indicates the solidification temperature of a pure component or a eutectic mixture. A "break" indicates a point corresponding to the temperature at which solid first appears at the given composition on the liquid curve.

Type 1 : **Fig. 6-2a** shows the cooling curve for a pure substance. When solid begins to form, we have two phases present and there are no degree of freedom. So the temperature is arrested or remains constant until all liquid has been converted into solid. The resulting solid will then cool at a rate proportional to the temperature difference of the object and its surroundings.

Type 2 : **Fig. 6-2b** shows the cooling curve for a typical mixture of two components. *AB* portion corresponds to the cooling of the liquid phase where no solid formation

takes place. The slope is determined by the specific heat of the melt and the temperature difference between the surroundings and the melt. When crystallization begins, there is a change in slope. The slope of the cooling curve is much less than that for cooling of a single phase. The abrupt change in slope, which occurs when a pure solid begins to form, is called a "break". The heat of fusion released slows down the cooling process. As the solid continues to form, there is a continuous lowering of the freezing point. The temperature becomes constant and there is no degree of freedom when the second solid appears at *C*.

Type 3 : Fig. 6-2c shows the cooling curve for a eutectic mixture. The temperature at which two solids coexist in the presence of the liquid is termed eutectic temperature and the composition of the melt is termed eutectic mixture. If we start with a melt consisting of the eutectic mixture, the cooling curve would have the same characteristics as the cooling curve of a pure substance. (Fig. 6-2a)

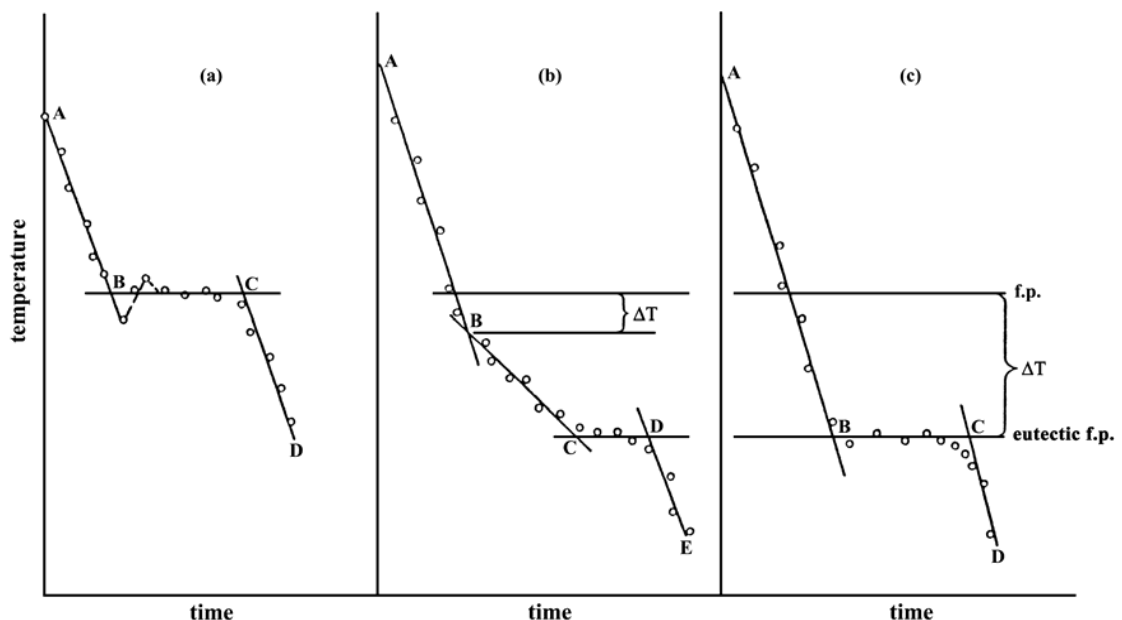


Fig. 6-2a.

Fig. 6-2b.

Fig. 6-2c.

When we discuss the diagram in Fig. 6-1, we have the following equation for the solid-liquid curve ("liquidus curve") starting from the left at T_A , the melting point of *A*:

$$T \cong T_A + \frac{RT_A^2}{\Delta \bar{H}_A} \ln(1 - x_B) = T_A + \frac{RT_A^2}{\Delta \bar{H}_A} (x_B + \frac{x_B^2}{2} \dots) \quad (2)$$

where $\Delta \bar{H}_A$ is the heat of fusion of *A*. Clearly this theoretical curve starts with a finite negative slope determined by the melting point and heat of fusion of pure component *A*; the slope increases in steepness with increasing x_B , so that the curve is concave downward. Similarly, for the liquidus curve starting from the right at T_B

we obtain

$$T \cong T_B + \frac{RT_B^2}{\Delta H_B} \ln x_B \quad (3)$$

The eutectic composition and eutectic temperature are given by the intersection of the two liquidus curves and can be estimated by solving simultaneously Eqs. (1) and (2), on the assumption that the liquid represents an ideal solution with respect to both components over its entire composition range. This assumption is often not even roughly valid, especially in metal systems.

Apparatus and Chemicals :

Eight test tubes; two test-tube clamps; rack; air jacket; 100°C thermometer; two 600-ml beakers; glass bar; spatula; heating vessel.

p-Dichlorobenzene; biphenyl.

Procedures :

- (1) Prepare eight test tubes containing different composition of p-dichlorobenzene and biphenyl. The compositions are 0, 15, 30, 45, 60, 75, 90, and 100 percent biphenyl by weight and the total weight is 2g for each mixture.
- (2) One of the prepared tubes is heated in a beaker of hot water until the mixture is completely melt and a thermometer is put into place. Wipe the tube dry, then the tube is placed in air jacket and the whole assembly is dipped into water contained in the beaker.
- (3) Stir continuously. Obtain cooling curve for the mixture by recording the temperature of the mixture at 10 sec interval. Record 20 more temperature readings until the sample has solidified.
- (4) At the end of the experiment, do the following steps in sequence. Liquefy the mixture by warming the test tube in warm water. Pour the contents into a designated disposal container.

Calculations :

- (1) Plot temperature vs. time to obtain corresponding arrest temperature (melting point or eutectic point) or break temperature (first melting point of a mixture).
- (2) Convert weight-percentage compositions to mole fractions.
- (3) Plot the break and arrest temperatures against the overall composition (mole fraction of biphenyl). Draw the eutectic line and the liquidus curves to obtain the eutectic composition and temperature. Label all fields to show the phases present.
- (4) Using the experimental data of mole fraction and freezing point, prepare a graph using the logarithms of the mole fractions of p-dichlorobenzene and biphenyl as

ordinates and the reciprocals of the absolute temperatures as abscissas. Obtain the slope of the curves at the melting points of pure p-dichlorobenzene and biphenyl and calculate the average molar heat of fusion of each component using Eq. (1).

References :

- (1) **P. W. Atkins and J. de Paula**, "*Physical Chemistry*," 9th ed., pp. 185-186, Oxford University Press, U.S.A (2010).
- (2) **D. P. Shoemaker, C. W. Garland, and J. W. Nibler**, "*Experiments in Physical Chemistry*," 5th ed., pp. 238-246, McGraw-Hill, Singapore (1989).
- (3) **F. Daniels** and others, "*Experimental Physical Chemistry*," 6th ed., pp. 116-121, Europe-Asia book company, Taiwan (1956).
- (4) **O. F. Steinbach and C. V. King**, "*Experiments in Physical Chemistry*," pp. 110-114, American book company, U.S.A. (1950).