A Binary Solid-Liquid Phase Diagram  
Experiment Including Determination of Purity,  
Enthalpy of Fusion and True Melting Point

In a study of the thermodynamics of solution of various solutes in liquid mixtures of \( n \)-tetracosane (\( C_{24} \)) and di-\( n \)-dodecyl thiourea (\( C_{24}S \)) a question arose regarding the extent of non-ideality of the solvent mixture. Because of the low vapor pressures of these substances, and the fact that we were working in the temperature range only slightly above the melting points of the mixtures, it was decided that an examination of the solid-liquid binary phase diagram of \( C_{24} \)-\( C_{24}S \) mixtures might provide the information we needed.

The experimental set-up used was so simple, and the results so good, that we think it offers an attractive alternative to the undergraduate experiments described in popular laboratory texts. These seem limited to high temperature metal systems, or lower temperature systems involving objectionable or unstable materials (e.g. naphthalene:diphenylamine; \( p \)-dichlorobenzene: \( o \)-cresol).

Advantages of the experiment described herein are as follows:
1. The systems were never heated over 80°C. Cooling in undisturbed, room-temperature air leads to very satisfactory temperature-time curves.
2. The compounds in question are stable for years when stored without any precaution beyond using a closed container.
3. They are commercially available at better than 97% purity \(^1\) (Humphrey Chemical Co., New Haven, CT)
4. They are not hazardous chemicals.
5. Only small amounts are required (1–1½ g per cooling curve).
6. Quite respectable-looking phase diagrams are obtained without stirring, presumably due to the thinness of the sample under study.

An extension of the usual experiment, which to our knowledge has not been described in undergraduate laboratory texts, is the estimation of purity of each "pure" component of the series of mixtures. It involves no extra data collecting and is based on the same principle as the rest of the experiment. \(^2\)

**Experimental**

Convenient mole fractions of the thiourea are 0.0, 0.2, 0.4, 0.6, 0.8, 0.9, 0.95, and 1.00. Samples are weighed directly into 3-in. test tubes which are chosen to fit closely onto the end of a thermometer gradu-ated in 0.1°C intervals. \(^3\) The test tube full of the solid mixture is heated carefully with a heat lamp until all of the sample is melted. For the test tubes we used, the shrinkage of the sample on melting was compensated for by insertion of the thermometer. The latter is removed and inserted several times to provide adequate mixing of the components, and a wire (common bell-wire is good) looped around the test tube under its lip is attached to the top of the thermometer to hold the sample in place. The unit is then placed in a clamp on a ring stand. The heat lamp is used to heat the sample to about 75°C, turned off and removed from the vicinity of the experiment. When the mercury hits 65°C, a stop watch or timer is turned on, and readings are taken every 10 or 20 sec until room temperature is approached.

Interpretation of the curves is described adequately in many laboratory texts. We observed the eutectic mixture at a \( C_{24}S \) mole fraction of 0.88, and \( t \approx 34.9°C \). (See Fig. 1.)

**Estimation of Purity**

The estimation of purity will be illustrated with our data for "pure" \( C_{24}S \). The cooling curve is shown in Figure 2. The mole fraction of the impurity in the sample is related to the slope of a plot of equilibrium temperature versus the inverse of the fraction, \( F \), of the sample melted. The relationship may be derived as follows:

The fundamental equation on which the experiment is based may be written

\[
\frac{dT}{d \ln x} = \frac{RT^3}{\Delta H_f}
\]

where in the present instance, \( x \) is the mole fraction of the

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\(^1\) The \( C_{24}S \) was recrystallized from EtOH before use.
\(^3\) We used a Sargent-Welch Cat. No. S-80210-B, which, being a total immersion thermometer, requires the addition of a small stem correction to the break and arrest temperatures.
sample in solution with a small amount of unknown impurity. We use the approximation that for  

\[ x \approx 1, \ln x = -(1 - x), \]  

which may be written \(-x_{imp}\), the mole fraction of impurity present. Thus,  

\[ \frac{dT}{dx_{imp}} = \frac{-RT^2}{\Delta H_f} \tag{2} \]

Now as long as the impurity is excluded from the crystals as the sample solidifies, \( x_{imp} \) at any time may be expressed in terms of the impurity mole fraction in the original sample, \( x^0_{imp} \), and the fraction of the sample remaining uncrystallized, \( F \):  

\[ x_{imp} = x^0_{imp}/F \tag{3} \]

Substituting into the above expression, we may write  

\[ \frac{dT}{d(1/F)} = \frac{-RT^2}{\Delta H_f} x^0_{imp} \tag{4} \]

where the left-hand side is, for a small range of temperature, the slope in question.

\( F \) is estimated by drawing three straight lines over the cooling curve as indicated in Figure 2. The left intersection is assumed to correspond to \( F = 1 \), the right intersection to \( F = 0 \), and intermediate values are assumed linearly proportional to the distance between the end points. In choosing values \((1/F, T)\) for the plot, two considerations must be kept in mind: (1) For reasonably pure samples, temperatures near the left end will vary so slightly with \( F \) that the thermometer will not detect any change; (2) as the right end of the solid-liquid region is approached, the impurity becomes more and more concentrated in the liquid phase, and the assumption upon which the linearity of the plot is based becomes untenable. Thus, we desire points as close to the left side as will allow detectable changes in equilibrium temperature. Figure 3 shows a plot of the points indicated in Figure 2. The temperature corresponding to \( 1/F = 1.0 \) represents the actual melting point of an absolutely pure sample; 40.18°C in this case. Perhaps the best way to appreciate the latter is to consider the integrated form of eqn. (2):  

\[ T = \frac{-RT^2}{\Delta H_f} x_{imp} + C = \frac{-RT^2}{\Delta H_f} x^0_{imp}(1/F) + C \tag{5} \]

We evaluate the constant of integration, \( C \), by noting that when \( x_{imp} = x^0_{imp}(1/F) = 0, T \) represents the melting point of the sample under study, and that at \( 1/F = 0, \) the melting point of an absolutely pure sample. In terms of Figure 3, the intercept should be thought of as the value of \( T \) corresponding to \( x_{imp} = 0 \), rather than the temperature at which the fraction melted is infinite.

In order to use eqn. (4), we need a value for \( \Delta H_f \) for \( C_z4S \). The student should recognize that eqn. (1) can provide that value given equilibrium temperatures for solutions of \( C_z4S \) with known amounts of impurities. But these are precisely the data which he or she has already obtained. The “impurity” is \( C_z4S \). By plotting \( \ln x \) versus \( 1/T \) for the \( x = 0.9, 0.95, \) and 1.0 solutions, we find excellent linearity (the solutions are apparently very nearly ideal in this range) and an enthalpy of fusion of 7.76 kcal mol\(^{-1}\). This value substituted into eqn. (4) along with our slope \((-0.132 \text{ K})\) and \( T \) (313.33 K) yields \( x^0_{imp} = 0.0053 \) for our sample of \( C_z4S \).

There is some uncertainty about the location of the point at which \( F = 0 \) in Figure 2, but it is not a quantity upon which the “true” melting point and the calculated purity of the sample depend strongly. For example, we also chose the intersection of the vertical right line with the cooling curve itself as the point corresponding to \( F = 0 \). The resulting analysis gave the “true” melting point as 0.04° higher, and the purity as 0.002 lower in mole fraction.

The additional estimation of purity and evaluation of “true” melting point add much to the conventional experiment, since in many actual cases such an analysis provides the researcher with the most reliable estimate of the purity of a substance. Furthermore, it illustrates the somewhat paradoxical fact that, as long as no solid solution forms, thermodynamic analysis allows the measurement of the melting point of a perfectly pure substance using an impure sample.

As a postscript, it might be pointed out to the student that proper use of the method involves an adiabatic calorimeter (which insures thermal equilibrium and a reliable estimate of \( F \)) and a thermometer that measures in millidegrees. It is the prohibitive cost of such equipment that forces us to settle for a more approximate experiment which still does a good job of illustrating the principles involved.

**Acknowledgment**

Dr. Jurgis A. Anyšas provided helpful suggestions which improved the quality of this paper.

\*Strictly speaking, of course, we should divide both sides by \( T^2 \) before integrating; however, the range of \( T \) is so small in this application that treating \( RT^2/\Delta H_f \) as a constant has no practical effect whatever on our results.