Purity and Identification of Solids Using Melting Points

Stew Dent
CH 337, Section 059
Department of Chemistry
Portland State University
Portland, OR

Abstract

Class-obtained melting points were used to create a melting point diagram of naphthalene and biphenyl. The eutectic point was estimated by extrapolation to be at 45 mole percent naphthalene. Unknown "A" was determined to be benzophenone by mixed melting point method.

Introduction

Melting points are used to help determine the purity and identification of solids. A melting point is the temperature at which a material melts at atmospheric pressure.[1] Melting points are usually expressed as a range between when the material begins to melt and when it has completely melted. A material is said to have a sharp melting point if the range is less than 5ºC, and a material is said to have a broad melting point if the range is greater than about 5ºC. Pure compounds characteristically have a sharp melting range while most mixed or impure compounds have a broad melting range. The notable exception is a eutectic mixture, which is a unique mixture that nevertheless has a sharp melting range. Another characteristic of melting points is their depression upon introduction of impurities or mixing. This can sometimes allow a pure compound to be distinguished from a eutectic mixture.

Melting point depression is useful in identifying unknown solid compounds. Simply ascertaining the melting point of an unknown compound is insufficient to identify the unknown because many chemicals have the same, or very similar, melting points. For positive identification of an unknown substance a mixed melting point must be performed by combining the unknown substance with different known substances and taking the melting points of the mixtures. Melting point depression will not be exhibited only if the unknown and known substances are the same compounds, allowing for positive identification.

Experimental

The experimental procedures for this lab are found in the PSU lab manual.[2] All chemicals used were obtained from the PSU Chemistry Stockroom.

Small samples of 100% biphenyl, 90% biphenyl/10% naphthalene mixture and 50% biphenyl/50% naphthalene mixture were obtained and placed in a spot plate. All three samples were pulverized, loaded into a standard closed end capillary tube and labeled. The capillary tubes were then placed in a Mel-Temp apparatus where they were gradually heated (0.1º/sec). The temperatures were recorded at the sign of the first drop of liquid and when the sample had turned completely to liquid. Two trials were done for each sample.
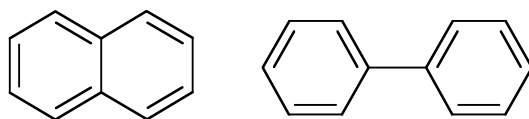

Figure 1: Naphthalene and Biphenyl

Data were collected from other students in the class for the following compounds and mixtures: 100% naphthalene, 90% naphthalene/10% biphenyl, 70% naphthalene/30% biphenyl, 50% naphthalene/50% biphenyl, 30% naphthalene/70%

biphenyl, 10% naphthalene/90% biphenyl, 100% biphenyl. The initial and final temperatures were averaged for each sample and reported on the melting point diagram.

Mole percentages were calculated from mass percentage using the following equation: (N=naphthalene, B=biphenyl)

$$\text{Mole\% N} = \frac{\text{mass\%N x (1 mole/128 g)}}{(\text{mass\%N x (1 mole/128 g)}) + (\text{mass\%B x (1 mole/154)) g))}}$$

The melting point diagram was constructed by plotting the average initial and final melting points against the mole % of naphthalene using Excel.

A small sample of unknown "A" was obtained and placed in a spot plate. The sample was pulverized and loaded into a standard closed-end capillary tube. It was gradually headed (0.1°/sec) using a Mel-Temp device. The temperatures were recorded at the sign of the first drop of liquid and when the sample had turned completely to liquid. This melting range was then compared to the melting points of eight "knowns." Small samples of the solids that had similar melting points were obtained and placed in a spot plate. An equal amount, by mass, of Unknown "A" was added to each sample and each of the mixtures was mixed and pulverized. Each mixture was placed in a closed-end capillary tube, labeled and the melting point determined using a Mel-Temp. The initial and final melting points were recorded.

Results and Discussion:

From the class melting point data, the melting point diagram was constructed (Table 1). The pure compounds in the graph show the smallest melting range and all the mixtures exhibit broader melting ranges and overall melting point depression as compared to the pure solids. The eutectic point appears to lie between 33% and 75% (mole %) naphthalene.

Figure 2:
Melting Point Diagram of Naphthalene and Biphenyl
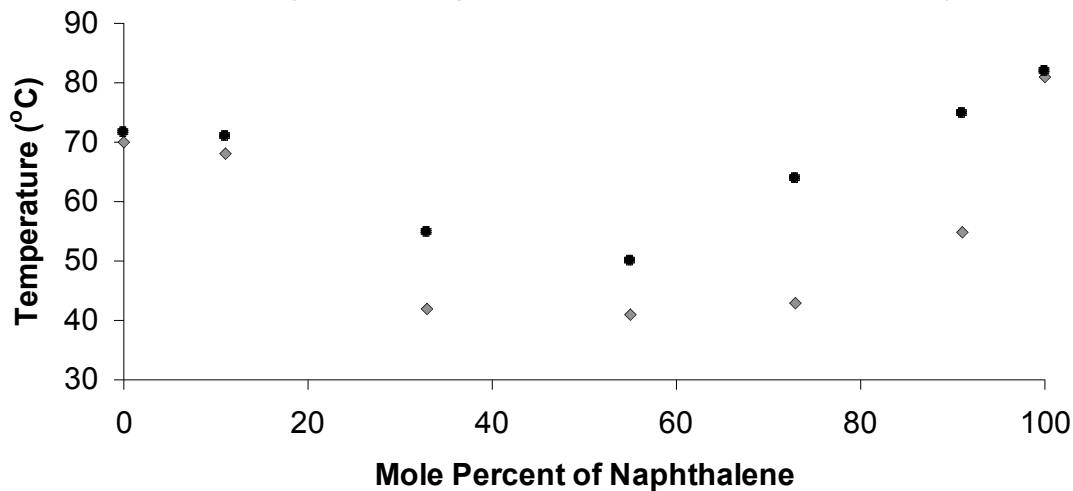
Several more melting points of mixtures between these would be needed to narrow the range. With the given data, an extrapolation of a eutectic point around 45% naphthalene and a temperature around 30º seems most probable. Discrepancies in the data may reflect the many different experimenters, equipment, and rates of heating. Each of these random errors could allow for movement of the data in either direction. In spite of the lack of precision among the various trials, the average melting ranges from the class data for pure naphthalene (80.0-82.7ºC) and pure biphenyl (68.8-72.0ºC) correspond well to the literature values for these compounds, which are 80.2 ºC[3] and 71.0,[3] respectively.

Unknown "A" was found to have a melting range of 44.7 to 46.3 ºC. The only two given pure compounds with similar melting ranges were benzophenone (47 ºC) and hydrocinnamic acid (47 ºC). The mixture of the unknown and benzophenone produced a mixture that melted at 45.2-46.7 ºC and the mixture of the unknown and hydrocinnamic acid produced a mixture that melted below room temperature. The melting point depression of the hydrocinnamic acid mix indicates that it is acting as an impurity. This rules out hydrocinnamic acid as the unknown. The benzophenone mixture had a melting point similar to both pure benzophenone and the unknown. This indicates that unknown "A" is benzophenone.

Conclusion

Purity and identity can often be determined using melting pints. The sharp melting points of pure naphthalene and biphenyl, the depression and broadening of the melting points of their mixtures, and the eutectic point near 45% naphthalene illustrate the characteristics of melting points. Melting points also determined that unknown "A" was benzophenone.

References
[1] Fessenden; Fessenden; and Feist, Organic Laboratory Techniques, 3rd Ed, Brooks Cole: California, 2000

[2] PSU Chemistry 337 Lab Manual, 2006

[3] CRC Handbook, CRC Press: New York, 1999