Purity Analysis of Highly Purified Materials by Time-Temperature Cryometry

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Visual observation of the freezing and melting of compounds in cells used for the determination of purity has uncovered some heretofore unexpected behavior. This behavior has been correlated with certain difficulties experienced in the measurement of purity, particularly when the sample is very pure. Means for partially reducing these difficulties are proposed and procedures for increasing the accuracy of purity measurements are described.

1. Introduction

The usefulness of cryometry as a method of determining the purity of a compound has been well established. The time-temperature apparatus and technique developed by Rossini and coworkers [1] have been widely and successfully used. However, several years ago both Cines [2] and Mathieu [3] published comparisons between the results as obtained by the time-temperature techniques and those obtained by the use of a precision adiabatic calorimeter. Samples of various compounds were analyzed and serious differences between the two methods were found to exist. The differences in the results obtained by the two techniques were particularly significant when the more highly purified materials were analyzed. In these comparative studies, there appeared to be reasonable evidence supporting the view that, under the experimental conditions employed, the results obtained by using the adiabatic calorimeter were more reliable.

Enclosed freezing point cells [4], improved sample transfer [5], and a new method of analyzing data [6] have greatly improved the precision and accuracy of the time-temperature cryometric analysis.

This paper describes techniques used to explore further the utility of time-temperature cryometry into the region of highly purified materials, an area wherein previous work exhibited the most serious discrepancies. It will be seen from section 5, table 1, that the apparatus and techniques described give highly accurate results when used in the determination of purity of simple organic compounds.

2. The Freezing-Melting Curve

The apparatus and general experimental details discussed in this paper are modifications of those discussed in references [1, 4, and 5]. The success of any time-temperature cryometric determination of purity is dependent upon introduction of the sample without contamination, establishment of good thermodynamic and thermal equilibrium during the freezing process, and proper analysis of the experimental data. Under the experimental conditions imposed, the time-temperature freezing curve should be hyperbolic, and when materials of moderate purity are analyzed in the apparatus and by the procedures described in [4] the freezing curve exhibits normal behavior. However, with high purity material (99.99+ percent), after initial recovery from supercooling, the observed temperature continues to rise until a large fraction (approximately 50 percent) of the sample is frozen. Beyond this point, the temperature falls rapidly. If the sample is melted after being about 35 percent frozen, the melting experiments produce the normal hyperbolic curves. These melting curves may be used to establish the sample purity, but in general such determinations are less accurate than those obtained from a well-performed freezing curve.

These anomalies in the freezing curves of highly purified materials have been observed for several years. At first they were thought to be associated with specific compounds, but as more materials of high purity were analyzed, it became strongly indicative that the unusual behavior was a result of the purity itself. Figure 1 depicts the general type of phenomenon observed during freezing and melting as described previously. This type of behavior has been observed with highly purified samples of benzene, titanium tetrachloride, carbon tetrachloride, dimethyl phthalate, dichlorostyrene, isopropyl alcohol, certain metallo-organic compounds, and various isomers of dichloroethylbenzene.

Since the accuracy of the time-temperature cryometric measurement in the stirred cells is so dependent upon the ability to analyze the freezing curves, an investigation into the causes of the abnormal character of such curves was undertaken. For this work, unsilvered cells were used so as to permit visual observation of the freezing process. Samples of materials ranging in purity from 99.0 percent to 99.999 percent were used. It was observed that crystallization in the stirred cells always commenced on the inner surfaces of the
The crystal was strong enough to stop the stirrer. The crystalline mantle surrounding the thermometer well also continued to grow, but the liquid quickly became opaque and gave the appearance of having a very large number of small crystals in suspension.

Contrariwise, with the very pure materials, the sheath was a clear hard mass which was not dislodged by the stirrer action. Instead, it continued to grow from the wall and, encroaching upon the stirrer space, the crystal was strong enough to stop the stirrer. The crystalline mantle surrounding the thermometer well also continued to grow, but the dendritic growth disappeared. Because of poor stirring the dendritic crystals sank to the bottom and were incorporated into the crystalline mass growing there. As crystallization continued, the crystal sheath adhered tenaciously to the thermometer well. A typical time-temperature freezing curve resulting from this type of freezing behavior is shown in Figure 1. An approximate temperature scale is shown, corresponding to the temperature changes which occur when a material of high purity, 99.999 percent, is frozen and melted.

The melting process was also watched. If the sample was warmed as it reached point C (fig. 1), the first effect was the melting of the outer crystalline mantle. As this solid became detached from the cell walls and was included in the liquid, much better stirring was achieved. During this initial melting period the crystalline mantle around the thermome-
these particles is not known. They appear to act as crystal supports, suspended in the liquid. The crystalline mantles are quickly broken up and the large amount of suspended crystal causes thermal equilibrium to be obtained. It is probable that other materials could be satisfactorily used for this purpose; samples of diatomaceous earth added to samples of carbon tetrachloride or benzene exhibited no apparent effect.

3. Data Processing

The end result of the time-temperature freezing experiment is, of course, the determination of purity of the sample. The thermodynamic relationships, the theoretical proof that the experimental curve should be hyperbolic, and the usual methods of fitting the curve are well known and will not be discussed here. Basically, the analyst is interested in determining two numbers, the freezing temperature of the particular sample and the freezing point of the sample had there been no impurity present. Both of these numbers are obtained by fitting the data to the equation of a hyperbola. Extrapolation of this curve to the intersection of the liquidus cooling curve provides the freezing point of the sample, and further extrapolation to the asymptotic value provides the temperature at which the sample would have frozen had there been no impurity present.

When one is analyzing several samples of the same material but of different purity levels, the freezing points of the individual samples will vary as a function of the impurity present, but the extrapolated value for \( T_{f0} \), the freezing point of the pure material, should be invariant. This rule provides a valid test for any curve fitting technique. With this as a criterion, several hundred freezing point curves were analyzed, using a series of rather arbitrary curve-fitting rules. As a result it was found that only within the limits of 10 percent and 30 percent frozen, was the value of the experimentally determined \( T_{f0} \) invariant with respect to the purity of the particular material. The need for the lower limit follows directly from the argument that there must be a critical ratio of crystal area to liquid volume before temperatures corresponding satisfactorily to thermodynamic equilibrium can be registered by the thermometer. The upper limit of fraction frozen is the result of increased stirring energy and decreased stirring efficiency. These limits, imposed by particular apparatus and experiment design, seem to hold for all materials analyzed to date.

Other corrections which must be considered by the analyst include factors such as the significant change in heat capacity of the sample on freezing. Because of the difficult theoretical evaluation of the effect of these corrections on the freezing point equation, perhaps the best and most elegant method of fitting the data to an empirical curve is that of Saylor [6]. In this method, a series of positive transparencies of hyperbolae whose asymptotic intersection produces an angle of from 90 to 95° are first made. These 4 x 5 in. transparencies are placed in a photographic enlarger. The recorded freezing curves are placed under the enlarger so that by increasing or decreasing the magnification, the projected curve can be made to coincide with the experimental curve. Special holders for the transparencies and the recorded freezing curves are used. They allow the movement of each independently, without changing the coordinate interlock between the two. When the "best fit" is obtained, the experimental curve and the coinciding projection are photographed using a 35 mm camera mounted adjacent to the projector. The developed film serves as a permanent record, and the enlarged print may be used to calculate the purity.

By applying the fitting limit rules described previously, and by selecting the correct hyperbolic transparency, the fitting and subsequent calculation of purity is made very easy. Since, usually only 30 to 35 percent of the sample is frozen, the liquid cooling slope is used. The errors introduced by this substitution are negligible.

4. Experimental Detail

When compounds are less than 99.9 mole percent pure, inadvertent contamination during transfer is a relatively minor problem. As long as the samples do not react with air or water and if the containers are reasonably clean and dry, little relative contamination results from pouring or pipetting the sample from one container to another. However, with materials which have a total impurity of less than 10 parts per million, water in the atmosphere or adsorbed on the walls of the container, cell, and transferring manifold can easily increase the amount of impurity by a factor of 10 or more. It is obvious that if complete exclusion of water and air is desired, the sample must be transferred by and analyzed in a closed, evacuated system. The following describes a technique for transferring high-purity samples from a glass ampoule, equipped with a breakoff tip, to the freezing-point cell.

4.1. The Transfer of Highly Purified Materials

The transfers were carried out in all-glass evacuated systems containing no lubricated joints. Such a system is shown in figure 2. All parts were treated with hot chromic acid, water-rinsed, cleaned with warm, concentrated nitric acid, and finally rinsed several times with distilled water. The powdered glass, mentioned previously, was treated in the same fashion as the other glassware and placed in the cell prior to final assembly. The apparatus was then assembled and dried by evacuation to \( 10^{-6} \) mm Hg while being continuously heated at 150 °C for 24 hours. Previous experience [5] indicated that even after this treatment for the 24-hour period some water was still adsorbed on the inner glass surfaces.

The manifold was flame-sealed at constriction F after evacuation. Then the breakoff tip of ampoule I was broken and a portion of material similar in composition to the sample was distilled throughout the system. This wash liquid was returned to the ampoule after several hours of refluxing. As much
of this material as possible was poured back into the
ampoule by turning the entire apparatus manually.
The remaining material was distilled into the
ampoule by cooling container I with liquid nitrogen.
This ampoule was then removed by sealing at E.
The breakoff tip of ampoule A was broken, and the
desired amount, usually 40 ml, was poured into the
graduated tube J. After both A and J were cooled
to liquid nitrogen temperature, the sample ampoule
A was removed by sealing at D. The melted sample
was poured into the cell and again frozen. Next
the measuring tube J was removed by sealing at K.
The breakoff tip L was used in removal of the
sample from the cell after the analysis had been completed.

Previous experience [5] had shown that the pour-
ing operation is to be preferred to distillation since
there can be no change in composition induced in
transfer by pouring, but if the impurity is sufficiently
nonvolatile serious compositional changes could
occur during a transfer by vacuum distillation.
The powdered glass may selectively adsorb some of
the impurity present in the wash sample. Whether
this happens is not known but since the wash sample
was similar in composition to the sample being
analyzed there was no evidence of a detrimental
adsorption-desorption process taking place when the
sample is introduced.

4.2. The Freezing-Point Cell and Thermometric
System

Freezing-point cells of the type described pre-
viously [4, 5] were used. The cells were closed so
that samples could be analyzed in the absence of
air and water vapor. The double helically wound
stirrers were constructed of platinum-iridium, and
stirring was achieved by means of a reciprocally
moving external electromagnet which was coupled
with the platinum-encased iron armature attached
to the stirrer shaft. Figure 2 depicts a cell attached
to the filling manifold. Constant-temperature freez-
ing or warming baths were used. These baths were
selected so that their temperatures differ from the
freezing point of the sample by approximately 50°.
The freezing rates were controlled by evacuation of
the outer jacket of the cell to the appropriate pressure
as determined by a Pirani gage.

A 25-ohm, bifilar, helical, glass-sheathed platinum
resistance thermometer was used. The G-2 Mueller
Wheatstone bridge used in this work was modified
as described in [7]. The extreme stability which
was achieved as a result of these modifications
allowed automatic recording of the bridge output
without the necessity of frequent zeroing. With
this apparatus temperature differences of 0.00002 °C
were detectable.

The freezing curves were recorded automatically
in order to obtain a continuous record, to eliminate
the tedious manipulation of dials, and to reduce
operator bias. A considerable gain in both precision
and accuracy was achieved by this recording method.
The output from the nearly balanced Wheatstone
bridge was amplified using a high-gain, d-c amplifier
equipped with two duplicate sets of gain controls
with external-switching mechanisms.

In our experience it has been extremely helpful to
program automatically the freezing sequence. For
this purpose the recorder was equipped with four
switches. There were two limit switches at the oppo-
site ends of the chart, a switch that was direction-
activated by the appropriate direction change of the
recorder pen, and a switch that could be preset to
operate at any selected portion of the recorder span.
These switches, together with a stopping switch and
a repeating, adjustable cycle switch, were used to
program the freezing-point experiment. Program-
ing of the freezing or melting sequence can be a
valuable, timesaving aid for the analyst who is en-
gaged in the determination of purity of many samples
of one material wherein the expected range of purity
is quite small. The precision obtained by program-
ing is always improved in comparison to the non-
programed experiment sets. However, the basic
accuracy is not necessarily improved, and the de-
cision of whether to program or not should be made
upon the number of replicate analyses expected.

The programing mechanisms may be of any vari-
ety of forms. Figure 3 depicts a real freezing curve
showing the programing points. Through ABC one
set of amplifier gain controls is adjusted so that a
single recorder span corresponds to 5 °C. At point
B the direction-sensitive switch is actuated. This
starts a timed sequence of events. After a preset
period of time (point C) the amplifier gain controls
are switched to high sensitivity by advancement of
the stepping switch. Again after a preset interval,
the appropriate dial on the Mueller bridge is turned
(point D) by one of a pair of electromagnets so as to
determine the sensitivity. The selection of this
point is important in that it should be prior to 10
percent frozen but after the highest recorded temperature has been reached. At time $F$ the dials are automatically returned to their original position, by the other electromagnet. Point $H$ represents approximately 35 percent frozen, and at this point the limit switch interrupts the bridge current, producing the zero plot from points $I$ to $J$. The zero should not be taken in this fashion until the experiment is complete, since interruption of bridge current causes hysteresis effects which are not completely eliminated until approximately 10 minutes have elapsed.

### 5. Experimental Results

The most rigid test of the reliability of the general method described in this paper was imposed by participation in a cooperative project on purity control organized by the Commission on Physicochemical Data and Standards, International Union of Pure and Applied Chemistry. In this program 20 laboratories analyzed replicate samples of benzene to which controlled amounts of contaminant had been added. The list of participants included government, university, and industrial laboratories from 6 countries. The results of this investigation, as yet not published, were reported before the Calorimetry Conference in August 1961 at Ottawa, Canada. Table 1 lists the most probable purity value for each sample as decided by the Committee, together with the results as obtained by this method.

It is sufficient to point out that there is excellent agreement from purity ranges of 99.999 mole percent down to 99.0 mole percent, and to note that among the several participants using the Glasgow, Streiff, Rossini technique, the methods suggested herein were the only ones which gave excellent agreement for all samples and, incidentally, agreed with those results obtained from application of precision adiabatic calorimetric techniques.

### 6. Summary

This paper discusses in detail the changes in technique which were necessary to extend the time-temperature cryometric method of purity determination to the realm of very highly purified materials. These changes in technique are summarized as follows:

1. The samples were transferred and analyzed in closed, evacuated systems.
2. The systems were rigorously cleaned, dried, and preconditioned with a portion of the sample to be analyzed.
3. Ground glass was added to insure the attainment of equilibrium in the freezing cell.
4. The time-temperature curves were automatically recorded.
5. When large numbers of replicate analyses were performed, the freezing experiments were programed.
6. Selection rules were devised to insure that the best portion of the time-temperature curve was used in the curve-fitting.
7. The optical projection method of curve-fitting was employed to eliminate operator bias and give more reliable results.

### 7. References