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Cryostat for measuring the triple point of trichlorofluoromethane (refrigerant 11) under adiabatic conditions[1]

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Abstract

We present the design of a cryostat that houses trichlorofluoromethane triple-point cells. The apparatus was used to measure the triple point adiabatically and then compare results with the values obtained using the continuous melting technique.

Keywords: Cryogenic triple point; Resistance thermometry; Trichlorofluoromethane triple point

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1. Introduction

Conventional melting experiments are performed using the continuous melting technique, in which the sample is first frozen. Next the temperature of the sample's surroundings is adjusted to be slightly higher than the melting point. This provides a source of heat sufficient to ensure that the melting point will eventually be reached and that the sample will melt. The temperature is monitored and one knows that the melting process is taking place when the temperature tends to a steady value: the melting point.

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The length (melting time) of the plateau depends on the total heat of fusion, heating rate, size of the sample, thermal gradient configuration, etc. The total melting time and the heating rate are used to estimate the total heat of fusion and the solid-to-liquid ratio. The melting range, defined here as the temperature difference between the extremes of the plateau, along with the melting curve itself, is used to estimate the proportion of impurities in the sample.

The experimental arrangement uses a concentric cylindrical configuration with the heat source on the exterior, the sample on the interior and the thermometer at the center. In the course of the experiment, the greater part of both the solid and the liquid material can be at considerably different temperatures from the solid–liquid interface. Consequently, the thermometer indicates temperatures that may be quite different from the melting point. What relation do these thermometer readings have to the melting points accurately measured when solid, liquid and vapor states are in stable equilibrium?

An adiabatic calorimeter was built to obtain the triple point temperature of three samples of trichlorofluoromethane (CCl_3F; R11). Results obtained here are compared with those obtained in a previous work [1] using the same cells and the continuous melting technique.

2. Apparatus

The design of an adiabatic calorimeter to house trichlorofluoromethane (CCl_3F; R11) is shown in Fig. 1. The R11 cells have dimensions similar to those of ordinary water triple-point cells (5–6 cm diameter, 30–40 cm long).

The sample holder (SH) is made of a copper tube of 6.4 cm diameter and 39 cm length. The bottom of the tube is sealed using indium wire with a 1-cm-thick brass flange using 6 screws. Copper is used to reduce the vertical temperature gradients along the cell. The top end of the SH is welded to a stainless steel cup. A manganin sample heater is wound bifilarly around the SH.

The sample container is suspended from the support flange using a 0.8-cm diameter thin-walled stainless steel tube. This tube serves as a thermometer well and also insulates the sample from its surroundings. Copper foil is inserted between the cell and SH in order to improve thermal contact.

The SH is surrounded by a cylindrical copper heat shield of 10 cm diameter. The shield is suspended from the top flange by three cotton threads. A heating element is wound around the cylinder with careful attention to its uniform distribution, so that heat is applied equally to all parts of the cylinder surface. A differential copper–constantan thermocouple, with its junctions at the shield and the SH respectively, is used to control the shield temperature. The thermocouple is connected across a microvoltmeter whose output in turn controls the power supply connected across the shield heater.

The SH and the shield are housed in a 12.7-cm-diameter stainless steel vacuum chamber, attached to the top flange using 8 screws. It is sealed with indium wire. Two 0.9-cm-diameter stainless steel tubes are welded between the top and the support

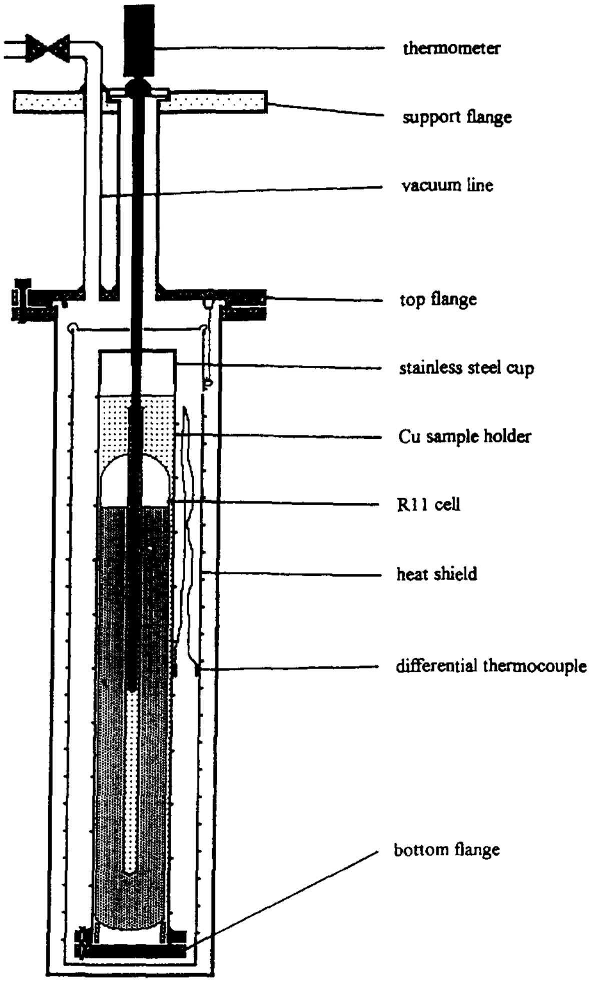

Fig. 1. Cryostat arrangement.

flange: one is used for heater wiring and the other for thermocouples. An extra stainless steel tube, 1 cm in diameter, is used either to fill the cryostat with helium exchange gas or to evacuate it.

Temperature is measured with a 25.5-Ω long-stem SPRT (Rosemount model 162CE) and an ASL F18 bridge.

3. Experimental

In a melting experiment it is possible to obtain equilibrium temperatures at any solid-to-liquid ratio, if the heat exchange between the sample and its surroundings is cancelled. To achieve this result, we surrounded the sample with a shield whose temperature can be controlled. By adjusting the temperature of the shield to correspond to the temperature on the outside wall of the cylinder holding the sample, we eliminate the transfer. Thus the sample can gradually approach a homogeneous temperature throughtout its entire bulk at any given solid/liquid ratio.

Of course such a state can only be approached because one can only minimize, not eliminate, the heat exchange: there are remaining heat leaks through the sample support, thermometer stem, connection leads, etc. When working with R11 these problems are further aggravated by its characteristics as a thermal insulator, because of which residual heat leaks can gradually build up local temperature gradients within the sample.

To tune up the calorimeter we have to determine the temperature setting for the shield, either by fixing certain values and making a large number of arbitrary tests, or else by using a differential thermocouple which measures the temperature difference between the sample container and the shield in order to solve the problem. When in our apparatus the temperature of the outside cylinder wall rose relative to the shield, the signal from the thermocouple was used to apply heat to the shield, until the temperatures were equal. Heat exchange is thus reduced.

By patient "tuning" of the cryostat, one can in practice minimize heat leaks to a level at which the temperature drift of the sample becomes negligible for all practical purposes. The temperature of the sample can only be altered if heat is supplied by heat deliberately applied to the sample.

The cryostat was lowered into a dewar filled with liquid nitrogen. The liquid nitrogen level was maintained 2.5 cm above the top flange. The sample was cooled from room temperature with one atmosphere He exchange gas in the vacuum chamber. The total cooling time required to freeze the sample was 4–5 h. Afterwards, the He exchange gas was evacuated and the temperature regulation of the heat shield begun. By trial and error, an appropriate bias voltage for the thermocouple was found such that the sample drift became less than 1 $\mathrm{mK\,h^{-1}}$.

Sufficient heat was supplied with the sample heater to warm the solid sample to its melting point and to supply about 20% of its total heat of fusion. The time to reach stable sample temperatures was about 20 h. This implies that a very long time would be required if one were to obtain an equilibrium melting curve with a number of points along the curve, clearly illustrating the experimental problems caused by the low heat conductivity of such samples.

It is seldom practical to obtain a full melting curve, but fortunately an accurate determination near the liquidus point can serve most purposes. This is the method we have adopted. To obtain points in this region we have used the following methods:

A. Cool the sample till it supercools and recalescence is first observed. Then, evacuate the vacuum chamber and maintain the shield temperature at that of the sample. A shell of solid phase is then induced around the thermometer well by inserting liquid-nitrogen-cooled metal rods. A crude estimate of the solid/liquid ratio can then be made.

B. Cool the sample to about 4 K below its freezing point, evacuate the vacuum chamber, maintain the shield at the sample temperature and then insert five liquid-nitrogen-cooled metal rods into the thermometer well. About 10% solid is thus formed in the supercooled liquid sample.

4. Results and conclusions

Once the triple point was thus established, PRTs at room temperature were placed in the thermometer well. The successive insertions gradually increased the thermometer indication such that 6–8 insertions resulted in about a 20 mK higher apparent triple point temperature. Fig. 2 shows a plot of PRT resistance on repeated insertions into cell 85A. The three curves represent three different demonstrations of the triple point near the liquidus point of the cell. The temperature in these demonstrations was 162.677 ± 0.003 K (ITS-90). The scatter is too great for accurate thermometry.

An "immersion test" (to determine the sample temperature along the thermometer well by raising the PRT in 2.5 cm increments until it is 10 cm higher than its lowest location in the well) indicated a sample temperature uniform within 0.25 mK.

On repeatedly measuring the triple point of the cells (3 cells marked 85A, 86 and 91 were used), a reproducibility of about 20 mK was obtained. This range of reproducibility is similar to that obtained by us in 1992 using the same cells with the continuous melting technique [1].

Due to the very long times required to reach thermal equilibrium once the thermal state of the sample is disturbed, the cell design should be improved to shorten

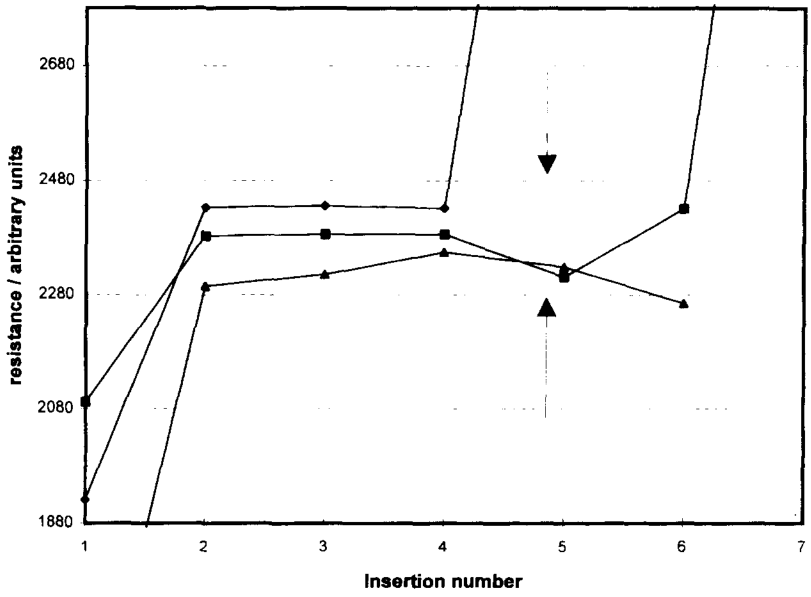

Fig. 2. Triple point stability near the liquidus point. Arrows show a 2 mK range for successive insertion of the PRT from room temperature.

relaxation times. Nevertheless, adiabatic calorimetery can reliably be used to determine the triple point near the liquidus point.

Even though this cryostat was designed to house our R11 cells, it can be used in the range of − 200 to 100°C for any other substance. The apparatus is, however, best suited for substances of high heat of fusion and high thermal conductivity.

Reference

[1] E. Méndez-Lango, M.L. Chávez and F. Guzmán, Temperature (New York), 6 (1992) 277.