viscometer to give high precision without unnecessary sacrifice of convenience and speed in operation are discussed.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY]

The Freezing Point of Methanol; A Simple Type of Cryostat Applicable to Freezing Point Determinations

BY EDWIN E. ROPER

A very pure sample of methanol had been prepared by Jones and Fornwalt[1] for their work on the relative viscosity and on the density. It appeared desirable to determine some physical constants as accurately as possible. Since a cryostat had been constructed by the author and a standardized resistance thermometer was available, Professor Jones requested a determination of the freezing point of their best samples of carefully purified methyl alcohol. The reported physical constants in the literature for methanol appear to be somewhat erratic and, in view of the difficulty involved in thoroughly freeing this material from water, in all probability the main cause of the discrepancies may be assigned to the presence of this impurity.

Experimental Procedure

Temperature Measurement and Standardization.—The temperature of the alcohol sample was measured by means of a four-lead coiled-filament 25-ohm platinum resistance thermometer.[2] The thermometer resistance was measured by a standardized Mueller type Wheatstone bridge, which was thermostated (25.0 ± 0.1°) in an oil-bath. The reproducibility of the measurements was *ca.* 0.0001 ohm, corresponding to 0.001°. The thermometer was standardized by accepted methods[3] at the sulfur boiling point, the steam point, the ice point and compared against the vapor pressure thermometers of carbon dioxide and of oxygen. The temperatures of the fixed points above 0° were taken as recommended by the International Temperature Scale specifications[3] and below 0° as given by Heuse and Otto.[4] The temperature of the ice point on the thermodynamic temperature scale was taken as 273.16°K.[5] The thermometer constants fulfilled all specifications[3] for pure platinum. The absolute accuracy at $-100°$ is probably ±0.02° and the precision ±0.001°. A single junction copper–constantan thermel was used as an aid in adjusting the cryostat. This thermel was standardized at the same fixed points as was the resistance thermometer, with the exception that the freezing point of a National Bureau of Standards sample of tin replaced the sulfur boiling point. The e. m. f. of the thermel was determined with a special type K potentiometer to one microvolt. The e. m. f. was converted into temperature by the accepted method of constructing a deviation curve[6] in conjunction with the reference tables of Southard and Andrews.[7] The accuracy is about ±0.05°.

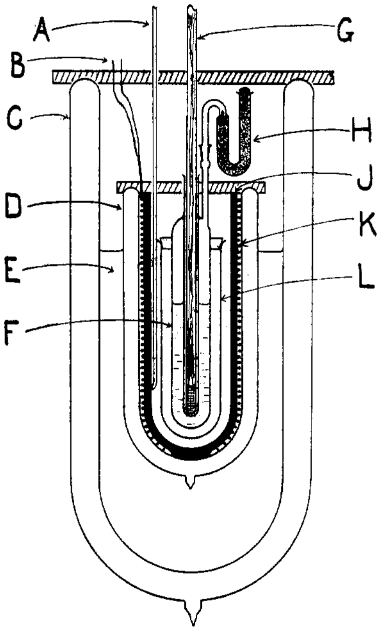

Fig. 1.—Freezing point apparatus showing details of cryostat. A is the environment thermel, B the heater leads, C the outer Dewar containing the refrigerant, D is the inner Dewar, E is the refrigerant, F is the freezing point tube, G the resistance thermometer, H a protective tube of Dehydrite, J is the copper tube, K is the heater wound on the surface of J, L is a glass jacket about the freezing point tube. Not drawn to scale.

Temperature Control.—The cryostat, somewhat similar to the one of Southard and Andrews,[7] is shown diagrammatically in Fig. 1. The copper shell J was 4 mm. wall thickness, 52 mm. outside diameter and 200 mm. long. The outer surface was so machined that after the heater winding was in place, the assembly fitted quite closely

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[1] Jones and Fornwalt, THIS JOURNAL, **60**, 1683 (1938).

[2] (a) Meyers, *Bur. Stds. J. Res.*, **9**, 807 (1932). (b) This thermometer and bridge are the same as were used for the ice point investigation, Roper THIS JOURNAL, **60**, 866 (1938).

[3] Burgess, *Bur. Stds. J. Res.*, **1**, 635 (1928).

[4] (a) Heuse and Otto, *Ann. Physik*, **9**, 486 (1931); (b) *ibid.*, **14**, 181, 185 (1932).

[5] (a) Heuse and Otto, *ibid.*, **2**, 1012 (1929); (b) Roebuck, *Phys. Rev.*, **50**, 370 (1936).

[6] "Inter. Crit. Tables," Vol. I.

[7] Southard and Andrews, *J. Franklin Inst.*, **207**, 323 (1929).

into the Dewar tube D. The heater winding K consisted of 14.1 meters (136 ohms) of number 30 D. S. C. constantan wire wound non-inductively on the tube J, a good thermal contact being ensured by coating the completed winding with Bakelite lacquer, which was subsequently baked. Two slide resistances and an 0–150 milliammeter in series with the heater served to control the energy input. A lag of but a few seconds was found between the heater and the thermel. A glass test tube L about F served to damp out sudden temperature changes in J; this baffle introduced a thermal lag of sixty to eighty seconds between J and F. The outer Dewar tube C was 13 × 52 cm., while the smaller Dewar was 5.4 × 21 cm., both inside dimensions. Liquid air was placed in the outer Dewar to serve as a cold reservoir; the rate of cooling could be controlled within limits by varying the liquid air level. Approximately 100 milliamperes (1.36 watts) d. c. in the heater was sufficient to maintain the assemply at −100°. A given temperature setting could be held constant for several hours, but during this time the decrease in the liquid air level had to be compensated by a manual decrease in the energy input to the cryostat. However, this type of cryostat is particularly suited to freezing point determinations below 0°, where a slow but steady decrease in the environment temperature is required.

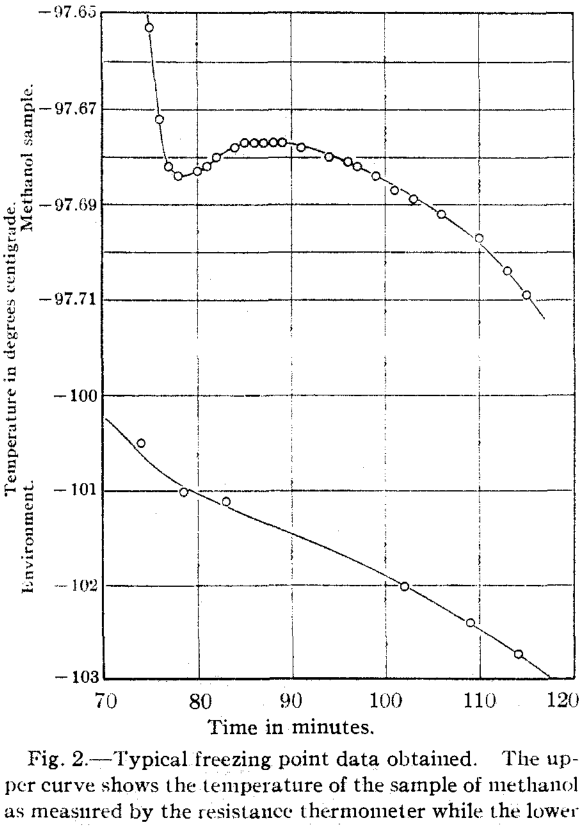

Fig. 2.—Typical freezing point data obtained. The upper curve shows the temperature of the sample of methanol as measured by the resistance thermometer while the lower curve is the course of the environment temperature measured by means of the thermel.

Methanol Samples.—The freezing point of two different portions was investigated. The data on the original samples as determined by Jones and Fornwalt are presented in Table I. The sample no. 31 contained some water as shown by means of the relative viscosity and the density. The sample no. 37 was classed as anhydrous by these investigators. The alcohol was distilled directly into the freezing point tube through the ground joint at the top and then the protective tube of Dehydrite immediately placed in position. Fifty cc. of alcohol was used in the freezing point tube F; this covered the thermometer with 5 cm. of alcohol, which should be sufficient to eliminate heat conduction down the thermometer leads.

TABLE I

Sample	Relative viscosity	Density, $d^{25}{}_4$, g./ml.
31	0.6094	0.786 65
37	.6084	.786 53

Procedure.—The alcohol was precooled to *ca.* −90° and the freezing point tube placed in position in the cryostat, which was at about the same temperature. The energy input to the heater was then decreased so that an approximately constant rate of cooling ensued. The temperature of the environment as indicated by the thermel was closely followed. Upon nearing the freezing point, readings of both the thermel and the resistance thermometer were taken at suitable intervals of time. If the environment temperature is not known and carefully controlled, there is no means of predetermining (if no supercooling takes place) whether the freezing point "flat" has been reached or whether the sample is merely approaching the temperature of the environment.

Results Obtained

Figure 2 gives a typical set of data obtained for one particular determination of the freezing point. It can be seen that the temperature of the alcohol sample is constant to 0.01° for twenty-four minutes, while during the same interval the environment temperature dropped 1.1°. The temperature of the alcohol sample does not fall off as abruptly as would be expected, and this might indicate slight traces of water. However, this falling off is a function of the thermal head and conductivity between J and F. Mair[8] takes as the principal criterion of purity the slope of the approximately horizontal portion of the freezing point curve. Table II gives the freezing points found for the two samples and also rough calculations of the amount of water present in sample no. 31 on the assumption that sample no. 37 is anhydrous. The value based on the relative viscosities was calculated on the basis of an estimate made by Jones and Fornwalt[9] on the effect of water upon the viscosity of methanol. The value obtained from the difference in densities was calculated on the basis of a linear relationship be-

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(8) Mair, *Bur. Stds. J. Res.*, **9**, 459 (1932).

(9) Jones and Fornwalt, THIS JOURNAL, **57**, 2041 (1935).

tween density and composition, while the value calculated from the observed freezing point depression was obtained by the application of the approximate thermodynamic equation connecting the mole fraction of impurity, the true freezing point, the freezing point depression and the heat of fusion, the latter value being taken from the calorimetric work of Kelley.[10]

TABLE II

Sample	Freezing point, °C.	Percentage of water in sample from: rel. vis.	density	f. p. dep.
31	−97.75 ±0.02	0.04	0.06	0.05
37	−97.68 ± .02	(.00)	(.00)	(.00)

Discussion

It is very probable that the value −97.68° represents the true freezing point of anhydrous methanol to within the thermometric accuracy in relation to the thermodynamic temperature scale, namely, ±0.02°. An attempt has been made to correlate the freezing point with the density of methanol. Table III gives data taken from three other precision researches and Fig. 3 shows the data plotted, a rough estimate of the estimated accuracy being shown by the diameters of the plotted points. It can be seen that the results of Parks and of Timmermans and Hennaut-Roland are not in agreement with the data of Kelley and of this research. The latter two appear to be the more precise measurements and the density–freezing point curve has been passed through the data as shown.

TABLE III

Freezing point, °C.	d^{25}_4, g./ml.	Author
−97.8 ±0.1	0.7864[a]	Parks[11]
−97.88 ± .05	.786 75	Kelley[10]
−97.0	.786 75	Timmermans & Hennaut-Roland[12]
−97.68 ± .02	.786 52	This research
−97.75 ± .02	.786 65	This research

[a] Calculated value from that given for 22°.

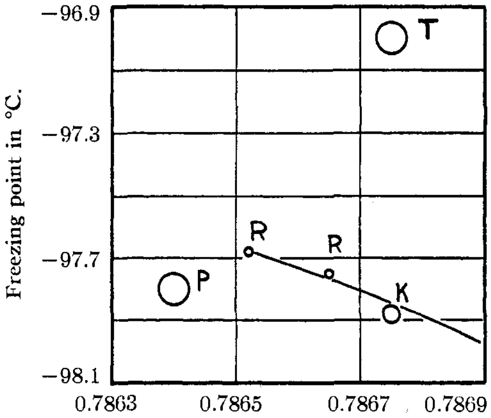

Fig. 3.—Data of different investigators plotted in order to attempt to determine the course of the freezing point–density of the liquid curve: K, Kelley; P, Parks; R, Roper; T, Timmermans.

Acknowledgments.—The author wishes to express his appreciation to Professor Arthur B. Lamb, in whose laboratory the cryostat was developed, for the use of the resistance thermometer, the cryostat and other apparatus and facilities. Professor Grinnell Jones and Dr. H. J. Fornwalt kindly supplied the methanol samples and furnished data concerning their respective relative viscosities and densities. Dr. Fornwalt filled the freezing point tubes with the samples and aided in measuring the environment temperatures in part of the determinations.

Summary

A simple cryostat is described which is applicable to the determination of freezing points below 0° and data are appended describing the operation of the cryostat during the freezing point determination of a methyl alcohol sample. The freezing point of a particularly pure sample of methanol prepared by Jones and Fornwalt was determined to be −97.68 ± 0.02°. A short discussion is given of the freezing point–density relationship.

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[10] Kelley, THIS JOURNAL, **51**, 180 (1929).

[11] Parks, *ibid.*, **47**, 338 (1925).

[12] Timmermans and Hennaut-Roland, *J. chim. phys.*, **27**, 401 (1930).