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THE TRANSITION TEMPERATURE OF CARBON TETRACHLORIDE AS A FIXED POINT IN THERMOMETRY

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In a recent paper[1] McCullough and Phipps have suggested the use of the transition point of carbon tetrachloride[2] as a fixed point in thermometry and have given this transition temperature as $-48.54 \pm 0.02°$. For reasons which will appear below it seemed advisable to redetermine this transition temperature and the value found by us is $-47.55 \pm 0.12°$.

Method.—Our observations were made by means of a special cooling curve and heating curve apparatus which will be described in detail in a paper now being prepared for publication by one of us (E. L. S.). The apparatus involves a cryostat whose temperature can be very accurately regulated and in which a 0.7–1.0 g. sample is suspended in an hermetically sealed "freezing point tube." The latter is made of extremely thin-walled glass tubing (0.05 mm. wall thickness) in order that its heat capacity may be negligibly small with respect to that of the sample, and is so constructed that the temperature of the sample may be followed by means of a single-junction thermocouple one element of which fits snugly into a thin-walled capillary tube extending down into the center of the sample. The cold junction is kept at 0°. The readings are made to the nearest microvolt (0.03°) by means of a Leeds and Northrup Type K potentiometer.

Calibration and Materials.—The thermocouple, which is made of No. 30 constantan and No. 36 copper wire (B. and S. gage) was calibrated at the ice point, at the freezing point of pure mercury (−38.87°),[3] at the sublimation point of carbon dioxide (−78.51°)[3] and at the boiling point of oxygen (−183.00°).[3] The last two points were established by measuring the vapor pressure of the carefully purified substances in a

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[1] McCullough and Phipps, THIS JOURNAL, **50**, 2213 (1928).

[2] The existence of this transition point was recognized previously by Goldschmidt [*Z. Krist.*, **51**, 21 (1912); THIS JOURNAL, **50**, 3390 (1928)] and by Latimer [*ibid.*, **44**, 90 (1922)]. Neither of these investigators, however, was interested in the exact measurement of the transition temperature.

[3] "International Critical Tables," Vol. I, p. 53.

constant temperature cryostat in which the thermoelement was immersed.[4] In each case the purity of the sample was tested by evaporating to one-half volume and then redetermining the vapor pressure. The calibration at the mercury point was carried out in the same apparatus as the freezing points and under identical conditions.

In order to further corroborate the accuracy of our calibration in the range to be considered, we are recording below the freezing point data obtained by our method on samples of carbon tetrachloride and chlorobenzene kindly supplied to us "for thermocouple calibration" by Professor Jean Timmermans. This same sample of carbon tetrachloride was used for our determination of the transition point in question.

Results.—A number of cooling curves and heating curves were obtained on chlorobenzene at its freezing point, and on carbon tetrachloride at its freezing point and at its transition point. The data given in Cols. 2 and 3 of Table I are the values obtained from these curves using our own thermocouple calibration; those in Col. 4 are the values as determined independently by Timmermans on the same samples for the purpose of thermometric standardization.

TABLE I

FREEZING POINT AND TRANSITION POINT DATA

Substance	Phenomenon	Temperatures, °C. Heating curve	Cooling curve	Timmermans
Carbon tetrachloride	F. p.	−22.84	−22.87	−22.9
Chlorobenzene	F. p.	−45.20	−45.23	−45.2
Carbon tetrachloride	Tr. p.	−47.43	−47.67	......

It will be noted that whereas the freezing point values as obtained by the heating and cooling curves show very good agreement, the corresponding values for the transition point differ by 0.24°. It was found that the heating curve value was fairly reproducible but that the value obtained by cooling curves varied from −47.67 to −47.99°, depending on the conditions, that is, on the degree of supercooling and on the rate of cooling. In cases such as this, where one cannot establish equilibrium by stirring due to the fact that the change takes place in the solid state, it is, of course, to be expected that the proper degree of supercooling before the transition takes place is very important.[5] Our best curves for this point were obtained with a supercooling of 3 to 4°, the rate of cooling being about 0.3° per minute.

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[4] The details of this method have been fully described by Keyes, Townshend and Young, *J. Math. Phys. Mass. Inst. Tech.*, **1**, 302 (1922); see also Loomis and Walters, THIS JOURNAL, **48**, 3101 (1926), and Henning, *Ann. Physik*, **43**, 282 (1914).

[5] Nernst [*Z. physik. Chem.*, **15**, 681 (1894)] discusses the dangers of supercooling too little or too much in cryoscopic determinations in dilute solutions; see also Findlay's "Practical Physical Chemistry," 4th ed., Longmans, Green and Co., London, **1926**, pp. 114–115.

Discussion

Our results show that the transition point of carbon tetrachloride is −47.55 ± 0.12°; that is, it must lie between the temperature, −47.43°, the value obtained from heating curves, and −47.67°, the highest value from cooling curves.

The large discrepancy between our value for this point and that reported by McCullough and Phipps is probably not due to a difference in the purity of the sample used, judging from their freezing point data. It may be caused in part by the fact that their thermometer calibration at the sublimation point of carbon dioxide was not done by the accepted method. It is very likely chiefly due, however, to the inadequacy of their method of obtaining cooling curves. This seems probable at least from the fact that their diagram of the cooling curve for their best sample shows that there was no supercooling.

From the results of our investigation it seems improbable that the transition point of carbon tetrachloride will be entirely satisfactory for general use as a fixed point in thermometry. Except in the case of hydrates, transition points do not lend themselves to this purpose due to the difficulty of attaining a definite equilibrium in the solid state.[6]

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Summary

The transition point of carbon tetrachloride has been redetermined on a very pure sample in a special apparatus using a thermocouple whose calibration has been very carefully checked. The transition takes place at −47.55 ± 0.12°, about one degree higher than reported by McCullough and Phipps.[1] This transition phenomenon is apparently not suitable as a fixed point for thermometry.

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[6] Wyatt [*Trans. Faraday Soc.*, **24**, 429 (1928); **25**, 43, 48 (1929)] suggests the suspension of the carbon tetrachloride in a liquid for reproduction of a definite temperature at the transition point. On the basis of values so obtained he places the transition point of carbon tetrachloride at "about −48°C." He used a thermometer in his temperature measurements whose stem-emersion calibration was based upon McCullough and Phipps' value for the transition temperature. Timmermans [*Bull. soc. chim. Belg.*, **37**, 409 (1928)] has also worked on such binary systems and reports that the transition point of carbon tetrachloride in cyclohexane, chloroform and acetone is −46°; in carbon disulfide, −46.5°.