

The authors wish to express their appreciation of the helpful suggestions of Professor W. F. GIAUQUE pertaining to the specific heat measurements, the skilful execution of the mechanical design by Mr. G. F. NELSON, the work on the heat of solution of cesium alum by Dr. F. D. ROSSINI, and the laboratory assistance of Mr. J. E. AHLBERG.

Summary

The heat capacity of cesium alum, $\text{CsAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, has been measured from 18 to 300°K.; the molal entropy at 298.1°K. is computed to be 163.8 cal./deg.

The activity of dilute solutions of rubidium and cesium alums has been determined from freezing point measurements.

The entropy ($H^+ = 0$) of Al^{+++} in hypothetical 1 *M* solution at 298.1°K. has been determined as -70.9 cal./deg./mole.

The electrode potential at 298.1°K. of aluminum, $\text{Al} = \text{Al}^{+++} + 3\text{E}^-$, has been calculated from thermal data to be $+1.69 \pm 0.01$ volts.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM SEVERANCE CHEMICAL LABORATORY OF OBERLIN COLLEGE]

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

BY JAMES C. McCULLOUGH AND HARRIS E. PHIPPS¹

RECEIVED JUNE 22, 1928

PUBLISHED AUGUST 4, 1928

An enantiotropic or reversible transition has been discovered when carbon tetrachloride is cooled below its freezing point. This solid-solid transition is a change from the cubic to the monoclinic system and takes place at $-48.54 \pm 0.02^\circ$. The hold in the time-temperature curve (Fig. 1) is of approximately the same duration as that at the freezing point. With proper precautions the transition temperature is as constant as the freezing temperature. Since the freezing point of carbon tetrachloride is given as a fixed point in thermometry,² the transition point should be equally valuable. The purification of one substance would thus serve to fix two points on the thermometer scale, saving the purification of a second material, such as chlorobenzene.

No reference has been found in the literature indicating that more than one solid form of carbon tetrachloride has been known at atmospheric pressure. Tammann,³ working with high pressures, at one time believed that he had found three solid forms. Later, in "Kristallisieren und Schmelzen,"

¹ This paper represents part of the work done by Mr. Phipps in meeting the requirements for the degree of Master of Arts.

² (a) "International Critical Tables," Vol. I, p. 54; (b) Timmermans and Martin, *J. chim. phys.*, **23**, 747-787 (1926).

³ Tammann, "Kristallisieren und Schmelzen," E. Barth, Leipzig, 1903, p. 222.

zen," he retracted his former statements, and explained the irregularities which he had observed when carbon tetrachloride solidified at various temperatures and pressures by assuming the existence of two polymorphic forms. Bridgman,⁴ using very high pressures, found three solid forms of carbon tetrachloride. Extension of his curves indicates that the second form should exist below -48° with one atmosphere pressure. In this connection Bridgman says: "It should be possible to realize the phase II at atmospheric pressure at low enough temperatures. Such an attempt was made by cooling CCl_4 in carbon dioxide snow to -80° , but the depression of temperature was not sufficient to overcome the viscous resistance to the reaction." There are two possible explanations as to why Bridgman did not observe the solid-solid transition: (1) he may have failed to identify it and (2) the solid may have supercooled. If the third phase recorded by Bridgman exists at atmospheric pressure, the transition temperature would probably be close to absolute zero.

The transition was first observed by us with a polarizing microscope equipped with a cold stage. Samples of carbon tetrachloride from three different sources were examined. Each exhibited the same behavior. The first crystal form is cubic, as is well known. The form existing below -48.54° appears to be monoclinic, for it exhibited a biaxial interference figure and both parallel and oblique extinction with polarized light.

Apparatus

The apparatus used in measuring the transition temperature consisted of two large test-tubes, made from heavy walled Pyrex tubing, one of which slipped inside the other. These were then placed in a one-quart thermos bottle of the wide-mouthed type which was filled with solid carbon dioxide and ether. A four-terminal, compensated lead, platinum resistance thermometer and Mueller type bridge, made by the Leeds and Northrup Company were used for the major portion of the work. This pyrometer was calibrated at the sulfur boiling point by the method of Mueller and Burgess,⁵ at the steam and ice points, and at the sublimation point of solid carbon dioxide.⁶ Since no information could be found regarding the calibration at the sublimation point of solid carbon dioxide, the technique is here given in detail.

The solid carbon dioxide was purchased from the Dry-Ice Corporation in the usual form of a dense cube about ten inches on an edge. The resistance thermometer was placed in a one-quart thermos bottle of the wide-mouthed type which was filled with small pieces of solid carbon dioxide. The bottle was closed with a cork which fitted the thermometer loosely. The cork had a second hole about 4 mm. in diameter so as to ensure atmospheric pressure without undue circulation of air. Equilibrium was reached in about two hours. The readings could be checked by this method. The temperature of the solid carbon dioxide in the thermos bottle was also measured by a pentane thermometer which had been calibrated at -40° and other temperatures by the U. S. Bureau of Standards. The value obtained with this thermometer agreed with the published value for carbon dioxide in the solid state, as given in the "International

⁴ Bridgman, *Phys. Rev.*, (2) 3, 126-141, 153-203 (1914).

⁵ Mueller and Burgess, *Bureau of Standards Scientific Paper*, 339.

⁶ Ref. 2 a, p. 53.

Critical Tables.”⁶ It was first thought that the sublimation temperature of the solid carbon dioxide could best be obtained by placing the thermometer in a deep hole drilled in the cake of Dry-Ice. This was done and after equilibrium was established, which took about seventeen hours, a temperature of -97° was obtained. It appears that this must be due to the escape of carbon dioxide gas and the rapid sublimation of the solid. If the solid carbon dioxide were not in equilibrium with its vapor, the temperature at the surface of the block would naturally fall. This point was tested by placing some pieces of solid carbon dioxide in a thermos bottle and rapidly drawing off the carbon dioxide gas by means of a suction tube extending nearly to the bottom of the bottle. A temperature of -102° has been obtained by this method and further study of it is under way.

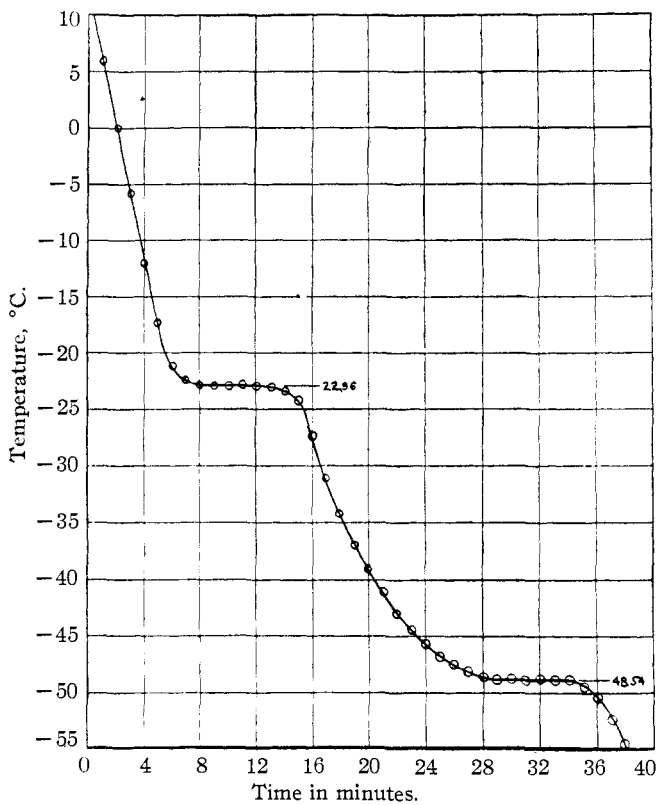


Fig. 1.—Enantiotropic transition of carbon tetrachloride. E. K. Co., 444-A.

Procedure and Results

Time-temperature curves were made by cooling various samples of carbon tetrachloride, some of which were purified by fractional distillation. A Young pear-head fractionating column was used and the temperature of the condensing vapor was taken with a mercury thermometer calibrated by the U. S. Bureau of Standards. The boiling point was calcu-

lated to atmospheric pressure (760 mm.) by the method of Smith and Menzies.⁷ When freezing, the liquid carbon tetrachloride was vigorously stirred until it was nearly all in the solid state. After it had all solidified and the temperature was again falling, the tube containing the solid carbon tetrachloride was occasionally removed from the freezing bath and gently tapped. When this was done the temperature was fairly constant even with an impure sample. The temperatures recorded in the table below are the average temperatures obtained, plus or minus the fluctuations observed during the hold. The platinum resistance thermometer was accurate to 0.006°.

TABLE I
BOILING, FREEZING AND TRANSITION POINTS OF CARBON TETRACHLORIDE

Thermometer	Sample of CCl ₄	B. p., °C.	F. p., °C.	Transition point, °C.
Resistance	444	-22.946±0.008	-48.563±0.006
	444	-22.967±0.01	-48.551±0.007
Pentane	444	-22.97	-48.5
Resistance	444-A	76.8	-22.968±0.005	-48.541±0.005
	444-B	76.8	-22.973±0.006	-48.531±0.008
	444-C	76.8-77.3	-22.889±0.02	-48.395±0.02
	P.W.R.	-23.225±0.3	-48.925±0.3
	P.W.R.-A.	76.6-76.8	-23.14±0.2	-48.71±0.3
Pentane	P.W.R.-A.	76.6-76.8	-23.0 to -23.2	-48.7 to -48.9
	Stock		-22.9 to -23.5	-48.6 to -49.2

Sample 444 was obtained from the Eastman Kodak Company and is listed as E. K. Co. 444 carbon tetrachloride; 444-B was a sample obtained by fractional distillation; 444-C was a small amount of the higher boiling fraction; 444-A was obtained in the same way as 444-B but a more efficient pear-head fractionating column was used. The P.W.R. was a sample of the Powers-Weightman-Rosengarten Company product marked purified. The sample marked stock was a cheap commercial grade.

Summary

The results obtained show quite definitely that carbon tetrachloride has a solid-solid transition. The change from the cubic to the monoclinic system takes place at -48.54 ± 0.02 when pure material is used. It is suggested as a fixed point in thermometry, since the hold is as constant and as fixed as the freezing point which is given as a fixed point in "International Critical Tables" and elsewhere.

OBERLIN, OHIO

⁷ Smith and Menzies, *THIS JOURNAL*, **32**, 907 (1910).