tetrahedral radii for these elements. These values, 2.28 and 2.64 Å., would be shorter than the distances observed in the corresponding manganese compounds. It is planned to prepare several of these substances and to investigate their magnetic susceptibilities and crystal structures in these Laboratories.

Acknowledgment.—The author wishes to thank Professor Linus Pauling for his interest and help in this investigation; his suggested interpretation of the magnetic measurements of Haraldsen and Klemm proved especially valuable. The author also wishes to thank Dr. James H. Sturdivant for his kind advice concerning the preparation of the powder photographs.

Summary

The crystal structures of manganese diselenide and manganese ditelluride have been investigated with x-rays and found to belong to the pyrite type of structure. The cubic unit of manganese diselenide has the dimension $a_0 = 6.417 \pm 0.005$ Å. and the parameter $u = 0.393 \pm 0.001$. For manganese ditelluride the corresponding values are $a_0 = 6.943 \pm 0.002$ Å. and $u = 0.386 \pm 0.002$.

The results obtained suggest that in the pyrite type structures the manganese–non-metal bonds are either ionic or resonate between ionic and covalent, the covalent part involving 4*d* orbitals from the manganese rather than 3*d* orbitals.

The magnetic susceptibility measurements of Haraldsen and Klemm,[7,8] on the sulfides of manganese, cobalt, and nickel, are interpreted as supporting the results of the X-ray investigation, and, further, as showing that cobalt and nickel probably form covalent d^2sp^3 bonds in these compounds.

PASADENA, CALIF. RECEIVED JULY 19, 1937

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY No. 394]

Comparison of Platinum–Rhodium Resistance Thermometers with the Helium Gas Thermometer from 11 to 300 °K. An Improved Cryostat. Low Temperature Studies, No. 2

BY R. W. BLUE AND J. F. G. HICKS, JR.

Introduction

In the program of low temperature research now in progress in this Laboratory a prominent place has been assigned to the precise measurement of specific heats. The establishment of an accurate and reliable secondary temperature scale is of fundamental importance in these measurements. The purpose of this paper is to describe the construction and calibration of resistance thermometers and thermocouples for use as secondary standards.

The cryostat used for this research embodies several important features of the apparatus described by Southard and Brickwedde,[1] while the arrangement of radiation shields and reservoirs follows closely that employed by Keyes, Gerry and Hicks[2] in the hydrogen liquefier described recently. The method which we used for transferring refrigeration was suggested by an apparatus of Mendelssohn, Ruhemann and Simon.[3] Since the cryostat has some advantages over those in common use and is readily adaptable for many kinds of low temperature measurements, it is described here in considerable detail.

Construction of Resistance Thermometers.—As secondary standards for specific heat work we have chosen platinum–10% rhodium resistance thermometers of the strain-free type, described by Meyers.[4] That such thermometers are suitable for low temperature specific heat measurements has been demonstrated by Southard, Brickwedde and Milner.[5] Platinum–10% rhodium wire has a relatively high resistivity and a satisfactory temperature coefficient of resistance. The residual resistance at low temperatures is sufficiently high to permit the thermometers to be used readily as heaters. Four resistance thermometers were calibrated. They were designated by their nominal ice-point resistances, R197, R222, R140 and R145. Number 40 B. and S. gage wire was used for all thermometers. R197 and R222 were wound on mica crosses (7.5 × 0.8 × 0.01 cm.) each of which was enclosed in a copper tube (9 cm. long × 1.3 cm. o. d.; wall thickness 0.2 cm.). The ends were closed with copper disks, the top disk being fitted with four platinum tubes through which the leads were sealed with lead glass. The upper disk

(1) Southard and Brickwedde, THIS JOURNAL, **55**, 4378 (1933).
(2) Keyes, Gerry and Hicks, *ibid.*, **59**, 1426 (1937).
(3) Mendelssohn, Ruhemann and Simon, *Z. physik. Chem.*, **158**, 121 (1931).
(4) Meyers, *Bur. Standards J. Research*, **9**, 807 (1932).
(5) Southard and Milner, THIS JOURNAL, **55**, 4384 (1933).

was silver-soldered to the walls of the case. The bottom disk, which was soft-soldered in, was fitted with a copper tube for the admission of helium. These thermometers were annealed at the boiling point of sulfur for ten days, filled with helium and alternately cooled to 80°K. and warmed to room temperature until the ice-point resistances showed no further change with this treatment. The thermometers were slipped into snugly fitting cylindrical holes in the gas thermometer block, thermal contact being obtained by means of stopcock grease. No lag in attaining temperature equilibrium with R140 and R145 was ever observed. Thermometers R140 and R145 were wound on mica crosses (6.3 cm. × 0.87 cm. × 0.01 cm.) and enclosed in snugly fitting nickel-silver tubing closed at the ends with copper disks. The fittings of the thermometer cases were the same as for R197. Thermometer R140 was annealed in the case (with bottom disk removed) by passing 0.6 ampere through it for a few seconds. Thermometer R145 was annealed on the mica cross before it was sealed into the case. Annealing was accomplished by heating the thermometer in a quartz tube at 600–700° for three hours. The drop in resistance caused by annealing was approximately the same for R140 and R145. Several coolings with liquid air caused no change in the ice-point resistances.

The resistance thermometers were compared with a 100-ohm standard resistance by the potentiometer method, a Wenner potentiometer (0.1 volt range) being used for all measurements. The potentiometer resistances were intercompared after the first series of measurements (Run II).

The Cryostat.—The essential parts of the cryostat (shown diagrammatically in Fig. 1) are the liquid-air reservoir, L, the liquid-hydrogen reservoir, H, and the protective shields, S(1), S(2) and S(3). S(1) which was always warmer than reservoir H was heated continuously to keep it at a constant temperature. Control was maintained by means of a difference thermocouple with junctions on S(1) and on the thermometer block, B. S(2), a thin-walled copper cylinder in good thermal contact with the reservoir L, served to protect the inner parts of the cryostat from radiation. This device was so effective that the loss of liquid hydrogen by evaporation during the measurements was only 400 cc. per day. The floating shield, S(3), served to protect the reservoir L from radiation.

It will be observed that the familiar wide-mouthed glass Dewar vessel has been eliminated. As pointed out by Keyes, Gerry and Hicks,[2] this improvement results in a marked decrease in liquid air consumption.

The apparatus was suspended in a heavy-walled brass cylinder, E, which was closed at the ends with brass plates. The bottom plate was soldered in while the joint, A, was made with picein wax and coated with glyptal lacquer. The cylinder, E, was evacuated in order to isolate the various parts of the apparatus from each other and from the surroundings. When it was desired to cool the shield S(1) and the thermometer block B, the reservoir H was filled with liquid nitrogen and oxygen gas was admitted to the cooler chambers, III and IV, through the thin-walled nickel-silver tubes, T(5) and T(6). Liquid oxygen condensed in the tubes and dropped into the cooler chambers where it evaporated, cooling the shield and block. Three kilograms of copper was cooled by this refluxing device from room temperature to liquid air temperature in six hours. The same procedure was used for cooling to liquid hydrogen temperature except that reservoir H contained liquid hydrogen and hydrogen gas was admitted to the cooler chambers. Block and shield could be cooled from 60 to 20°K. in a few minutes. Hydrogen was condensed in the cooler chambers and frozen by evaporation under vacuum. Cooling block and shield to 10.5°K. required only half an hour.

In the conventional type of cryostat, refrigeration is transferred by gas conduction, the conducting gas subsequently being removed by evacuation of the working space. This method requires that a large vacuum tight joint be made inside the apparatus whenever the calorimeter or other device in the working space is removed or altered. Frequently this vacuum tight joint is the cause of trouble or delay. In our apparatus the only large, demountable, vacuum tight joint is on the outside of the apparatus where wax may be used very conveniently. Any defect in this joint is repaired readily after the apparatus is completely assembled. Thus a very large apparatus may be built into the working space without any difficulty. The new cryostat also has the advantage that highly purified helium gas, which is ordinarily used for cooling purposes, is not required.

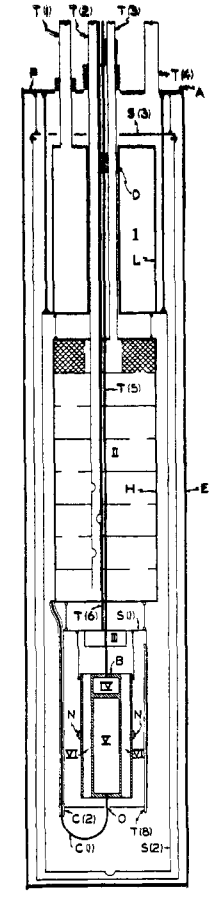

Fig. 1.– The cryostat.

In the new cryostat all electrical leads readily may be brought into thermal contact with the refrigeration reservoirs, thus diminishing the heat leak into the working space and conserving liquid hydrogen. Because of the extremely high thermal conductivity of copper at low temperatures this advantage is sometimes of considerable importance.

The thermometer block, B, was fashioned from a solid block of copper. The cooler space, IV (15 cc.), and the thermometer bulb, V (81 cc.), were closed at the ends with copper plates, soft-soldered in. Four cylindrical holes, VI, accommodated the resistance thermometers. Thermometers R197 and R222 were brought into thermal contact with low vapor pressure grease while thermometers R140 and R145 were soldered in by means of nickel-silver ferrules (not shown), thermal contact being obtained by helium gas admitted through a tube (not shown) which could be pinched off. Four bolts on the sides of B accommodated thin copper washers to which thermocouple junctions were soldered.

The thermometer bulb, V, communicated with the manometer by means of a 0.5 mm. o. d. × 0.1 mm. wall nickel-silver capillary, C(1). Surrounding this was a 0.139 mm. i. d. × 0.1 mm. wall nickel-silver capillary, C(2). C(2)

was connected to an auxiliary manometer and served as a measure of the mean reciprocal temperature[6] of C(1). C(2) was brought into fair thermal contact with S(1) and H by means of paraffin. The inside volume of that portion of C(1) contained in C(2) was 1.15 cc.

Manometer.—The manometer was made from 19.5 mm. i. d. tube of Pyrex chemical-resistant glass, the short arm and long arm being coaxial. The constant part of the dead space including 90 cm. of 1 mm. i. d. glass capillary and a short length of 0.5 mm. o. d. nickel-silver capillary was 1.56 cc. The variable dead space, including the gas below the crown of the meniscus, was approximately 0.25 cc.

The height of the mercury column was measured by means of a brass scale and a Société Génévoise cathetometer with micrometer eye-pieces on the telescopes. The brass scale was compared with an invar scale which had been calibrated by the Bureau of Standards, and found to be accurate to within 0.03 mm.

Procedure.—The thermometer bulb was filled with helium which had been purified by passing through two charcoal traps in series at liquid-nitrogen temperatures. The ice-point pressures for the several fillings are indicated in Table I. It will be observed that helium was lost at a rate of about 0.1% per week when the bulb was at room temperature, and at the rate of about 0.04% per week when the bulb was at liquid air temperatures. In the absence of positive information whether this loss was caused by a leak or by diffusion we elected to eliminate the uncertainty with regard to the amount of helium in the thermometer by frequent standardization. It is apparent that no uncertainties equivalent to our accuracy of measurement remain.

TABLE I

Run no. and temp. range, °K. Date of meas.	Dates of standardization	Reduced pressure, mm.
I		
300–90	12-10-36	824.84
12-11-36	12-10-36	824.85
Value used, 824.85		
	12-13-36	1859.53
	12-13-36	1859.74
II	12-15-36	1859.63
11–140	12-15-36	1859.63
12-19-36 to	12-16-36	1859.65
1-8-37	12-16-36	1859.68
	1-5-37	1859.56
	1-5-37	1859.48
Value used, 1859.57		
III	1-25-37	796.52
90–273	1-25-37	796.52
1-30-37 to	2-2-37	796.39
2-1-37	2-2-37	796.44
Value used, 796.47		
IV	2-3-37	2358.24
10–90	2-3-37	2358.28
2-5-37 to	2-6-37	2358.25
2-9-37	2-6-37	2358.16
Value used, 2358.23		
IV′	3-19-37	2357.35
54–110	3-19-37	2357.29
3-17-37 to	3-20-37	2357.38
3-20-37	3-20-37	2357.41
Value used, 2357.36		
V	3-23-37	904.83
90–303	3-23-37	904.85
3-22-37 to	3-24-37	904.72
3-23-37	3-24-37	904.82
Value used, 904.82		

Calculations based on the gas thermometer data were made in the conventional manner.[6] Meniscus volume corrections were made on the basis of data given in "International Critical Tables."[7] Corrections for capillary depression were based on the Lohnstein formula.[8] Correction for thermal expansion of copper was made with the aid of an empirical equation[9] derived for us by Dr. H. T. Gerry from the data of Keesom, Van Agt and Jansen.[10,11] We have used 273.19°K.[12] for the melting point of ice in calculating our results.

Correction to the absolute temperature scale was accomplished with the aid of the Keyes[13] equation of state for helium.

The resistance thermometers were used to standardize the gas thermometer both at the ice-point and at 90°K. The ice-point resistances had been determined before the thermometers were placed in the cryostat and the resistances at 90°K. were determined in terms of the ice-point by means of the gas thermometer. The boiling point of oxygen was determined by condensing pure oxygen[14] in the cooler space, IV. During a measurement of the oxygen boiling point the entire cryostat with the exception of the thermometer block was maintained at temperatures

(6) This is the method used in this Laboratory by Beattie and associates, and is described in a paper to be published shortly.

(7) "I. C. T.," Vol. I, p. 73.

(8) Lohnstein, *Ann. Physik*, **33**, 296 (1910).

(9) The equation is $V_T = V_0 (1 + 10^{-5}T \times 10^{0.725 - 50/T})$.

(10) Keesom, Van Agt and Jansen, *Leiden Comm.*, No. 182A.

(11) The formulation of these data by Southard and Milner[5] contains an arithmetical error (private communication).

(12) Prof. J. A. Beattie in a private communication has recommended 273.19 as a provisional value.

(13) Private communication from Professor F. G. Keyes of unpublished equation of state. However, the corrections are the same within our experimental error as those recommended by Henning, *Z. ges. Kälte-Ind.*, **37**, 169 (1930).

(14) The oxygen was prepared by heating potassium permanganate and passing the gas over potassium hydroxide pellets and phosphorus pentoxide. The product was condensed and the middle portion was distilled into the thermometer block.

above the boiling point. Oxygen was allowed to escape through a small tube into the atmosphere and the barometric pressure was measured with an accurate barometer. A similar procedure was followed in determining the hydrogen boiling point.

The temperatures obtained for the normal boiling point of oxygen, the normal boiling point of ordinary hydrogen and the triple point of ordinary hydrogen are 90.20, 20.37, and 13.94°K., respectively. These values agree with those obtained by other investigators within our limit of error.[15] All intercomparisons were made with the thermometer block at very nearly constant temperature. With the exception of eight comparisons, during which the drifts were slightly higher, all points were taken when the drift of the thermometer block was less than 0.04° per hour. Conditions such as room temperature, mercury temperature and shield temperatures were kept as steady as possible for at least one-half hour before a comparison was made. All measurements were made independently by two observers. Resistances were compared with an empirical equation obtained from our data by Dr. H. T. Gerry. The equation used for R197 is

$$\frac{R}{R_0} - \frac{R^0}{R_0} = \frac{T}{498.24 + 0.191T + 1.89 \times 10^4 T^{-4} + 0.6173 \times 10^8 T^{-8}}$$

where R_0 is the ice-point resistance, R^0 is the residual resistance at low temperatures, and T is the gas thermometer temperature. For use with the other thermometers the right-hand side was multiplied by a factor and a convenient value was chosen for R^0/R_0. The resistance measurements of Southard and Milner[5] on a platinum–10% rhodium thermometer were found to be in good agreement with a function of this type. The maximum departure of calibration points of this research from the smooth deviation curve was 0.03°, the average departure being less than 0.01°. A deviation plot was made for each thermometer and the smooth deviation curve was used to obtain the temperature scale for R197, a few values from which are given in Table II.

(15) For a summary of the literature, see Henning and Otto, *Physik. Z.*, **37**, 635 (1936). Our values are based on 273.19°K. for the ice-point.

The departure of the calibration points from the smooth deviation curve is indicated in Fig. 2. The ordinate is the difference between the temperature calculated from the measured resistance and the temperature indicated by the gas thermometer.

TABLE II

T	R	dR/dT	T	R	dR/dT
273.19	197.0827	0.3325	30	112.4883	0.1874
200	172.3764	.3445	20	111.1556	.0796
100	136.4367	.3779	14	110.8452	.0285
80	128.8396	.3800	12	110.7998	.0177
50	117.8879	.3310	10	(110.7728)	(.0101)

We believe that temperatures measured with R197 will be accurate to 0.02° between 20 and 90°K., and to 0.02% at higher temperatures.

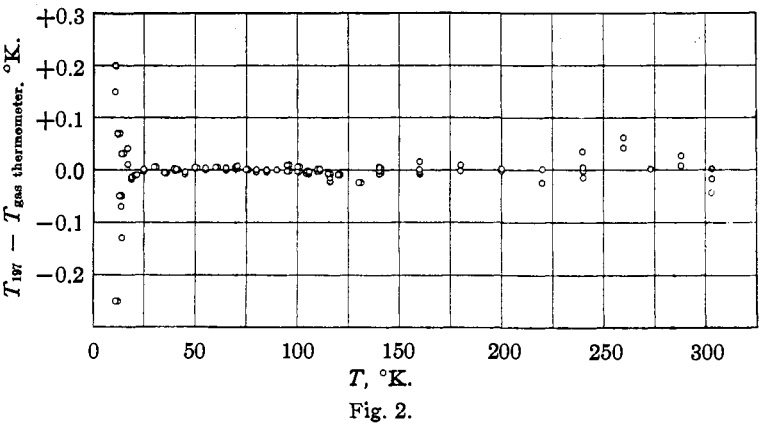

Fig. 2.

Because of the insensitivity of the resistance thermometer at the lower temperatures the error in temperatures measured with R197 may be 0.05° between 14 and 20°K., and 0.3° between 10 and 14°K.

We are indebted to Dr. H. T. Gerry for his valuable assistance in the design of the apparatus and the treatment of the data, and to Professor F. G. Keyes for his constant interest and encouragement.

Summary

The construction of platinum–10% rhodium resistance thermometers has been described and the calibration of thermometer R197 has been given in terms of the helium gas thermometer corrected to give thermodynamic temperatures. The normal boiling point of oxygen, the normal boiling point of ordinary hydrogen and the triple point of hydrogen have been found to be 90.20, 20.37, and 13.94°K., respectively, on the basis of 273.19°K. for the melting point of ice.

An improved cryostat has been described.

CAMBRIDGE, MASS. RECEIVED JULY 1, 1937