Huffman, Parks and Daniels between 90 and 300°K. well within the limits of accuracy claimed by them (1%). Furthermore, there is no tendency for one curve to be consistently higher or lower than the other up to 250°K. It should be pointed out while Huffman, Parks and Daniels used a "vacuum" calorimeter, their method of operation was entirely different and it seems probable that their corrections for radiation lead to the divergence at the higher temperatures.

It is interesting to note that the value Huffman, Parks and Daniels obtained by extrapolation from 90 to 0°K. for the entropy at 90°K. was 12.69 e. u. while the value found here is 12.52 e. u. with an extrapolation of only 0.43 e. u. from 15 to 0°K.

Acknowledgment.—The authors are indebted to Dr. R. T. Milner for his helpful suggestions in the construction of the apparatus and for his assistance in measurements on the empty calorimeter. They are indebted to Mr. J. W. Cook for liquefying the hydrogen and to Mr. R. A. Nelson for assisting in the measurements and calculations on naphthalene.

Summary

1. An improved adiabatic calorimeter for the measurement of specific heats of liquids and solids between 14 and 300°K. has been constructed. It can be used with a precision of about 0.1% and is particularly suited to the study of slow transitions and thermal changes.

2. The molal heat capacity of naphthalene was determined between 14 and 300°K. and the entropy and free energy of formation at 298.16°K. calculated to be 39.89 ± 0.12 e. u. and +48.5 kg. cal., respectively.

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Low Temperature Specific Heats. II. The Calibration of the Thermometer and the Resistance of Platinum, Platinum–10% Rhodium and Constantan between −259 and −190°

BY J. C. SOUTHARD AND R. T. MILNER

In the determination of a thermal property, the temperature scale and the thermometer that are used are of such fundamental importance that they deserve special consideration. The International Temperature Scale[1] was used for the specific heat measurements described in this series in the range over which it is defined, that is, above −190°. Below this temperature there is no accepted or established scale except that obtained by the use of a gas thermometer. This paper describes a helium constant volume thermometer that was used in a relatively simple manner to obtain

(1) G. K. Burgess, *Bur. Standards J. Research*, **1**, 635 (1928).

a knowledge of the resistance of specimens of platinum, platinum–10% rhodium and constantan at temperatures below −190°.

The resistance of platinum down to −259° has been measured at Leiden[2] and at the Reichsanstalt,[3] by comparison with gas thermometers. The relation between resistance and temperature below −190° is of a complex nature and up to this time has not been represented by an equation containing only a few constants. Simple deviation formulas to account for differences between various samples of platinum have been proposed[4] but there have been no detailed comparisons with experiment. Since the standard platinum resistance thermometer is used from −190 to 660°, it would be desirable to use this same metal below −190° if possible. Others have used copper–constantan thermocouples[5] and lead resistance thermometers. The latter were calibrated[6] by comparison with a platinum thermometer.

Apparatus

The gas thermometer bulb of 20 cc. capacity is formed by a very heavy-walled, cylindrical copper container (5 × 5.5 cm., wt. 760 g.). The inner surface of the bulb was machined smooth but not polished. The platinum cases of the resistance thermometers were soldered in holes in the heavy wall of the bulb. The bulb is connected to a manometer by a capillary tube (0.27 mm. i. d.) one meter long, made of a copper–nickel alloy of low thermal conductivity. The copper container is surrounded by a thermostated shield which can be so controlled that its temperature will not change 0.001° during periods of over half an hour.[7] All leads to the thermometers enter through a spiral groove in the shield. The capillary which passes through the outer bath which is below the temperature of the bulb has on it a separate difference thermocouple and heater which can be controlled so that the temperature gradient in the portion of the capillary next to the bulb is negligible. The bulb and shield are suspended in an evacuated brass jacket which is immersed in liquid hydrogen or liquid air. The liquid bath is enclosed by another jacket to which a vacuum pump may be attached.

The resistance thermometers are of a so-called "strain-free" four lead type, recently developed at the Bureau of Standards.[8] Wire of about 0.1 mm. diameter is wound into an open helix of approximately 0.5 mm. outside diameter which in turn is wound around a notched mica cross. After annealing the wire on the cross, the thermometer is slipped into a snug fitting cylindrical platinum case (5 × 45 mm.). The leads are brought out through a soft glass cap on the open end in such a manner that they are insulated from each other. After the case has been evacuated and filled with helium to about one-third atmosphere, the glass cap is sealed off close to the case. Two pure platinum thermometers (K_2 and K_V), a platinum–10% rhodium thermometer (K_4) and a constantan thermometer (K_5) were so constructed. K_V and K_5 were wound on the same mica cross and placed in a single tube together. The resistances of the ther-

(2) Cath, Onnes and Burger, *Comm. Phys. Lab. Univ. Leiden* 52 c, 1917; "I. C. T.," Vol. VI, p. 130. See also *Communications Phys. Lab. Univ. Leiden* Suppl. 58 (1926).

(3) Henning and Otto, *Z. ges. Kälte-Ind.*, **39**, 86 (1932).

(4) Nernst, *Sitz. preuss. Akad. Wiss. Physik-math. Klasse* 311 (1911); Henning, *Naturwissenschaften*, **16**, 617 (1928).

(5) Giauque, Buffington and Schulze, THIS JOURNAL, **49**, 2343 (1927).

(6) Clusius and Vaughen, *Z. ges. Kälte-Ind.*, **36**, 215 (1929).

(7) Southard and Brickwedde, THIS JOURNAL, **55**, 4378 (1933).

(8) C. H. Meyers, *Bur. Standards J. Research*, **9**, 807 (1932).

mometers are measured by comparison with a 100-ohm standard coil by means of a White double potentiometer and a type H. S. Leeds and Northrup galvanometer. Both the 100-ohm coil and the potentiometer had been calibrated by the electrical resistance section of the Bureau of Standards less than a week before use.

The U-type manometer was constructed from selected Pyrex tubing (10 mm. i. d.) of very uniform bore. The metal capillary was connected to one limb through a brass plug bearing a platinum pointer 1 mm. long to which the mercury meniscus was adjusted by means of a leveling bulb mounted on a traveling screw device. The other limb of the manometer was connected to a high vacuum system. The height of the column was read on a mirror-back calibrated glass scale to about 0.1 mm. with the unaided eye. As shown in the discussion later this precision of reading was ample.

Procedure

The copper bulb was first cooled to liquid air temperatures, helium admitted to a pressure of about one atmosphere, and the manometer filled with mercury through the leveling bulb. The helium had been purified by passing it first through activated charcoal immersed in liquid air and then through a spiral filled with charcoal immersed in liquid hydrogen.

The apparatus was then cooled to the triple point of hydrogen, the jacket evacuated to a pressure of less than 10^{-5} mm., and the shield regulated to maintain its temperature constant. A series of five resistance measurements was made on each thermometer while a number of manometer readings were being taken. During the time required for these readings the temperature of the bulb did not change by an amount detectable with either the manometer or the resistance thermometers. The block and shield were then heated from two to five degrees and the above procedure repeated.

Discussion of Results

In this type of gas thermometer there are three interconnected volumes which may be considered as being at three different temperatures.[9] If the temperature of each of these is considered uniform, and if the gas is assumed to obey the law pv/T = constant, then

$$p\left(\frac{V}{T_V} + \frac{v_m}{T_m} + \frac{v_c}{T_c}\right) = C \qquad (1)$$

where p is the pressure, V the volume of the bulb of the gas thermometer, v_m the volume in the manometer, v_c the volume of the capillary, T_v, T_m and T_c the temperatures of these respective volumes, and C depends on the total mass of gas. Here T_c represents the average or effective temperature of the capillary. If V is expressed as a function of temperature, $V = V_0(1 + \alpha\,(T_v - T_0))$ where V_0 is the volume at any reference temperature T_0, and α is the coefficient of expansion of copper, equation (1) becomes

$$T_v = \frac{pV_0}{C}\left[1 + \alpha\,(T_v - T_0) + \frac{v_m T_v}{V_0 T_m} + \frac{v_c T_v}{V_0 T_c}\right] \qquad (2)$$

as a sufficient approximation between 90 and 14°K. where α is 6.28×10^{-5}. Although T_v occurs on both sides of this equation, it is found on the right only in "correction" terms, so that successive approximations give T_v to any desired exactness. V_0/C is a constant which may be determined from

(9) For a more complete discussion see Henning, "Hand. d. Physik," Verlag Julius Springer, Berlin, 1926, Vol. IX, p. 532.

measurements at any reference temperature where T_v may be taken by definition. In this case the boiling point of oxygen was selected as the reference temperature and T_v obtained from the observations on thermometers K_2 and K_v which had been calibrated previously against an oxygen vapor pressure thermometer in a bath of boiling oxygen. The normal boiling point of oxygen is $-182.97°$ on the international temperature scale and with 273.16°K. for the ice point, this is 90.19°K.

With an initial pressure of 1 atmosphere at 90°K., a precision of 0.1 to 0.2 mm. in the manometer readings is equivalent to 0.01 or 0.02° in T_v. The calculation of the change of volume of the bulb with temperature is entirely dependent on measurements made at Leiden,[10] which appear to be uncertain by a factor of 1×10^{-4} at the lowest temperatures. The equation $V = V_{90}(1 + 6.28 \times 10^{-5}(T-90))$ was found to fit the data for copper satisfactorily below 90°K. Corrections for the manometer and capillary spaces appear in equation (2) as $v_m T_v / V_0 T_m$ and $v_c T_v / V_0 T_c$. Since $v_m / V_0 = 0.0073 \pm 0.0002$ and $T_v / T_m < 0.3$, uncertainties in the manometer space correction are negligible. Although v_c / V_0 is small (1.1×10^{-3}), the uncertainty in the mean temperature of the capillary T_c is such that an error of 0.01° in T_v may result from the capillary space correction.

Errors in resistance measurements were of the order of 10^{-4} ohm, involving an uncertainty of less than 0.01° in T_v in most cases. The reduction of values of T_v obtained from Eq. (2), which assumes a perfect gas, to the thermodynamic temperature scale was made using the data given by Henning,[11] which according to him are exact to a few thousandths of a degree for a pressure of one meter at 0°. Since the pressure used was equivalent to 2.4 meters at 0°, this uncertainty may amount to 0.01°.

Mendelssohn[12] has used a thermometer similar to this one for measurements at helium temperatures. He could not detect the Knudson[13] thermal pressure gradient when using capillaries of only 0.1 to 0.15 mm. diameter.

The results of the measurements are presented in Table I. A plot of these data would be too small to show deviations of observed values from a smooth curve and the complexity of the curve. Instead, a table of R/R_0 for platinum (K_2) has been constructed (Table II) by fitting two simple cubic equations over different parts of the range, plotting deviations from these and adding the two values algebraically. Figure 1 shows the differences between tabular and observed values. For K_2 the deviation from the axis gives an estimate of the precision while for K_v, with an R/R_0 curve differing from K_2, the deviation from a smooth curve is the criterion. A tabulation for the constantan thermometer K_5 covering the narrow range 14

(10) Keesom and Van Agr, *Leiden Comm.*, No. 182A.
(11) Henning, *Z. ges. Kälte-Ind.*, **37**, 169 (1930).
(12) Mendelssohn, *Z. Physik*, **73**, 482 (1931).
(13) Knudson, *Ann. Physik*, **31**, 205, 633 (1910); **33**, 1435 (1910).

to 26°K. in which it seems most useful is also given (Table II) and the resistance temperature curve shown in Fig. 2. A table similar to that of K_2 has been constructed for K_4 and the deviations are found to be of the same magnitude.

TABLE I

OBSERVED VALUES OF R/R_0 OF PLATINUM, PLATINUM-10% RHODIUM AND CONSTANTAN FROM 14.44 TO 97.06°K.

0°C. = 273.16°K.

Gas thermometer $P_{corr.}$, cm.	Gas thermometer T, °K.	R/R_0 K_2 Platinum R_0 = 24.8262 ohms	R/R_0 K_4 Pt-10% Rh R_0 = 53.4330 ohms	R/R_0 K_V Platinum R_0 = 19.2149 ohms	R/R_0 K_5 Constantan R_0 = 94.6220 ohms
12.46	14.44	0.003529	0.552698	0.003949	0.968158
14.85	17.20	.004664	.553280	.005100	.970853
15.82	18.33	.005289	.553615	.005736	.971944
17.09	19.77	.006255	.554144	.006726	.973320
18.71	21.65	.007786	.554979	.008276	.974934
21.56	24.95	.011415	.556935	.011951	.977324
25.47	29.47	.018412	.560620	.018985	.979570
29.55	34.20	.028422	.565712	.029019	.981046
33.79	39.10	.041315	.572068	.041956	.982313
37.92	43.89	.056166	.579234	.056852	.983431
42.17	48.83	.073285	.587287	.073906	.984440
46.54	53.91	.092334	.596183	.092969	.985468
50.81	58.88	.111995	.605288	.112631	.986453
55.04	63.81	.132320	.614655	.132980	.987432
17.60	20.36	.006707	.554388	.007177	.973852
23.28	26.94	.014201	.558423	.014751	.978390
27.26	31.54	.022492	.562731	.023065	.980222
31.67	36.65	.034580	.568774	.035181	.981713
35.74	41.37	.048191	.575397	.048816	.982858
39.88	46.17	.063864	.582869	.064466	.983905
44.28	51.29	.082425	.591583	.083061	.984959
48.35	56.01	.100599	.600033	.101229	.985904
52.64	61.00	.120848	.609379	.121489	.986900
77.77	90.32[a]	.246195	.666828	.246850	.992395
56.33	65.32	.138833	.617649	.139480	.987744
60.70	70.41	.160431	.627567	.161062	.988737
65.17	75.62	.182642	.637757	.183269	.989730
69.50	80.69	.204522	.647779	.205169	.990680
73.61	85.50	.225230	.657257	.225877	.991549
77.62	90.19[a]	.245635	.666570	.246267	.992376
72.78	84.61	.221540	.655563	.222182	.991383
77.66	90.33[a]	.24632	.666880	.246964	.992379
80.60	93.77	.26111	.673642	.261749	.992973
83.40	97.06	.27537	.680153	.276025	.993525

[a] Calibration point.

To check the accuracy of the gas thermometer measurements the temperature of liquid hydrogen boiling under atmospheric pressure was determined. This was accomplished by admitting helium to the surrounding jacket and allowing the thermometers to come to equilibrium in a bath of liquid hydrogen. The vapor pressure of the bath was determined by reading the barometer, since the pressure coefficient near the boiling point is about 230 mm./degree and even an error of 1 mm. could be neglected. At 750 mm. pressure the helium thermometer gave a temperature of

TABLE II

RESISTANCE OF PLATINUM (FROM 14 TO 109 °K.) AND CONSTANTAN (FROM 14 TO 25 °K.) AT ONE-DEGREE INTERVALS. READ FROM SMOOTHED DEVIATION CURVES

0 °C. = 273.16 °K.

T, °K.	R/R_0	T, °K.	R/R_0	T, °K.	R/R_0
Platinum Thermometer K_2. R_0 = 24.8262 ohms					
14	0.003400	46	0.063288	78	0.193032
15	.003724	47	.066774	79	.197341
16	.004110	48	.070323	80	.201652
17	.004566	49	.073931	81	.205965
18	.005099	50	.077594	82	.210279
19	.005716	51	.081309	83	.214594
20	.006423	52	.085073	84	.218910
21	.007226	53	.088883	85	.223227
22	.008130	54	.092747	86	.227545
23	.009140	55	.096643	87	.231864
24	.010260	56	.100579	88	.236184
25	.011493	57	.104552	89	.240505
26	.012842	58	.108560	90	.244826
27	.014309	59	.112601	91	.249147
28	.015896	60	.116673	92	.253468
29	.017604	61	.120774	93	.257789
30	.019432	62	.124902	94	.262110
31	.021379	63	.129055	95	.266431
32	.023444	64	.133231	96	.270751
33	.025625	65	.137428	97	.275071
34	.027920	66	.141644	98	.279390
35	.030326	67	.145877	99	.283708
36	.032841	68	.150125	100	.288014
37	.035464	69	.154386	101	.292328
38	.038190	70	.158658	102	.296639
39	.041016	71	.162939	103	.300947
40	.043939	72	.167227	104	.305251
41	.046955	73	.171520	105	.309551
42	.050060	74	.175817	106	.313846
43	.053250	75	.180117	107	.318136
44	.056521	76	.184420	108	.322421
45	.059869	77	.188725	109	.326701
Constantan Thermometer, K_5. R_0 = 94.6220 ohms					
14	0.967710	18	0.971654	22	0.975234
15	.968701	19	.972610	23	.976002
16	.969692	20	.973532	24	.976710
17	.970678	21	.974409	25	.977355
				26	.977924

20.36°K. This value corrected to 760 mm. gives 20.40°K. or −252.76°. This is an excellent agreement with the −252.78° of the Reichsanstalt and −252.75° of Leiden.[14]

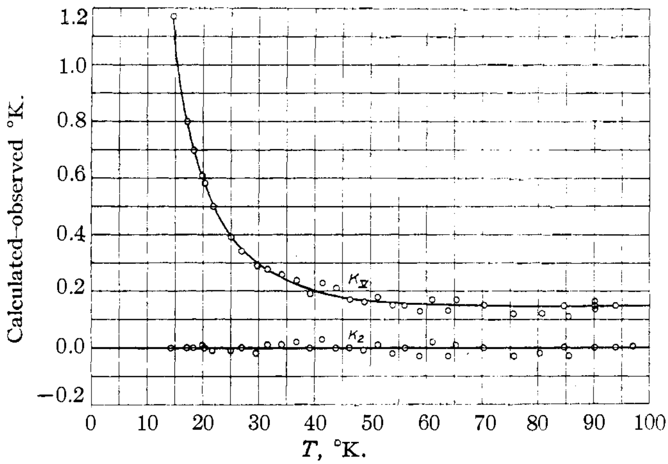

Fig. 1.—Deviation of platinum resistance thermometers K_2 and K_V from values given in reference table (II).

To show that the bulb had come to the temperature of the bath the resistances of the two platinum thermometers were compared with values previously obtained by direct immersion in a bath of boiling hydrogen. After making the proper correction for pressure differences, K_2 gave a resistance 0.0001 ohm higher and K_v 0.0001 ohm lower than previously, these variations being within the limits of error of the measurements.

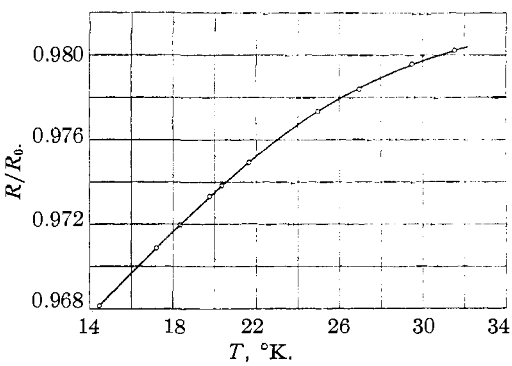

Fig. 2.—R/R_0 values for a constantan thermometer in the region of high sensitivity.

Henning[4] has published the deviation formula $R/R_0 - R'/R'_0 = (T - 273)[A - B/(T + 10)]$ for the range 20 to 80°K. without presenting data on which it was based. R/R_0 and R'/R'_0 refer to two thermometers at absolute temperature T; A and B are constants. The data of Table I furnish a test of this equation. Using K_2 and K_v for the two thermometers and evaluating A and B from the data for 21.66 and 90.19°K., no deviation equivalent to greater than 0.01° in $R/R_0 - R'/R'_0$ was found from 20 to 97°K.

(14) Heuse and Otto, *Ann. Physik,* [5] **9**, 486 (1931); Keesom, Bijl and van der Horst, *Leiden Comm.*, No. 217 (a); *Proc. Amst. Akad.*, **34**, 78 (1931).

Henning and Otto[3] have recently given values of R/R_0 at eight temperatures between 14 and 80°K. for four Reichsanstalt thermometers and one from Leiden. If this formula and the table for K_2 are used to calculate values of R/R_0 for these thermometers, no difference between observed and calculated values equivalent to more than 0.07° is found for any of the three thermometers of the purest platinum even though the values of R/R_0 at 20°K. vary from 0.0065 to 0.0092. For their thermometer No. 35, for which the values of R/R_0 are most nearly equal to those for K_2, the difference does not exceed 0.03°. We believe that the reference table given for K_2 together with Henning's formula should give values correct within 0.05° in the range 20 to 90°K., providing the unknown thermometer is calibrated at the boiling points of hydrogen and oxygen and has characteristics similar to those of K_2. For exact work, however, a direct comparison such as here carried out must be recommended.

The simplified four constant equation recommended by Henning and Otto[3] was also tested on K_2. Errors of as much as 0.11° were found in the computed values. When the temperatures chosen for evaluation of the four constants were changed, the constants were changed in both sign and magnitude.

The authors are indebted to Dr. F. G. Brickwedde for his help and encouragement in this work. The assistance of Mr. R. A. Nelson in the measurements and calculation, and of Mr. J. W. Cook in liquefying the hydrogen, is gratefully acknowledged.

Summary

1. A constant volume gas thermometer for use in the calibration of resistance thermometers between 14 and 90°K. has been constructed.

2. The resistance of specimens of platinum, platinum–10% rhodium and constantan has been determined in this range with an estimated error of about ±0.02°.

3. A reference table of R/R_0 for platinum between 14 and 109°K. and for constantan between 14 and 26°K. has been constructed giving values for every degree in this interval.

4. The usefulness of Henning's two constant deviation formula in conjunction with this reference table has been demonstrated.

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