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COPPER-CONSTANTAN THERMOCOUPLES AND THE HYDROGEN THERMOMETER COMPARED FROM 15 TO 283° ABSOLUTE

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One of the most important tasks of a laboratory engaged in low-temperature calorimetric and other measurements is the maintenance of a secondary thermometric standard.

Since 1918, the secondary standard of this Laboratory has been the four-junction copper-constantan thermocouple calibrated between 60 and 300°K. to an accuracy of 0.1° by Eastman and Rodebush.[2]

This thermocouple has been compared frequently with the freezing point of mercury since the original calibration, and has always been in closer agreement than the stated limits of accuracy.

However, for a number of reasons, the preparation of a new secondary standard has seemed necessary, the chief of these being the extension of the obtainable temperatures by the use of liquid hydrogen.

The gap between 15 and 60°K. has in some cases been bridged by making use of the triple- and boiling-point temperatures of hydrogen, but at best this leads to large uncertainties. For this reason, considerable data have for some time been withheld from publication, pending the conclusion of the work presented in this article.

Most of the recent calorimetric work in this Laboratory has utilized resistance thermometers which can be made much more sensitive and suitable for temperature interpolation than are thermocouples. This is especially true at very low temperatures.

However, at least for the immediate future, copper-constantan thermocouples were again chosen as the reference standard. This was primarily

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[2] Eastman and Rodebush, This Journal, 40, 489 (1918).

because they are much more convenient, and also because the experience with the Eastman-Rodebush standard couple had been satisfactory.

The convenience of thermocouples depends largely on the fact that they may, after calibration, be soldered to a metal apparatus, thus insuring excellent thermal contact. Resistance thermometers which may be detached for calibration have sometimes been used, for example, by Keesom and Onnes.[3]

It is expected that most cryogenic work in this Laboratory will, at least for some time, make direct use of fixed-resistance thermometers which are continuously calibrated during measurements by means of an attached thermocouple. This permits a precision in the measuring of small temperature intervals beyond that possible with a thermo-element alone, and at the same time furnishes a valuable check on the temperature measurements.

The effective portions of a thermocouple are those located in temperature gradients, and it is important that no inhomogeneities of a physical or a chemical nature occur at such places. When possible, tests for the effect of inhomogeneities should be carried out at temperatures approximating those at which the thermocouple is to be used. We believe that the use of liquid air as described is an unusually severe test.

The Thermocouple Wire

The Laboratory supply of constantan, consisting of 58 spools of various sizes and amounts, including 20 spools of No. 30 B. and S. gage, was tested. The e.m.f. against copper between 83 and 273°K. was measured in each case, and in most cases a loop was run through liquid air and galvanometer deflections were noted as a measure of imperfections. Sharp turns were prevented by means of a submerged glass U with a radius of about 6 cm. The warm ends of the loop were attached to copper and kept in an ice-bath. About 1.5 meters of each sample was pulled through, and the procedure was then reversed.

Table I shows typical results on the best constantan wire of various sizes. The deflections in the case of the poorer wire went as high as 10 microvolts, even in the larger sizes. It is evident from the data that very small wire should not be used. The severe gradient imposed by the test would be somewhat greater in the case of small wires, but the same situation might arise in the normal use of thermocouples.

TABLE I

TESTS ON CONSTANTAN WIRE

Size, B. and S. gage	25	30	35	40
E.m.f. vs. Cu at 83°K., microvolts	5468	5810	5791	5609
Av. e.m.f., microvolts	0.24	0.35	0.87	1.84
Maximum	.7	.8	2.0	3.1

[3] Keesom and Onnes, *Comm. Phys. Lab. Leiden*, 143, **1914**.

Table II shows the e.m.f.'s of some copper-copper thermocouples with junctions at liquid air and ice temperatures in each case. It is evidently necessary to use the same copper for all couples when close agreement is desirable for intercomparisons.

TABLE II

TESTS ON COPPER WIRE

Size	20	24	28	36(a)	36(b)	36(c)	40(a)	40(b)
E.m.f. vs. No. 36(a) junctions 83 and 273°K., microvolts	+2.7	−0.5	−5.2	(0.0)	−0.2	−0.1	−27.1	+13.8

The Thermocouples

Since it was desired to solder the couples to apparatus, the use of multi-junction couples was eliminated. At the suggestion of Dr. D. H. Andrews, parallel constantan wires were used to average out, partially, small imperfections. This method has recently been used by Hovorka and Rodebush.[4]

Six thermocouples, designated as J, W, 15, 16, 17 and 18, respectively, were made. Each consisted of five No. 30 double-silk-covered constantan wires, and one No. 36 double-silk-covered copper leading to the variable junction. J and W each had five No. 36 copper leads to the individual constantan wires at the ice ends, while 15, 16, 17 and 18 had only one No. 36 copper lead from the ice end in each case. The five No. 30 constantan wires had about the same thermal conductivity as one No. 36 copper wire.

In addition to the above, one couple was made from another spool of No. 30 constantan, which gave 5494 microvolts when opposed to copper at 83 and 0°K. The loop test on this wire gave an average deflection of 0.34 and maximum deflection of 0.9 microvolt. Four parallel constantan wires with separate No. 36 ice ends were used. All of the couples, each of which was 268 cm. long, were wrapped with silk thread.

The Thermocouple Comparison Apparatus

All of the variable junctions were well soldered to a solid cylinder consisting of about 1 kg. of lead. This was suspended within a hollow lead and copper cylinder of about 1.2 kg., which was itself suspended within a brass container suitable for high vacuum.

Each couple was wound twice about the outer cylinder and three times around the inner one, 72 cm. being used in this way as a protection against heat leak into the junctions. The wires wound on the cylinders were heavily paraffined, and the whole was wound with adhesive tape.

Other details of construction and temperature control were quite similar to those of the final gas-thermometer apparatus, and will be described in that connection.

[4] Hovorka and Rodebush, THIS JOURNAL, 47, 1614 (1925).

Table III shows some typical results of the constantan comparison. Col. 1 gives the approximate e.m.f. against copper. Cols. 2–6, inclusive, give the differences between the various parallel groups of constantan wires. Cols. 7–10 show the comparison of the individual constantan wires contained in the parallel group of J. All differences were determined with a galvanometer, using the double-deflection method. The reversing switch was located at the apparatus, thus practically eliminating any error from electrical leaks.

Comparison of the results on single wires and on parallel groups shows that the latter are considerably more reliable, as was to be expected. The algebraic signs are all consistent; thus, when 15–Cu = 5220.00 and J–15 = —0.45, then J–Cu = 5219.55. Comparisons were made at intervals of about 10°.

Table III

Typical Results of Constantan Comparisons

(Values are given in microvolts)

15–Cu	J–15	W–15	16–15	17–15	18–15	5–6	5–7	5–8	5–9
6587	−0.63	−0.74	+0.11	+0.48	+0.30	−0.36	−0.42	−0.39	−0.46
6014	− .53	− .63	+ .17	+ .52	+ .32	− .51	− .44	− .44	− .54
5220	− .45	− .54	+ .13	+ .13	+ .52	+ .31	− .53	− .26	− .44
3185	− .44	− .36	− .02	+ .15	+ .06	+ .46	+ .00	− .37	− .48
− 2	+ .02	− .05	− .03	+ .03	− .03	+ .07	+ .09	+ .09	+ .02

The differences between the various copper wires, as shown in Table IV, were somewhat unexpected, since all of the wire was taken from the same spool (No. 36 a).

Table IV

Typical Results of Copper Comparisons

15–Cu	$W_{Cu}-J_{Cu}$	$15_{Cu}-J_{Cu}$	$16_{Cu}-J_{Cu}$	$17_{Cu}-J_{Cu}$	$18_{Cu}-J_{Cu}$
6518	+0.29	+0.76	+0.48	+0.97	+1.40
6336	+ .20	+ .36	+ .27	+ .62	+0.92
6014	+ .09	+ .10	+ .10	+ .37	+ .51
5220	+ .01	− .12	− .03	+ .14	+ .12
3185	− .06	− .20	− .10	− .05	− .10
− 2	− .02	− .04	− .01	− .04	− .02

Thermocouple 17 was selected for comparison with the hydrogen gas thermometer.

The Hydrogen Thermometer

The hydrogen-thermometer comparison apparatus used differs considerably from instruments used for this purpose by others. It was modeled after a calorimeter for the investigation of liquefied and solidified gases used by Giauque and Wiebe for a series of measurements soon to be published.

The apparatus is shown in Fig. 1.

D is a vacuum-tight monel container with connecting tube shown at A. The cover of D was equipped with a cup (not shown) which could be filled with water as a protection for the wires while the cover was being soldered on. B is a 6kg. block of lead. F is a hollow cylinder of lead and copper weighing about 7.5 kg. and supported from the cover of D by stout cords. G is a vacuum-tight 1.5kg. copper and lead container for the thermometer bulb. The spaces between D and F and between F and G could be evacuated. C is a German silver tube leading from G through F and then out at the top of Tube A. The 0.8mm. capillary leading from the 194.3cc. Pyrex bulb, shown at H, was taken out through Tube C. Hydrogen gas could be admitted through Tube C to the space around the capillary and bulb. A rough manometer was used in keeping this pressure approximately equal to that within the bulb, thus eliminating the necessity of pressure correction on the bulb volume. At Position E the tube C was securely soldered to Cylinder F, and the space between the capillary and tube was filled with Rose's metal for a length of 2 cm., with the exception of two very fine thin-walled glass tubes for the passage of hydrogen. Also, the capillary was wrapped at intervals of 2 cm. with narrow strips of adhesive tape until the space between the capillary and Tube C was nearly tight at these points.

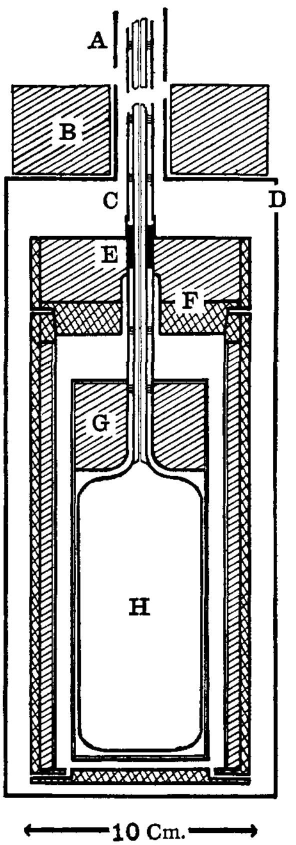


Fig. 1.

The purpose of the adhesive tape and of the Rose's metal was to minimize longitudinal and insure radial conduction. F and G were equipped with electric heaters for temperature control. Control thermocouples were attached to D, F and Tube C at points 20, 40 and 60 cm. above Position E. The temperature at 80 cm. above Position E was taken with a mercury thermometer in a cup attached to a copper case which also enclosed the capillary leading to the manometer. These temperatures were necessary in making the correction for the amount of gas in the capillary.

The top of Tube C was attached to the capillary by means of rubber tubing and de Khotinsky cement to avoid strain by unequal expansion. All wires were taken out through de Khotinsky cement.

Production and Control of Low Temperatures

All temperatures below room temperature were produced by either liquid air or liquid hydrogen at normal or reduced pressures. For example, at temperatures above 100°K., liquid air was used in small quantities, so that no great temperature difference existed between Container D and Cylinder F, Fig. 1. The apparatus was first cooled to the lowest desired temperature, Container D being filled with several centimeters' pressure of hydrogen to supply the necessary conduction. Container D was then evacuated to a pressure of about 10^{-5} mm. of mercury or better. Cylinders F and G were then easily adjusted to equal temperature by means of their electric heaters. The high vacuum reduced the heat leak to such an extent that the temperature of Cylinder G would not change by 0.01° during the course of a measurement.

Placing of Thermocouple

Thermocouple No. 17 was soldered to the lower portion or container G. It was also otherwise placed as nearly as possible in the same manner as that used in the comparison apparatus. Particular attention was paid to having the temperature gradient occur in the same portion of the wire.

The Manometer

The manometer and auxiliaries are shown in Fig. 2. J and L indicate the arms of the manometer, the inside diameter of each being about 1.2 cm. L also indicates a very close-fitting monel plug, carrying the thermometer capillary and cemented in with melted shellac and de Khotinsky cement. A 0.07cm. tip, which was off center in the line of vision, projected from the lower side of the monel plug as a reference point in adjusting the mercury level in that arm. See the description of the manometer used by Cath and Onnes.[5] A standard meter is shown at K. M shows the mercury reservoir with central stopcock at N. The capillary shown near O was a partial guard against rapid flow of mercury in case Stopcock O was opened while the manometer was out of balance. P shows a rubber tubing with clamp actuated by a screw worked by a series of reduction pulleys through Shaft Q. This permitted a fine adjustment of the mercury level. Tube I was attached to an evacuating system with mercury-diffusion pump and McLeod gage. The hydrogen was admitted through Tube I before filling with mercury.

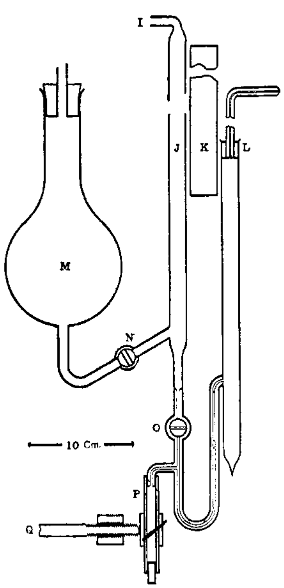


Fig. 2.

All of the apparatus shown in Fig. 2 was enclosed in a tight wooden case with a plate-glass window. The temperature of the case was controlled by a stream of air from the Laboratory compressed-air system. This gave a temperature which varied very slowly with time. The lighting of the menisci and meter was by means of focusing flashlights and a spotlight, all located far enough away to avoid large heating effects, and was used intermittently. The temperature of the mercury was obtained by means of four mercury thermometers.

[5] Cath and Onnes, *Comm. Phys. Lab. Leiden*, No. 156a, **1922.**

Pressure Measurements

The pressure measurements were made by using a Société Génevoise cathetometer for the comparison of the mercury menisci with the nearest millimeter ruling on the standard meter. The accuracy was 0.02 mm. The manometer case was tapped before each measurement to prevent sticking of the menisci. Since there was a high vacuum over the mercury in Tube J, direct pressure readings were secured. The correction for meniscus depression was that given in the International Critical Tables.[6] Since both arms of the manometer were of the same diameter, this correction was nearly balanced out.

Electrical Measurements

Two White double potentiometers were used simultaneously for the electrical measurements, one for the control thermocouples, and one of 10,000 microvolts' range with a galvanometer of low critical ramping resistance for the standard couple. The latter potentiometer was calibrated.

All wiring between the apparatus and potentiometer was supported from the lower side of highly insulating strips of Bakelite, and the whole system electrically shielded.

Temperature Variation of Bulb Volume

The correction for the diminution of bulb volume at low temperatures was made possible by the expansion measurements of Buffington and Latimer[7] on Pyrex. Their measurements extend only to liquid-air temperatures, thus necessitating considerable extrapolation. Fortunately, however, the nature of the correction is such that it becomes less important at very low temperatures.

The Obnoxious Volume

The obnoxious volume consists of the connecting capillary and the volume between the mercury meniscus and the monel plug. The latter volume was calculable from meniscus data in the International Critical Tables.[8] Data for this calculation were secured with each measurement.

In making the correction for the amount of gas in that section of the capillary within the temperature gradient, a graphical method was used.

Preparation and Purity of Hydrogen

The preparation of the electrolytic hydrogen was the same as that described by Latimer, Buffington and Hoenshel,[9] except that the rate of

[6] International Critical Tables, McGraw-Hill Book Co., New York, **1926**, vol. I, p. 70.

[7] Buffington and Latimer, THIS JOURNAL, **48**, 2305 (1926).

[8] Ref. 6, p. 72.

[9] Latimer, Buffington and Hoenshel, THIS JOURNAL, **47**, 1571 (1925).

flow over the nickel catalyst used for removing oxygen was 0.1 cu. meter per hour, and an extra tube of nickel catalyst was used as an added precaution. Although hydrogen prepared in the above manner contains less than 0.01% of oxygen, it was still further purified by standing over charcoal at liquid air temperature. The charcoal had previously been heated and pumped with a mercury diffusion pump.

Filling the Thermometer

The thermometer bulb was evacuated with a mercury diffusion pump and swept out with pure hydrogen several times before the final filling. The evacuation was slow because of the small diameter of the capillary. More than a week was required for the above procedure.

Reconstruction of Apparatus

After the completion of runs referred to as 1 and 2, one of the supports of the heavy cylinder gave way, and the capillary leading to the manometer snapped off. Also, after removal, thermocouple No. 17 proved to have developed a short circuit. The apparatus was repaired and Thermocouple J was used instead of immediately repairing No. 17. The silk insulation of 17 was easily repaired later. The bulb was refilled with hydrogen, and runs designated as 3, 4 and 5 were made. The reconstructed apparatus and new thermocouple proved to be a valuable check on the previous measurements.

The Ice Point

It was realized in the designing of the apparatus that the thermometer bulb could not be brought with sufficient accuracy to the ice point by surrounding the whole apparatus with ice; in fact, this experiment was not tried. However, it has been shown that the maximum difference in e.m.f. between any of the couples when the variable junctions were at the ice point was 0.07 microvolts, corresponding to 0.002°. This

Table V

Ice-Point Pressures

	Press., cm.	Valued used, cm.
Immediately after filling	97.916	
Before Run 1	97.924	
		97.926
End of Run 1	97.926	
End of Run 2	97.933	
	97.938	97.935
After refilling for Runs 3, 4 and 5	96.791	
	96.787[a]	
	96.783	96.783
Near end of Run 5	96.782	

[a] Heavy protective cylinder cooling rapidly.

enabled the ice point to be obtained by adjusting the temperature of the heavy cylinders until the thermocouple reading was zero, or nearly so. Table V shows the ice-point data.

The ice-point pressure gradually increased during Runs 1 and 2. The apparatus was known to be tight at the start by test with a McLeod gage before filling, but considerable difficulty was encountered in displacing the hydrogen by mercury in Tube P, Fig. 2, and small bubbles were observed on several occasions in the adjoining tube. The gas eventually rose into Tube J and was pumped off, but some apparently was carried into Tube L, Fig. 2, on the few occasions when the mercury moved rapidly through the capillary U. There is also some possibility that the plug in the bottom of Tube P leaked slightly, which might admit some air. If the gas were hydrogen it would make no difference as to the results, while even if it were air the effect would not exceed 0.01° in the most unfavorable case.

Before Runs 3, 4 and 5, Tube P was renewed and filled with mercury before hydrogen was admitted. The pressure then showed a slight decrease with time. The result marked *a* was obtained after rapidly heating the bulb from the neighborhood of liquid-air temperatures, and may indicate some temperature lag in bulb volume as well as the effect of other unfavorable conditions.

Most of the measurements were made by four observers simultaneously recording the various data.

Treatment of Results

The data were treated as follows. An approximate temperature scale (accurate to a few tenths of a degree) was calculated. The various corrections could then be applied, giving a table of e.m.f. and temperatures on the hydrogen scale. The data of Cath and Onnes[5] were used for correcting the temperatures from the hydrogen to the thermodynamic scale.

A plot of $\Delta\epsilon/\Delta T$ against T was constructed. Approximate $\mathrm{d}\epsilon/\mathrm{d}T$ and ϵ values were chosen. First and second differences of the $\mathrm{d}\epsilon/\mathrm{d}T$ values were tabulated. The approximate table was used to calculate the individual points. Guided by the above comparison, the $\mathrm{d}\epsilon/\mathrm{d}T$ differences were smoothed, and the final Table VI was constructed for Thermocouple 17. Fig. 3 shows the comparison of the temperatures given by the gas thermometer with those calculated from the thermocouple readings by means of Table VI. No absolute significance is to be attached to the data in Table VI, but it should prove useful in the construction of deviation plots for interpolating data of other thermocouples when only a few points are available. This is the method suggested by Adams,[10] but his data extend only to liquid-air temperatures. An

[10] Ref. 6, p. 57.

equation method could be used, but aside from the considerable difficulty in obtaining an equation to fit the observed data, we believe the deviation plot to be the more advantageous method.

Table VI

Temperature Conversion Table

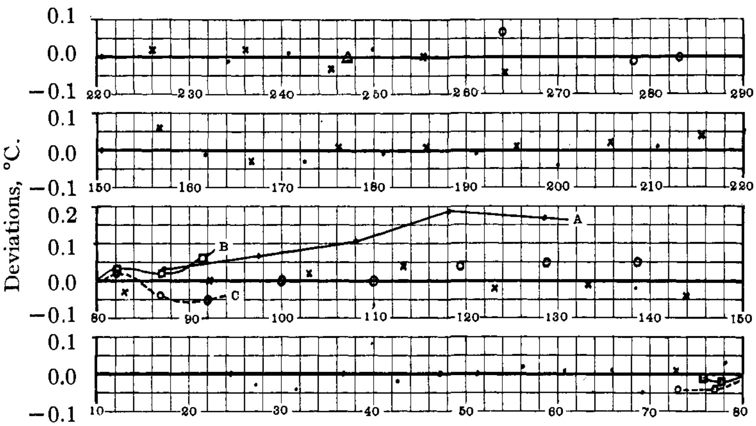
T, °K.	ε	Diff.	dε/dT	Diff.	T, °K.	ε	Diff.	dε/dT	Diff.
25	6586.0		7.10		160	3996.9		28.67	
		39.1		1.38			293.0		1.26
30	6546.9		8.48		170	3703.9		29.93	
		45.6		1.26			305.5		1.24
35	6501.3		9.74		180	3398.4		31.17	
		51.7		1.15			317.9		1.23
40	6449.6		10.89		190	3080.5		32.40	
		119.1		2.00			330.0		1.20
50	6330.5		12.89		200	2750.5		33.60	
		138.2		1.81			341.9		1.17
60	6192.3		14.70		210	2408.6		34.77	
		155.3		1.64			353.3		1.13
70	6037.0		16.34		220	2055.3		35.90	
		171.0		1.50			364.5		1.09
80	5866.0		17.84		230	1690.8		36.99	
		185.5		1.42			375.2		1.06
90	5680.5		19.26		240	1315.6		38.05	
		199.6		1.40			385.7		1.04
100	5480.9		20.66		250	929.9		39.09	
		213.6		1.39			396.0		1.01
110	5267.3		22.05		260	533.9		40.10	
		227.3		1.37			406.0		0.99
120	5040.0		23.42		270	127.9		41.09	
		241.0		1.35			415.7		0.96
130	4799.0		24.77		280	−287.8		42.05	
		254.3		1.32			425.2		(0.94)
140	4544.7		26.09		290	(−713.0)		(42.99)	
		267.4		1.30					
150	4277.3		27.39						
		280.4		1.28					

Since the completion of the work considered in this paper, Giauque, Johnston and Kelley have made a comparison of the scale here obtained with the hydrogen and oxygen vapor-pressure thermometers. This work, which is described in a following paper,[11] shows that the measurements below 25°K. are in error, presumably due to adsorption of hydrogen within the thermometer. We have accordingly extended Table VI only to 25°K. The extension of Table VI to 13°K., as well as a discussion of the adsorption effect, will be found in another paper.[11]

The results between 87 and 128°K. in Run 2 show the effect of neglect with regard to the ice junction. The ice had been in use for nearly 20

[11] Giauque, Johnston and Kelley, This Journal, **49**, 2367 (1927).

hours when this effect took place. The result at 264°K. in Run 5, which deviates by 0.07°, was taken after rapid warming from 138°K. and may indicate lag in the Pyrex bulb. The ice point immediately following this measurement was also off in the same direction. The greatest lack of agreement seems to be in the range where the obnoxious volume correction is most important, that is, at about 140°K. The effect of having the temperature gradient larger or smaller than was normal for the apparatus as used seems to be quite definite. It is difficult to segregate the effect on the gas thermometer from that on the thermocouple, but we suspect the latter. To our knowledge there is no theoretical or experimental reason to suppose that the irreversible heat flow which is necessarily



× Run 1. ● Run 2. △ Run 3. □ Run 4. ○ Run 5. A, new ice on junction; B, temperature gradient large as possible; C, temperature gradient small as possible.

Fig. 3.—Deviation graph.

present in thermocouples may not be contributing appreciably to the e.m.f., and if so the amount due to this factor may depend on the character of the gradient. The effect referred to is of course not to be confused with those due to inhomogeneity. However, regardless of the nature of the small disturbances always observed in the use of thermocouples, it is obviously desirable to calibrate thermocouples under conditions nearly the same as those which exist when they are used.

The agreement of results with Thermocouples 17 and J was satisfactory. All of the results with J are expressed in terms of No. 17.

In connection with other experimental work, as yet unpublished, initial comparison with the temperature scales of others is available. Giauque and Wiebe have measured the vapor pressure of hydrogen chloride, using Thermocouple 18 as a reference standard. The results agree with those of Henning and Stock[12] to one or two hundredths of a degree. This agreement is particularly significant since the work of Henning and Stock in the *Physikalisch-Technischen Reichsanstalt* was for the purpose of establishing thermometric standards. Their hydrogen chloride data extend from 156 to 186°K.

Before the hydrogen thermometer measurements were made, the e.m.f. of Thermocouple 17 in melting mercury had been measured. From Table VI this e.m.f. corresponds to a temperature of 234.18°K. The value given in the International Critical Tables is 234.23°K. The agreement is satisfactory, especially considering that the temperature gradient in this case was not in the same portion of the wire in which it occurred during the calibration. Other investigations in progress in this Laboratory will provide still other comparisons.

The results above 25°K. are believed to be accurate to 0.05°, which is considered quite satisfactory for present requirements.

The research described in this paper has been regarded as of a laboratory rather than an individual nature, and many besides the co-authors have contributed. We wish to express our thanks to W. M. Latimer, D. H. Andrews, H. D. Hoenshel, S. S. Shaffer, and particularly to R. Wiebe and H. L. Johnston, who assisted in making Runs 1 and 2.

Summary

The testing of constantan and copper wires for thermocouple use at low temperatures has been described.

The comparison of copper-constantan thermocouples with each other and with the hydrogen gas thermometer from 15 to 283°K. has been carried out, and considerable information is given as to what may be expected of carefully prepared thermocouples over the above range.

A gas thermometer has been described with which it is easily possible to obtain and maintain to 0.01°, for sufficient time, any temperature from that of liquid hydrogen to room temperature.

A table showing the properties of a typical copper-constantan thermocouple from 25 to 283°K. is included.

BERKELEY, CALIFORNIA

[12] Henning and Stock, *Z. Physik*, **4**, 226 (1921).