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CALORIMETRIC RESISTANCE THERMOMETERS AND THE TRANSITION TEMPERATURE OF SODIUM SULPHATE[1].

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I. Calorimetric Resistance Thermometers.

Of the methods in use for temperature measurement the variation in resistance of metallic wires affords probably the most accurate means of obtaining differences of temperature over a limited range. When the resistance material is a pure metal, resistance is in most cases a simple function of temperature. The metal generally used has been platinum, on account of its high specific resistance, high melting point and freedom from oxidation.

Construction of the Thermometers.—A form of resistance thermometer for calorimetric work was constructed as follows : four leads of thin copper strip about 15 cm. long, 4 mm. wide, and 0.12 mm. thick, are each fused[2] to a piece of 0.1 mm. platinum wire about 10 mm. long. The leads are then laid side by side, separated by thin mica strips, and one pair is connected to the ends of a coil of about 10 cm. of 0.02 mm. platinum wire wound in a flat coil on the end of one of the mica strips ; the other leads are connected by fusing together the ends of the short platinum

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[1] Published in full in Bull. Bureau of Standards, 3, 1907.

[2] In making up these thermometers it was found impracticable to wind the coils after fusing to the leads, and to overcome the difficulty of fusing wires so fine as 0.02 mm. in somewhat inaccessible positions an arc was used. The arc was formed between a small graphite pencil and one of the terminals to be fused, when the other terminal was brought up and the two connected. After a little practice this could be done quickly and neatly. This same method has since been used to advantage in fusing together wires of different materials and sizes. The platinum terminals also were fused to the copper leads by the same method. The fusing of copper wires is more easily effected when borax is used as a flux. It is necessary to regulate both the voltage and the resistance in series with the arc for different sizes of wire.

terminals. This second pair of leads is used to compensate for varying depth of immersion.

The leads and coil thus prepared were enclosed in a flat sheath of thin copper (0.12 mm. thick) and insulated from it by thin mica. The sheath was then soldered up along the side, copper-plated, and then gold-plated to protect it from oxidation. When finished it was about 7 mm. wide and 1 mm. thick, somewhat thinner at the coil. Finally it was sealed into a head of hard rubber, which serves to hold the flexible leads to the bridge, and covers containing a drying salt were also added.

This thermometer for calorimetric work has the following advantages : (a) very small time lag, (b) small water equivalent, (c) small thermo-electric effects due to the copper-platinum junctions, which are very close together, (d) high resistance (about 30 ohms in ice), (e) heat conduction by the leads affecting the temperature of the coil is not noticeable when the immersion is as much as 5 cm., (f) the resistance is made independent of depth of immersion by the use of compensating leads, (g) the insulation resistance has always been over 100 megohms.

Resistance Measurements.—Measurements of resistance were made by the Wheatstone bridge method using a bridge constructed especially for resistance thermometry. This bridge has an adjustable resistance of 110 ohms, the smallest coils being 0.01 ohm. In place of a bridge wire three shunt dials are used, giving steps of 0.001, 0.0001 and 0.00001 ohm respectively. The galvanometer used was of the Broca type and was so adjusted that a change of 0.0001 ohm, corresponding to 0.001° in temperature, gave a deflection of 1 mm. on the scale.

The bridge was calibrated several times during the progress of the work. All resistance measurements were made by reversing both battery and galvanometer connections to eliminate any small thermoelectric effects. A Griffiths thermoelectric key was used. The ratio arms were also reversed during each measurement.

Calibration of the Thermometers.—The formula proposed by Callendar

$$t - pt = \delta \left(\frac{t}{100} - 1 \right) \frac{t}{100} \quad \text{where } pt = \frac{R_t - R_0}{R_{100} - R_0} \times 100 \text{ was used as the}$$

basis of the calibration. The fundamental interval, $R_{100} - R_0$ was determined by measuring the resistance in ice and in steam in the usual manner. In Table I are given the values found at different times.

The constant δ was determined by comparing each resistance thermometer at 30°, 40°, 50°, 60°, 70°, with four primary standard mercurial thermometers of the Bureau of Standards. By an elaborate intercomparison the relation of each of these thermometers to the mean scale of the Bureau, which is defined by 16 thermometers calibrated at the International Bureau, and which have been shown to be in agreement with the Inter-

TABLE I.
VALUES OF $R_{100} - R_0$.

Date	Thermometer A		Thermometer B	
	R_0	$R_{100} - R_0$	R_0	$R_{100} - R_0$
10- 6-06	29.00548	9.75060	28.94158	9.76746
		9.75068		9.76755
10- 8-06	29.00498	9.75079	29.94128	9.76777
		9.75097		9.76777
10-12-06	29.00530	9.75055	28.94160	9.76747
		9.75055		9.76709
10-18-06	29.00570	9.75063	28.94202	9.76720
		9.75062		9.76720
1-18-07	29.00579	9.75091	28.94230	9.76717
		9.75062		9.76728
		9.75019		
2-27-07	29.00603	9.75111[1]	28.94260	9.76791[1]
		9.75115[1]		9.76800[1]
7-11-07	29.00564	9.75062		
		9.75068		
7-12-07	29.00568	9.75065	28.94200	9.76727
		9.75033		9.76735
		9.75051		
Mean		9.75062		9.76738
		± .00003		± .00003

national Hydrogen scale, had been established. Table II gives the results of this calibration, which shows that the platinum thermometers may be used to reproduce the International Hydrogen Scale to about $0°.002$.

TABLE II.
VALUES OF δ.

Thermometer A					Thermometer B				
Point	$t-pt$	δ	Obs.- mean	Residual in temp. C	Point	$t-pt$	δ	Obs.- mean	Residual in temp. C
30°	0°.3264	1.560	+.006	0°.0013	30°	0°.3276	1.565	+.009	0°.0019
40°	0°.3711	1.548	—.006	0°.0014	40°	0°.3707	1.547	—.009	0°.0021
50°	0°.3890	1.556	+.002	0°.0005	50°	0°.3897	1.559	+.003	0°.0008
60°	0°.3722	1.550	—.004	0°.0010	60°	0°.3742	1.558	+.002	0°.0005
70°	0°.3269	1.554	.000	0°.0000	70°	0°.3259	1.550	—.006	0°.0013
Mean		1.554	.004	0°.0008	Mean		1.556	.006	0°.0013

II. The Transition Temperature of Sodium Sulphate.

Since it has been shown that the relation between platinum temperature and the International Hydrogen Scale in the interval $0°$ to $100°$ may be given by a single constant (δ) it is evident that this constant might be equally well determined at a single temperature (in addition to the two fixed points) if the determination were made with sufficient accuracy. The work of Richards[2] and of Richards and Wells[3] has shown

[1] Not used in mean.
[2] Am. J. Sci., 6, 201, 1898.
[3] Pr. Am. Acad. Arts and Sci., 38, 431, 1902.

that the transition point of sodium sulphate serves to fix a definite temperature which would be suitable for such determinations.

The care with which this work was done and the small probable error deduced from the observations require that anyone attempting to repeat the work should have exceptional facilities for obtaining accurate results. On the other hand, it is very desirable to secure a further check on a point so important, in view of its proposed use in the calibration of calorimetric thermometers.

It was decided to use the two platinum thermometers, calibrated as above described, in a redetermination of this temperature. While this is an indirect method, it has certain advantages over a direct determination with mercurial thermometers. In the first place, the platinum temperature could be determined to about $0°.001$ by a single observation so that the errors in referring the point to the platinum scale become almost negligible and the whole problem is reduced to the relation between the platinum scale and the hydrogen scale, *i.e.*, the accuracy of mercurial thermometers.

Since the four thermometers used at each point have not only been calibrated at the International Bureau, but have been compared with a number of other primary standards also calibrated there and some of them directly compared with the standards of the International Bureau, they offer a means of reproducing the international hydrogen scale with the highest accuracy.

Moreover, the mercurial thermometers were used under conditions most favorable to attaining accurate results, *i.e.*, with total immersion, reading at principal calibration points where their indications are most reliable and reading with a rising meniscus. This avoids one of the largest sources of error in using mercurial thermometers, *i.e.*, the determination of a fixed point. In addition, as has been shown, the hydrogen scale represented by these platinum thermometers was obtained from the mean of observations taken at $30°$, $40°$, $50°$, $60°$, and $70°$, so that in fact, the determination of the transition temperature $32°.38$, rests upon observations of four thermometers at each of five points.

Method of Experiment.

The arrangement of the apparatus is shown in the accompanying figure, Fig. 1. (B) is a cylindrical brass case 6 cm. in diameter and 24 cm. long, which was immersed to the point (D) in a water bath ordinarily used for testing clinical thermometers. By this means the external temperature was regulated and could be maintained constant to $0°.1$ for any length of time. The salt was contained in a strong test tube (N), 3 cm. in diameter and 15 cm. long, holding about 100 grams. Smaller tubes holding about 50 grams were also used in some of the preliminary work. The head of the thermometer (T) was held in place by a cork

(C) fitted into a removable sleeve (S).   The salt was thus entirely enclosed in an air space at the temperature of the surrounding water.

The first experiments were made on a sample of "Kahlbaum" sodium sulphate.   Following the procedure of Richards, the crystals were first
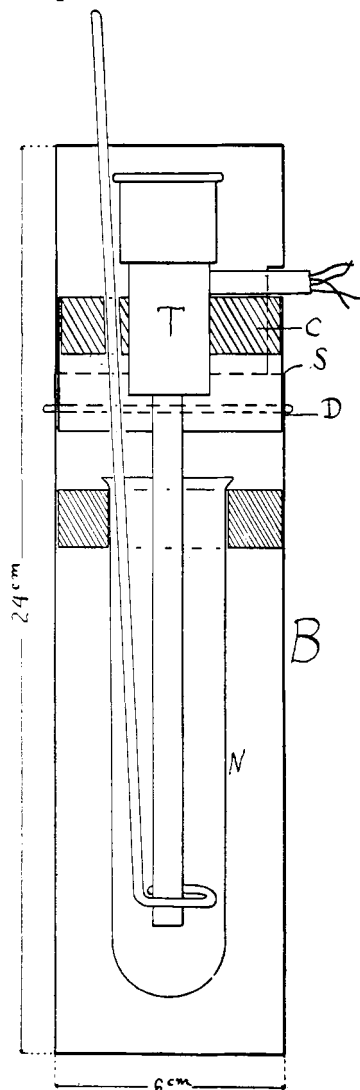

FIGURE 1

broken up rather fine in a mortar, then melted in the test tube by dipping in warm water until the mass could be readily stirred.   The tube was then placed in position, the thermometer inserted, and readings taken at intervals during several hours.   These observations showed that

no very definite equilibrium had been established. Stirring the contents of the tube and small changes in the external temperature produced changes amounting to over $0^\circ.01$ even after two hours. The procedure was therefore slightly modified, as follows : As the crystals seemed rather moist, a small quantity of the anhydrous salt was first added and the crystals were almost entirely melted. Recrystallization was then started by running cold water over the tube. In this way a perfectly definite temperature was secured within five minutes after starting the experiment. It was found later that the addition of anhydrous salt was unnecessary, as enough was formed during the process of preparing and melting. The procedure just indicated was followed in all subsequent experiments.

The Effect of External Conditions.

In one experiment the external temperature was kept at 33° for an hour and the temperature of the salt was observed at intervals. These observations showed variations of about $0^\circ.0005$. The temperature was then dropped to 32° for an hour, but no larger variations were observed. When the temperature was dropped to 23° and maintained for about forty-five minutes, until the salt could no longer be stirred, no changes exceeding $0^\circ.001$ were observed in the transition temperature. On raising the external temperature to 43°, a rise of about $0^\circ.003$ was observed after thirty minutes, but it was noted that the salt was almost completely melted. The temperature was again lowered to 33° and the original value was found. The experiment of lowering the temperature was tried a number of times with the same result. Richards found that lowering the outside temperature two or three degrees lowers the temperature of the salt by about $0^\circ.01$. It seems probable that the procedure followed in the present instance, whereby new crystals are formed by sudden cooling, makes the transition temperature more definite and less dependent on external temperature. In this connection it should be pointed out that when the cooling was omitted the variations were not larger than the accidental errors of mercurial thermometers. These irregular observations, moreover, fell on both sides of the final value.

To test further the influence of external conditions a smaller test tube was used. The salt was first melted in a large tube and the temperature observed ; some of it was then transferred to the smaller tube, where the same value was again found. This experiment further indicates that the effects of superheating, conduction down the thermometer stem, etc., were negligible. When the smaller tube was used, however, the external temperature had to be more carefully regulated, as a difference of 5 degrees from the transition point, if maintained for some time, began to affect the readings. Stirring the salt usually produced a small rise of less than $0^\circ.001$, which disappeared in two or three minutes.

Impurities.

It seemed desirable to determine directly the error which might be introduced by the presence of impurities in the salt. Since the transition temperature must be determined with a mixture of crystals and solution, and the effect of the impurity, except in some special cases, varies with the relative amount of the two present, it is evident that this effect will not remain constant. The values quoted in the table below are therefore *only approximate*, but serve to show what effect and range of variation may be expected in the transition temperature.

TABLE III.
EFFECT OF IMPURITIES.

Impurity	Lowering of transition point for the following—					
	0.2 per cent. NaCl	0.08 per cent. NaCl	0.05 per cent. NaCl	0.01 per cent. NaCl	0.1 per cent. K_2SO_4	0.1 per cent. $(NH_4)_2SO_4$
	0°.1885	0°.0873	0°.0505	0°.0147	0°.0620	0°.0937
	0°.1942	0°.1019	0°.0486	0°.0147	0°.0607	0°.0922
	0°.1942	0°.1019	0°.0490?	0°.0147		0°.0911
Mean lowering	0°.193	0°.100	0°.049	0°.015	0°.061	0°.092

From the preliminary determinations it may be concluded that: (*a*) the transition temperature of sodium sulphate is definite to 0°.001 ; (*b*) within a considerable range the transition temperature is not affected by external conditions (temperature and pressure); (*c*) the presence of 0.001 per cent. of other salts may lower the transition temperature by 0°.001. From the latter consideration it appears that if samples made by different methods give different values the higher is to be chosen as representing the purer salt.

Final Determination.

For the final determination four samples prepared by the chemical division of the Bureau of Standards, were used. No. 1 was prepared from Kahlbaum's sodium sulphate three times recrystallized. No. 2 was the same salt five times recrystallized. No. 3 was prepared by neutralizing the carbonate and was four times recrystallized. No. 4, was the same, five times recrystallized. Table V shows values obtained for the different samples with the two thermometers.

TABLE IV.

Date	Therm. "Kahlbaum"	Temp.	Mean	Date	Therm. No. I.	Temp.	Mean
1-4-07	A	32°.3812		1-12-07	A	32°.3832	
1-8-07	A	32°.3798			B	°.3841	32°.384
	B	°.3789		No. III.			
3-7-07	A	32°.3798		1-12-07	A	32°.3812	
	B	°.3773	32°.380		B	°.3818	32°.382
No. II				No. IV.			
1-7-07	A	32°.3798		1-5-07	A	32°.3855	
	B	°.3796			B	°.3860	
1-8-07	A	32°.3819		1-8-07	A	32°.3855	
	B	°.3813			B	°.3834	
1-12-07	A	32°.3799		1-12-07	A	32°.3812	
	B	°.3806	32°.381		B	°.3818	32°.384

32°.383

The agreement of the two thermometers and the constancy of the values for each sample taken at different times show that the differences observed represent real differences in the transition temperature for the different samples. There is reason to believe that sample No. 2, which gives a low value, had been accidently contaminated with some of the solution used in cleaning the tubes. It may be noted that the constancy of the indications for the various samples with varying conditions is not necessarily a proof of their purity, since any impurities which were not removed by recrystallization would have an effect independent of the relative amount of crystals and solution present. Samples prepared from the carbonate are less likely to contain impurities of this kind. Since differences between different samples are probably due to impurities which lower the transition temperature, the higher values may be taken as more nearly representing pure salt. The mean value from samples Nos. 1, 3, and 4 is 32°.383. But, for the reasons given above, the higher values are entitled to greater weight so that the most probable value from these observations is 32°.384.

Conclusion.

A special form of resistance thermometer, intended for calorimetric work, has been found applicable for general temperature measurement in the interval 0° to 100°. Two of these thermometers have been compared with eight primary standard mercurial thermometers, representing the mean temperature scale of the Bureau of Standards, at the temperatures 30°, 40°, 50°, 60°, and 70°. This calibration has shown that the Callendar formula $t-pt=\delta(\frac{t}{100}-1)\frac{t}{100}$ may be used to define the relation between the platinum scale of these resistance thermometers and the mean scale of the Bureau of Standards to within 0°.002. By using these calibrated thermometers the transition temperature of sodium sulphate has been determined and found to be **32°.384** for the purest salt. Resistance thermometers for use in the interval 0° to 100° may be calibrated to the highest degree of accuracy by using the Callendar formula and determining the constant δ from the transition temperature of pure sodium sulphate, 32°.384. These thermometers may be used to reproduce the international hydrogen scale of temperature to within 0°.002 or 0°.003.

In conclusion the authors wish to express their obligations to Dr. C. W. Waidner for many valuable suggestions throughout the course of the present investigation, to Dr. F. A. Wolff, who had charge of the calibration of the resistance bridge, and to Dr. Helen Isham, who prepared the samples of sodium sulphate used in determinations of the transition temperature.