[CONTRIBUTION FROM THE DEPARTMENT OF THE INTERIOR, BUREAU OF MINES, CRYOGENIC RESEARCH LABORATORY]

THE ESTABLISHMENT OF THE TEMPERATURE SCALE TO —193° BY MEANS OF PLATINUM-RESISTANCE THERMOMETERS[1,2]

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Introduction

One of the difficult problems involving the thermodynamic properties of fluids at low temperatures is the establishment of an accurate temperature scale. The ultimate standard for this purpose is, of course, the gas thermometer, giving results reproducible to 0.01° or 0.02° at low temperatures. However, the technical difficulties involved in gas thermometry are many, and it is desirable to establish the scale in terms of a secondary thermometer, such as a platinum-resistance thermometer, based on accurate gas thermometer observations by some one who has made a careful study of the problem. Henning,[4] and Henning and Heuse[5] have provided us with a very convenient method of calibration based upon the standard thermometer No. 32 of the Reichsanstalt which, in turn, has been compared with the hydrogen and helium thermometers at a large number of temperatures.

It is well known that the temperature scale defined by the Callendar equation is the same as the thermodynamic scale within the range —40° to +600° to the accuracy of measurement of the latter. This equation reads: $t = pt + \delta(0.01t - 1)0.01t$, where t is the centigrade temperature, pt is the so-called platinum temperature and δ is a constant. The term pt is defined as $100\ r_t - r_0/F.I.$, where r_t is the resistance at any temperature t, r_0 is the resistance at the ice point, and $F.I.$ is the fundamental interval, namely, the resistance corresponding to the interval between the steam and ice points. From this it is seen that a third point is still necessary to determine the constant δ, and we have used the normal boiling point[6] of naphthalene for this purpose.

It has been shown by Henning[4] that the Callendar equation no longer defines a reproducible temperature below —40° and that temperatures calculated from the Callendar equation are more than 2° too low at liquid-

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[1] Published with permission of the Director of the Bureau of Mines.

[2] Presented at the Washington Meeting of the American Chemical Society, April, 1924.

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[4] Henning, *Ann. Physik,* **40,** [4] 635 (1913). Also *Z. Instrumentenk.,* **44,** 349 (1924).

[5] Henning and Heuse, *Z. Physik,* **23,** 95 (1924).

[6] *Bur. Standards Circ.,* **35** (1919).

air temperatures; moreover, this amount of departure from the thermodynamic scale is not the same for all thermometers.

The value of Henning's contribution consists in the fact that he has studied the behavior of platinum of various origins at low temperatures and has given us a complete correction curve and calibration table in which the resistance ratio is represented as a function of the absolute temperature, to be applied as correction to the temperature as calculated by the Callendar equation. Henning and Heuse,[5] from a recent comparison of their platinum-resistance thermometers against a constant-volume helium thermometer, obtained substantially the same results as in Henning's earlier work, with a constant-volume hydrogen thermometer, and now recommend that the resistance ratio R be expressed as a function of the temperature between 0° and —193° by means of an equation of the type $R = r/r = 1 + at + bt^2 + ct^4$, where a, b and c are constants. For pure platinum ($\alpha > 0.00386$ and $\delta < 1.51$) the constant c may be put equal to -5.08065×10^{-12}, so that only a and b need be determined by calibrating at two fixed points, say at the normal sublimation point of carbon dioxide ($t = -78.51°$) and at the normal boiling point of oxygen ($t = -183.00°$). However, if both α and δ are known—and they should both be determined in order to test the thermometer for purity of wire and absence of strain—Henning and Heuse suggest that we calculate the resistance at the fixed point of freezing mercury (—38.87°) by means of the Callendar equation and then only the oxygen point need be found to evaluate the remaining constant.[7]

Recently, Van Dusen[8] has published his work on this problem and his results with platinum thermometers of the strain-free type agree entirely with the results of Henning. Van Dusen also gives an equation involving an additional term to the Callendar equation, which fits the data equally as well as the equation of Henning and Heuse, and is of a simpler form for calculation. The equation is as follows,

$$t = \frac{1}{\alpha}\left(\frac{r}{r_0} - 1\right) + \delta\left(\frac{t}{100} - 1\right)\frac{t}{100} + \beta\left(\frac{t}{100} - 1\right)\frac{t^3}{100^3}$$

where α, δ, r, r_0 and t have the same meaning as above and β is an additional constant to be determined from a calibration at the oxygen point.

It is seen from the above that Henning has advanced a most convenient and labor-saving method of establishing the temperature scale, eliminating as it does all individual work with a gas thermometer. However, Keyes,

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[7] In a recent report from the Reichsanstalt [*Z. Instrumentenk.*, **44,** 517 (1924)] it is recommended that the constant c be placed for convenience equal to -5×10^{-12} rather than -5.08065×10^{-12}, the difference being absorbed in the other constants without significant change in the value given by the equation. In our calculations, however, we have used the more precise value of c.

[8] Van Dusen, THIS JOURNAL, **47,** 326 (1925).

Townshend and Young,[9] from a comparison of a flat-coil calorimetric type of resistance thermometer with the hydrogen constant-volume gas scale of temperature have found that the deviations between the scale as defined by the Callendar equation below the ice point and the gas scale, for their particular transfer instrument, did not follow the curve of Henning, the difference amounting to about 0.1° over a large part of its course. This amount of departure is large when it is remembered that gas thermometry is reproducible to 0.02° at low temperatures. Moreover, these investigators state that the deviations of a platinum-resistance thermometer must be, to a certain extent, dependent upon the particular instrument employed, and that the deviations of any particular instrument must be independently investigated, but express the belief that a type of support which would not set up strains in the wire under large temperature changes would be a great advantage and the deviations of a thermometer so constructed might possess a considerable degree of generality. It becomes, then, an important question to decide whether the particular instrument as employed by these investigators was strained and hence produced abnormal deviations or whether the method of Henning with all of its simplicity and rapidity of calibration should be discarded. We will show from our measurements that the flat-coil calorimetric type of thermometer, when properly constructed, offers a precise means of reproducing the thermometric scale at low temperatures by calibration at one low temperature point, and that our results along with those of Van Dusen establish the reproducibility of pure platinum as a thermometric resistance wire when used under strain-free conditions at low temperatures.

Experimental Method

Since it is necessary to determine only one low temperature point for the calibration of the thermometer by the Henning method, we may use the oxygen point for this purpose and utilize the other well-established point, the normal sublimation point of carbon dioxide, for purposes of comparison between the computed and the observed resistance. Since the correction curves of Henning and of Keyes, Townshend and Young differ by about 0.11° at this point, we shall have a good basis of comparison between the two curves, and shall have a conclusive test of the question whether the generality of Henning is valid or not, since a calculation at this point means a long interpolation between the two experimentally determined points, the oxygen point and the ice point. We have used both the equation of Henning and Heuse and that of Van Dusen for comparison of calculated and observed values at the carbon dioxide point. If the method of Henning is correct, the calculated and observed resistance at the carbon dioxide point should check.

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[9] Keyes, Townshend and Young, *J. Math. Phys. Massachusetts Inst. Tech.*, **1**, 243 (1922).

Experimental Details

The thermometers used throughout this investigation were of the flat-coil calorimetric type[10] made by loosely winding 0.1mm. pure platinum wire[11] on mica strips of sufficient thickness to prevent sharp bends,[12] with gold connecting wires to the head; a silver sheath rolled down loosely on the wire formed the casing, silver-soldered at the end and to a stem of Monel tubing. Near the head was a side tube for the purpose of attaching a small tube containing phosphorus pentoxide, so that the pressure in the thermometer was always atmospheric; we consider this an important precaution to prevent strain of the wire by external pressure on the sheath when low temperatures are being measured. After winding, each thermometer was alternately flashed and dipped in liquid air until the ice point showed no further change. The ice point of each thermometer was frequently checked and remained constant.

The bridge and commutator used were of the Meuller type, and were calibrated by the Bureau of Standards. The temperature of the bridge was kept at the calibration temperature of 27° in order to avoid errors due to the uncertainty of the temperature coefficient of the various coils.

The δ-Value.—The δ-value of each thermometer was determined from the ice, steam and naphthalene points. The ice point was reproducible to two or three thousandths of a degree when fine shavings of clear ice were used to make a thick bath with a deep Dewar flask as container and during good stirring. Water redistilled over alkaline permanganate was used to wash the ice and to form part of the bath.

The steam point was determined in a double steam jacket, the steam entering at the top from a boiler placed some distance away to prevent superheating; a large exit tube and wide passages for the steam made it possible to maintain atmospheric pressure on the system. The barometric height was read by means of an accurate cathetometer and the boiling temperature corresponding to this corrected pressure found from the Landolt-Börnstein "Physikalisch-Chemische Tabellen" (1923 edition). From this temperature the *F.I.* was calculated.

The naphthalene point was determined in a special insulated boiling tube with all the precautions used in the sulfur point determination.[13] The relation between boiling point and pressure for pure naphthalene is given by the expression[6] $217.96° + 0.058° (p-760)$.

Low-Temperature Points.—The normal boiling point of oxygen and the normal sublimation point of carbon dioxide were determined by methods that will be described in another paper.

Results

The results are given in Table I, Col. 1 referring to the thermometer number, Col. 2 the δ-value, Col. 3 the coefficient α, Col. 4 the resistance at the ice point, Col. 5 the resistance at the oxygen point, Col. 6 the resistance

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[10] In order to generalize our investigation as much as possible for the type of thermometer used, the four thermometers that we employed for the measurements were made by different persons, No. 1 by the authors, No. 2 by Dr. Gerhard Dietrichson of the University of Illinois, No. 3 by Mr. Frank Porter of this Laboratory, No. 4 by Dr. D. C. Bardwell of the Radium Laboratory of the Bureau of Mines.

[11] It is strongly recommended that the platinum wire be tested thermo-electrically by the Bureau of Standards before being made into a thermometer. It has been our experience that many samples of so-called pure platinum wire are unfit for use in thermometers.

[12] Sligh, *Bur. Standards Sci. Papers,* **407** (1921).

[13] Mueller and Burgess, *Bur. Standards Sci. Papers,* **339** (1919).

at the carbon-dioxide point, Col. 7 the value of β, Col. 8 the resistance at the carbon-dioxide point observed minus the resistance calculated for this point by the equation of Henning and Heuse, Col. 9 the same, using the Van Dusen equation.

TABLE I

RESULTS

Therm.	δ-Value	α-Value	r_0	r_{O_2}	r_{CO_2}
1	1.477	0.0038983	22.41619	5.59486	15.36960
2	1.490	.00391825	23.51560	5.77425	16.08203
3	1.489	.00391724	23.06820	5.66568	15.77611
4	1.487	.0039167	23.87065	5.86673	16.32669

β	r_{CO_2}(obs.) − r_{CO_2}(calcd.) Henning eq.	r_{CO_2}(obs.) − r_{CO_2}(calcd.) Van Dusen eq.
0.1065	+0.00275 (0.02_7°)	+0.0028_6 (0.02_9°)
.1056	+ .00099 ($.01_0$°)	+ .00115 ($.01_2$°)
.1080	− .00056 ($.00_6$°)	− .00071 ($.00_7$°)
.1076	− .00009 ($.00_1$°)	− .00020 ($.00_2$°)

Cols. 8 and 9 show that the agreement between the calculated and observed values of the resistance at the carbon dioxide point for Thermometers 2, 3 and 4 is well within the experimental error, while this difference for Thermometer 1 is slightly greater, assuming that temperatures in this region are reproducible to about 0.02°.

Conclusions

From the close agreement between observed and calculated resistances at the carbon-dioxide point for four platinum-resistance thermometers of the flat-coil calorimetric type, we must conclude that the proposed calibration methods of Henning[4] and of Henning and Heuse[5] are entirely satisfactory, thus corroborating entirely the results of Van Dusen[8] for thermometers of the strain-free type. Our results, together with those of Van Dusen, establish the reproducibility of pure platinum as a thermometric resistance wire when used under strain-free conditions at low temperatures; our results also show that thermometers of the flat-coil or calorimetric type, when properly constructed, can be used at low temperatures and calibrated in the same manner as the strain-free types which have been investigated at the Reichsanstalt and the Bureau of Standards. The results also furnish conclusive evidence that the flat-coil type of thermometer used by Keyes, Townsend and Young was anomalous in its behavior, and the deviations found for their particular transfer thermometer were due, as surmised by them, to strains.

Other general objections to their curve representing the deviations between the Callendar-computed-platinum temperature and the gas scale as a function of the temperature are pointed out by Henning and Heuse[5] and by Van Dusen.[8]

Summary

1. General methods of establishing the thermodynamic scale of temperature to —193° by means of platinum-resistance thermometers as proposed by Henning are discussed.

2. An experimental method is outlined which will enable us to decide between the results of Henning and those of Keyes, Townshend and Young regarding the validity of the proposed methods of calibration.

3. Our results using the flat-coil calorimetric type of platinum-resistance thermometer entirely corroborate those of Henning and of Van Dusen for the strain-free type of thermometer.

4. It is concluded that Henning's proposed methods of establishing the thermodynamic scale of temperature in terms of platinum-resistance thermometers, using thermometers of pure platinum and entirely strain-free, are entirely valid and reproducible.

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INFRA-RED ABSORPTION SPECTRA. SOLUTIONS OF NITROGEN PENTOXIDE AND NITROGEN TETROXIDE IN ORGANIC LIQUIDS

BY FARRINGTON DANIELS

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This investigation was undertaken originally, for the purpose of testing relations between reaction velocity and absorption spectra predicted on the basis of the "radiation hypothesis."[1] The unimolecular decomposition of nitrogen pentoxide in the gas phase and in various solvents has been measured,[2] and it seemed important to ascertain whether a change in the temperature coefficient of reaction rate is accompanied by a shift in the position of the significant absorption band, in agreement with this hypothesis. Confirmation of such a shift has been reported in the decomposition of triethylsulfonium bromide in solutions.[3]

Of more interest, however, than the testing of this hypothesis has been the study of the relationship between near infra-red absorption spectra and the structure of molecules. Furthermore, the study of solutions is rather new in the field of infra-red spectroscopy and nitrogen pentoxide and tetroxide with their distinctive spectra and high solubility offered unusually good systems for generalization.

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[1] A good statement of this hypothesis may be found in papers by Perrin and by W. C. McC. Lewis, *Trans. Faraday Soc.*, **17**, 500, 550 (1922).

[2] (a) Daniels and Johnston, THIS JOURNAL, **43**, 53 (1921). (b) Lueck, *ibid.*, **44**, 757 (1922). (c) Forthcoming publication.

[3] Taylor and Lewis, *J. Chem. Soc.*, **121**, 665 (1922).