[CONTRIBUTION FROM THE BUREAU OF STANDARDS, UNITED STATES DEPARTMENT OF COMMERCE]

PLATINUM-RESISTANCE THERMOMETRY AT LOW TEMPERATURES[1]

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In platinum-resistance thermometry temperatures above 0° centigrade are calculated by the use of the well-known Callendar equation,

$$t = \frac{1}{\alpha}\left(\frac{R}{R_0} - 1\right) + \delta\left(\frac{t}{100} - 1\right)\frac{t}{100} \qquad (1)$$

where R is the resistance at centigrade temperature t, R_0 is the resistance at 0°, and α and δ are constants depending upon the purity and treatment of the platinum. The fundamental coefficient α is determined from observations at the boiling point of water, while the constant δ is determined at some other fixed point, preferably at moderately high temperature. When δ is determined from observations at the boiling point of sulfur, the temperature scale defined by the Callendar equation is indistinguishable from the thermodynamic scale in the range —40° to 600°, to the accuracy with which the latter has been determined. If the thermometers are constructed of pure platinum mounted so as to avoid mechanical strain due to temperature changes and properly annealed, a temperature scale can be reproduced by them with much greater accuracy than has thus far been possible by the use of gas thermometers or other means.

Below the region of —40°, however, temperatures defined by the Callendar equation depart from the thermodynamic scale by amounts which increase very rapidly below —100°, the calculated temperatures being about 2° too low at liquid-air temperatures. Furthermore, it has been shown, notably by Henning,[2] that such deviations are not the same for all thermometers. In other words, the Callendar equation does not define an accurately reproducible scale at low temperatures.

Henning and Heuse[3] have recently published the results of later work on resistance thermometers and a review of the earlier work of Henning. They find that the resistance of platinum between 0° and —190° can be represented by an equation of the form,

$$R = R_0\,(1 + at + bt^2 + ct^4) \qquad (2)$$

where the constants a, b and c are determined from three fixed points, namely, the freezing-point of mercury, the normal sublimation point of carbon dioxide and the normal boiling point of oxygen. Since the constant c came out practically the same for all their thermometers, it was

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[1] Published by permission of the Director, Bureau of Standards, Department of Commerce.

[2] Henning, *Ann. Physik*, **40**, 635 (1913).

[3] Henning and Heuse, *Z. physik*, **23**, 95 (1924).

suggested that the value of this constant could be assumed for platinum of a certain purity and the calibration at the carbon dioxide point thus eliminated. Since it has not been possible to distinguish the Callendar scale of temperature from the thermodynamic at the freezing point of mercury, the resistance at this temperature can be calculated by means of the Callendar equation and actual calibration eliminated. Equation 2 can thus be obtained indirectly from a calibration at the boiling point of oxygen. Since this equation is rather cumbersome to use, it seemed desirable to attempt to find a simple modification of the Callendar formula in which the departures are expressed by a term containing a single characteristic constant determined from a single calibration below zero.

The following equation was found to satisfy these requirements.

$$t = \frac{1}{\alpha}\left(\frac{R}{R_0} - 1\right) + \delta\left(\frac{t}{100} - 1\right)\frac{t}{100} + \beta\left(\frac{t}{100} - 1\right)\frac{t^3}{100^3} \qquad (3)$$

For temperatures above zero the last term is omitted and the equation is then identical with the Callendar formula, with identical constants determined from the usual calibration in ice, steam and sulfur. The constant β is determined from a calibration at or near the normal boiling point of oxygen, and the term involving β is used only for temperatures below zero. The transition from one equation to the other is very gradual since the term involving β is very small throughout the range —40° to +100°.

In addition to the work of Henning and Heuse, a limited number of thermometer comparisons made at the Bureau of Standards in 1918 are available for testing the validity of this equation. These measurements consisted in the comparison of three platinum-resistance thermometers of high purity with oxygen and carbon dioxide vapor-pressure thermometers, as well as an intercomparison of the resistance thermometers at various intermediate temperatures.

Using Henning's data[4] on the vapor pressure of oxygen and carbon dioxide in the region of one atmosphere pressure, it was found that the results of the measurements could be satisfactorily represented by Equation 3.

In the following tables the results of the thermometer comparisons at the Reichsanstalt, as well as those made at the Bureau of Standards, have been re-computed on the basis of Equation 3. Table I gives the constants of the thermometers used. Table II gives the Reichsanstalt comparison of several platinum thermometers with constant volume hydrogen and

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[4] Henning, *Ann. Physik*, **43,** 282 (1914). Ref. 3, p. 105. In the calculations made for this paper the temperatures have been corrected to the thermodynamic scale and the following figures used for the two fixed points in question.

Normal boiling point of oxygen = —183.00°.

Normal sublimation point of carbon dioxide = —78.51°.

helium gas thermometers, temperatures on the gas thermometers being corrected to the thermodynamic centigrade scale.

TABLE I

CONSTANTS OF THERMOMETERS

Thermometer	$\alpha \times 10^3$	$\alpha \times 10^3$	δ	β	Approx. R_0 ohms
		REICHSANSTALT THERMOMETERS			
	(1913)	(1923)			
29	3.9146	3.9148	1.484	0.1091	12
30	3.9130	3.9129	1.486	.1124	12
31	3.9139	3.9141	1.482	.1055	12
32	3.9137	....	1.487	.1082	12
28	3.9128	....	1.491	.1034	12
27	3.9127	....	1.491	.1049	12
7	3.8870	....	1.492	.1037	12
1	3.8620	....	1.510	.1234	3
		BUREAU OF STANDARDS THERMOMETERS			
	(1918)				
C_{28}	3.9159	....	1.496	0.1093	2.5
C_{22}	3.9090	....	1.496	.1116	25
C	3.8984	....	1.499	.1186	25

TABLE II

REICHSANSTALT THERMOMETERS

t(Thermodynamic scale)—*t*(platinum thermometer)

t Thermo-dynamic scale °C.	From 1913 publication Calculated by Equation 5				From 1924 publication By Eq. 5	From 1924 publication By H. and H, Eq.
	29	30	31	32	32	32
		HYDROGEN THERMOMETER, 1912				
−183.02	−0.02	−0.05				
−183.03	+ .03	+ .03				
−183.04	+ .02	+ .01				
−193.21	− .06	− .08				
−193.16	− .06	− .08				
− 39.29			+0.03	+0.03	+0.04	+0.04
− 52.09			+ .02	+ .10	+ .06	+ .06
− 83.92			− .08	+ .01	− .03	− .03
− 95.95	+ .01			+ .02	+ .02	+ .01
−148.33	− .05			.00	− .02	− .03
−121.84	+ .01			− .02	− .01	− .02
−132.46		− .06		− .07	− .06	− .07
−109.50		+ .04		+ .02	+ .02	+ .01
− 21.73		.00		− .01	− .01	.00
− 82.14		+ .01		.00	.00	.00
− 50.24		+ .01		+ .01	+ .02	+ .02
−193.55		− .09		− .03		
−193.49	− .06		.00		− .02	− .01
−182.98	− .02		.00		.00	.00
−183.00		.00		.00	.00	.00

TABLE II (*Concluded*)

t Thermodynamic scale °C.	From 1913 publication Calculated by Equation 5				From 1924 publication	
	29	30	31	32	By Eq. 5 32	by H. and H. Eq. 32
−149.93		+ .05		+ .03	+ .04	+ .02
−148.99	+ .01		+ .02		+ .03	+ .01
−100.66		+ .04		+ .01	+ .03	+ .02
−104.18		+ .02		− .01	.00	− .01
−103.47	+ .02				+ .02	+ .01
− 52.53		− .03		− .03	− .03	− .02
− 51.97	− .03		− .04		− .03	− .02
− 34.73	− .03	− .11			− .07	− .06
− 34.38			− .02	− .01	− .01	.00
− 27.46			.00	+ .01	.00	+ .01
−193.19					− .05	− .04
−183.03					+ .02	+ .02
	HELIUM THERMOMETER, 1923					
−183.00	.00	+ .01				
−195.81	− .10	− .10				
			Av. Pt. therms.			
− 65.558	− .021	+ .019	−0.001			
− 55.087	− .006	− .013	− .010			
− 42.228	+ .027	− .009	+ .009			
− 40.749	+ .010	− .019	− .005			
− 36.051	+ .004	− .011	− .003			

Cols. 7 and 8 of Table II show that temperatures calculated by the method here proposed differ very slightly from those calculated by the equation of Henning and Heuse. As a matter of fact, the greatest difference between the two is only a little more than 0.01° at —120°,—well within the limit of accuracy of the temperature measurements. Cols. 6 and 7 should be the same to the nearest 0.01°, the former being calculated from the values of the Callendar temperature given in the 1913 publication, and the latter from presumably corresponding values of the resistance given in the 1924 publication. Two or three discrepancies greater than 0.01° appear which may be due to typographical errors. In the comparison with the helium thermometer at the bottom of Table II, the average of Thermometers 29 and 30 given in Col. 5 should be considered, not the individual readings, since a lateral temperature gradient existed in the bath, and the platinum thermometers were so disposed that their average reading would correspond to the reading of the gas thermometer. Below —183° systematic deviations appear which amount to about 0.1° at the boiling point of nitrogen (—195°). The proposed method of calculating temperatures, however, appears to be valid down to about —190° and is in agreement with the equation of Henning and Heuse as low as —200°.

Table III is an intercomparison of platinum thermometers in the low temperature range, Henning's published values of the platinum temperature, $\frac{1}{\alpha}\left(\frac{R}{R_0} - 1\right)$, being used directly in the calculation of the temperature. It will be noted from this table that the deviations of Thermometer 1 are consistently a little greater than the average errors of observation. This thermometer, however, has a low fundamental coefficient showing that the platinum is impure and no particular importance need be attached to the observation.

Table III

Intercomparison—Reichsanstalt Thermometers

t (Eq. 5) 32	Deviation from Thermometer No. 32 (by Eq. 5) 31	30	29	28	27	7	1
−192.78	+0.05	−0.03	−0.03				
−192.22			− .01			0.00	−0.03
−192.14			− .02	0.00	−0.01		
−184.31	− .01	− .01	+ .03				
−182.89			− .02			− .02	− .01
−182.86			+ .01	+ .02	+ .02		
−144.24			.00			− .05	+ .04
−142.90			− .01		.00		
−104.58			+ .01			+ .01	+ .07
−103.96			.00		+ .01		
− 53.49			.00			− .01	+ .03
− 53.25			.00		− .01		

Table IV gives a summary of the results of the intercomparison of three platinum thermometers and several carbon dioxide and oxygen vapor-pressure thermometers made at the Bureau of Standards, in 1918. No systematic deviations are to be found in the summary of the data, although as noted previously the work was rather limited in scope.

An objection which may be raised against the method of procedure outlined in this paper is the fact that a calibration of the thermometer above 100° is required for low-temperature use. In fundamental standardization work, at least, it is very desirable that the sulfur point be obtained, in order to check the thermometer as a standard instrument. Thermometers for precision work must necessarily be constructed in such a way (except for casing) that they can be heated to this temperature without injury in order to permit annealing. Laboratory thermometers for general use at low temperatures, however, need not necessarily be calibrated at the sulfur boiling point. The constant δ can still be determined, with some sacrifice of precision, at the freezing point of mercury and Equation 3 used as before in the calculation of temperature.

It should be acknowledged in conclusion that other important comparisons between resistance thermometers and gas thermometers have been made, but cannot be utilized here for various reasons. No calibration data above zero are given for the resistance thermometers of the Leiden

Laboratory; consequently the method of calculation here proposed cannot be used.

TABLE IV

BUREAU OF STANDARDS THERMOMETERS

t Thermodynamic scale oxygen vapor-press. therm. °C.	t (Therm. scale) $- t$ (Pt. therm.) by Equation 5 C_{22}	C_{28}	C
−185.24	−0.02		
−185.21	.00		
−183.21	+ .01		
−183.18	+ .01		
−183.20		0.00	
−183.19		.00	
−185.25			−0.02
−185.21			.00
−183.21			+ .01
−183.18			+ .01
CO_2 vapor-pressure thermometer			
− 80.37		.00	
− 80.35		.00	
− 80.42		+ .01	
− 78.36		.00	
− 78.35		+ .01	
− 80.35	+0.01		
− 80.43	− .05		
− 80.36	+ .03		
− 80.38	.00		
− 80.42	+ .03		
− 78.36	− .01		
− 78.36	.00		
− 78.47	.00		
− 78.47	− .01		

Intercomparison		
t °C.	Deviation from C_{22}	
C_{22}	C_{28}	C
−182.85	+0.03	−0.01
−165.33	.00	− .04
−148.65	− .02	+ .01
−147.55	− .01	
−129.45	− .01	
−111.00	− .02	+ .01
−104.12	− .01	
− 79.85	.00	

The resistance thermometer of Keyes, Townshend and Young[5] was of the flat-coil, calorimetric type which, unless very carefully annealed, is known to show a somewhat anomalous behavior above zero and therefore it need not be inferred that the behavior of this thermometer below 0° is typical of that of the strain-free type.[6] If the identity of the temperatures determined with the gas thermometer by Keyes, Townshend and Young, with those deduced by Henning and Heuse from their gas thermometers be assumed, then this thermometer is one out of eleven, ten of which yield data consistent with Equation 3, while the behavior of the one is such that it is impossible to represent it by an equation of that type. Although Keyes and his associates give no direct calibration of their

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[5] Keyes, Townshend and Young, *J. Math. Phys. Mass. Inst. Techn.*, **1,** 243 (1922).

[6] Sligh, *Bur. Standards Sci. Papers,* **17,** 49 (1922). (No. 407.)

thermometer in freezing mercury, consistency of their observations demands that such a calibration yield the value —38.83° for the Callendar temperature of the mercury freezing point. This value is of the order of 0.04° higher than that universally obtained with resistance thermometers of the strain-free type and the existence of such a difference relatively so near the ice point had not previously been observed, even for a flat-coil type of thermometer.

Summary

A simple modification of the Callendar equation used in platinum-resistance thermometry above 0° is given, which will express accurately the resistance of platinum as a function of temperature on the thermodynamic scale throughout the range 0°C. to —190°. The application of the new equation requires but a single calibration point below zero. Recalculations of data on resistance thermometers at low temperatures obtained by the Reichsanstalt and the Bureau of Standards are made, showing that the modified equation expresses the experimental results within the error of observation.

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[Contribution from the Chemical Laboratory of the University of California]

THEORY OF CERTAIN ELECTROMETRIC AND CONDUCTIMETRIC TITRATIONS

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In the familiar hydrogen-electrode titration curves (e.m.f. *vs.* volume of added acid or base) a point of inflection usually occurs in the vicinity of the end-point. When both the acid and the base are strong it is rather obvious that this inflection must occur exactly at the end-point. If there is a difference in strength of acid and base, or if both are weak, the exact coincidence of inflection-point and end-point is no longer obviously necessary or probable. And if either the acid or base is sufficiently weak the point of inflection does not appear at all. The limiting strength of acid or base necessary for the appearance of the inflection and the extent of its divergence from the end-point under various conditions are, therefore, questions which must be considered in the more general applications of the method. Similar questions appertain to the "break" in conductivity titration curves. Some years ago occasion was taken to study these problems analytically in connection with an investigation then in progress. Since that time the results of this study have often been found to be of value to investigators making use of these methods, and also in teaching. It has, therefore, been decided to offer a summary of them for publication, together with an outline of the procedures by which they were obtained.