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AN ADIABATIC METHOD FOR THE PRECISE ELECTRICAL CALIBRATION OF THERMOMETERS

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The continuous maintenance of precise adiabaticity in calorimetric systems, like thermostatic control, makes possible not only the exact measurement of a variety of thermal effects otherwise undeterminable, and a significant improvement of accuracy in other calorimetric measurements, but also the development of procedures not practicable under other conditions whereby a number of familiar types of experimental procedure may be methodically improved. In an earlier paper¹ the precautions which must be observed in order to establish and maintain a measurably invariable adiabatic condition for ten hours or more were discussed at length, and procedures were described by which this condition had been closely approached. More recent experiences in this Laboratory having more precisely defined the observations there recorded, and suggested improvements of method by which the desired end was at length attained, a few of the possibilities just referred to have been developed.

Among these are procedures for the minute calibration and for the standardization of thermometers, the first of which it is the purpose of this paper to describe. These procedures are easy, and are known from the results of several intercomparisons of data to be dependable. They insure the calibration and standardization of calorimetric thermometers to an exactitude of $\pm 0.0002^\circ$ or less on a centigrade scale of equal energy increments,² at points 0.01° apart on any selected temperature intervals within the lower physiological range (*ca.* 0° to 25°). The complete procedure is applicable to any type of thermometer, but has been thus far applied only to the standardization of mercury instruments. In the present paper, attention will be confined to a method recommended for primary calibrations of standard calorimetric instruments of this type.

¹ F. Barry, *THIS JOURNAL*, **44**, 899 (1922).

² The particular centigrade thermodynamic scale adopted as the standard in these operations is that defined by Joule's law in terms of the international electrical units and the mean specific heat of water in the fundamental temperature interval.

The method of primary calibration depends, as has already been implied, upon the possibility of maintaining for several hours in a calorimetric system a condition of practically complete adiabaticity or, alternatively, one of small and measurably constant thermal leakage.³ These conditions are now habitually established in all calorimetric work carried on in this Laboratory with condensed (solid-liquid) systems. By the employment of installations similar to the most efficacious of those described in the paper cited,⁴ the maximal total uncompensated thermal leakage or variability from constant leakage during ten hours or more in a system roughly equivalent to a liter of water is reduced to less than 0.1 calorie—that is, to a change in temperature of less than 0.0001° —and since this leakage is determinable with a somewhat greater precision, the temperature correction for incomplete adiabaticity is thus made, with reference to the present limit of thermometric precision, quite negligible.⁵ Moreover, the consistency of numerous varied results seems to show that the other errors in this type of measurement⁶ are no greater. If this is so, the heat developed by any influx of energy into a calorimetric system thus controlled will be, within the limits of accuracy of any calorimetric measurement now possible, completely conserved; so that, if adequate provision can be made to prevent significant lag in effecting its uniform distribution,⁷ it may be determined, with respect to both its total quantity and its rate of evolution, with a precision limited only by that of the means adopted for its generation and control, or by that of its thermometric measurement.

³ The condition of constant thermal leakage, which may be established by the same means that establish a strictly adiabatic condition, is convenient for many purposes, most obviously for the determination of thermal conductivity (Ref. 1, p. 914 and footnote 26; p. 931, footnote 42—last paragraphs. See also, in the present paper, Table IV, footnote *d*). It may be called, consistently with current usage and in contrast with the *adiabatic* and *merodiabatic* conditions which are those of common practice, the *isodiabatic* condition. Measurements made under this condition may be corrected to the strictly adiabatic standard by application of a leakage modulus similarly determined under the largest temperature gradients that cause no measurable convection. This defines for any calorimeter its characteristic change of temperature by conduction and radiation under a definite gradient sufficiently larger than those established in isodiabatic measurements to make error in the reduction of data so obtained negligible. (Ref. 1, pp. 918 *ff.*, Table V and Fig. 3.) For instance, the leakage modulus of the calorimeter used in the present measurements is $\approx 0.00011^\circ$ per minute per 0.1° thermal gradient, determined by a measurement of leakage under this head during an hour or more. Its uncertainty ($\approx 0.00001^\circ$) is therefore the same as that of a corresponding correction for a head of 0.01° continuously maintained for ten hours.

⁴ Ref. 1, pp. 901–909.

⁵ *Cf.* below, p. 3792. The data given in the tables (see Table IV, p. 3796) are affected by a larger uncertainty from incomplete adiabaticity, the higher precision of control having been more recently established.

⁶ Listed in Ref. 1, pp. 899–900.

⁷ *Cf.* below p. 3788, lines 7 *ff.*

For the direct thermal calibration of thermometers, two means at once suggest themselves: the introduction of an accurately measured electrical heating current into a calorimeter of known heat capacity, or the initiation and completion within it of some chemical process the reaction heat of which is precisely known. The first of these procedures is advantageously employed at present for determining the heat capacities of calorimeters with reference to a standard thermometric scale.⁸ The second has found a limited use for the calibration of thermometers in a standard calorimeter.⁹

Of the two, the electrical method is superior because it permits the development of energy within the calorimeter at a constant rate, and thus makes possible under continuous adiabatic control a calibration by continuous process. It is conceivable that a slow chemical process or a quick reaction frequently repeated (as by the dripping of one liquid into another) could be substituted for the electrical current; but practical difficulties at present insuperable stand in the way of such alternative procedure, which in any case would be awkward. The efficacy of the chemical method, therefore, is restricted to the determination of single temperature intervals (or at best two or three) for every separate assemblage of apparatus and material, and it thus remains insufferably laborious. The procedure herewith presented, therefore, is electrical; its novelty and demonstrable advantages over other methods of thermometric calibration are wholly due to the possibility of continuous adiabatic control.

Apparatus

Within an adiabatic calorimeter of the uniform type adopted for all protracted determinations (Fig. 1) an electric current, held constant within necessary limits, is passed through a heating coil of constant resistance, and raises the temperature of water in which the thermometer is immersed. The thermometer is placed axially, and is surrounded by the heating coil, which is a cylindrical helix of doubled manganin wire, silk-insulated, thickly shellacked, and embedded in Wood's metal within a copper tube of about 5 mm.

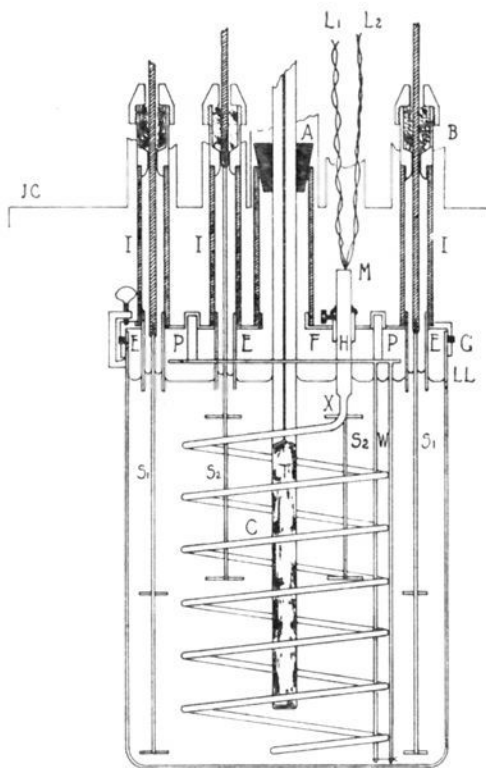


Fig. 1.

⁸ See W. P. White, "The Modern Calorimeter," A. C. S. Monograph, 1928, pp. 132 ff., and references there given.

⁹ Richards and Thorvaldsen, THIS JOURNAL, 37, 81 (1915).

external diameter.¹⁰ The diameter of the helix is such that, when the calorimeter water is still, and a current is passed through the coil, the heat developed is distributed as nearly as possible uniformly, so that in practice the necessary stirring of the system will be minimal; and for the same reason its axial length is such that it traverses all levels of the calorimeter water.

Provision is made for vertical reciprocating stirring by two two-stage stirrers, one within the coil, the other outside it, which may be operated independently, or together in the same or in opposite phases.¹¹ In practice the system is stirred at the rate of twelve strokes a minute; a measurably complete thermal homogeneity is thus quickly established, while the heat of stirring remains negligible during two hours or more.¹² The Wood's

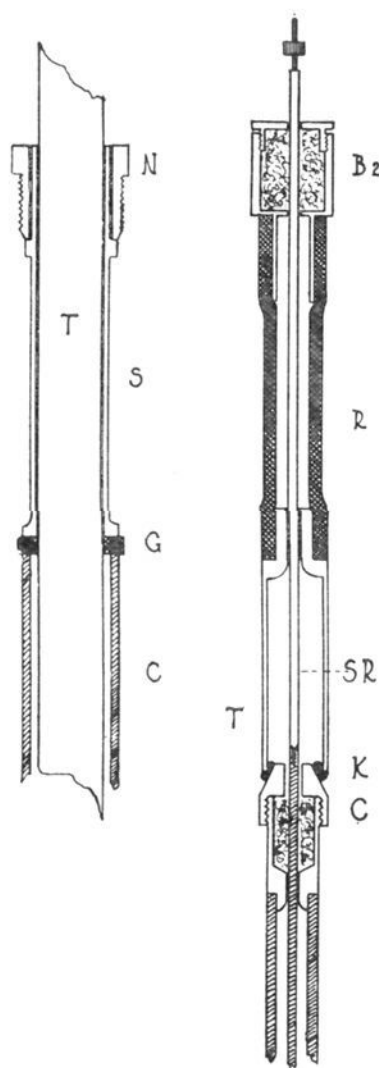


Fig. 2.—Insulations of thermometer and stirrer-rods for use when the air thermostat is not installed. The loose nut, N, engages the jacket chimney.

¹⁰ The shellacked wire was first drawn through the straight copper tube, which then was wound by hand upon a cylindrical block of wood of the required diameter held in the free chuck of a lathe, and was there pulled out to the requisite axial length, and evenly spaced. One open end of the tube—that near which the wire was doubled upon itself—was then fitted into the cap of a brass cartridge full of Wood's metal which was afterward sealed air-tight, and while held vertically with the tube above in a bath of boiling water, was slowly evacuated. The melted metal thus rose not too rapidly about the enclosed wires, and the results of comparative weighings later showed that only very minute air spaces could have been left in the tube. The coil was finished by pinching and soldering the casing-tube at a point about 3 cm. beyond the doubled end of the wire, fashioning the head (Fig. 1) at the other end, and gold-plating the whole. The manganin resistance was closely 13 ohms (*ca.* 260 cm. of No. 27 wire) and its insulation resistance was 9 megohms. Other forms of heating coils, in which, to reduce lag, the thinly insulated wires were not encased, had been previously tested; but though it seems not impossible to utilize dispositions of this sort, they are very fragile, and electrical leakage even if temporarily obviated may at any time be caused either by the fracture or by the chemical deterioration of the insulation.

¹¹ Rotary stirring is equally possible, of course, and has the advantage that it permits a complete closure of the system. The insulation of the reciprocating stirrers here described, however, had been found adequate to prevent measurable evaporation during the time occupied by the process, and the heat absorbed by it was negligible. It is obvious that in calibration of this sort, as in any precise measurement of a protracted process, the possible errors due **either** to evaporation or to irregularity of stirring **must** be shown by test in advance to be negligible.

¹² Ref. 1, pp. 909–916.

metal which surrounds the heating wire ensures a very slight lag in the coil itself: the total lag of the whole system is only a few seconds, and has no measurable calorimetric effect. The leads from the coil are so disposed that the very slight conduction of the wires will be practically constant under adiabatic control (Fig. 1). Two leads of very fine wire are attached to the current leads midway of the gap—that is, at the extremities of the heating wire—so that the potential drop across the heater may be measured while the current is flowing. Both these and the leads from the coil pass through the bath in thermal contact with it, and thus conduct very little heat either into or out from the system.

The electrical system consists of an 8-volt storage battery with control resistance, the calorimeter heater and a standard 10-ohm coil. The control resistance is made up of a 10-ohm fixed resistance and two variable resistances of 100 and 1000 ohms, respectively, all in parallel to permit rapid approximate and precise adjustments. The current through the calorimeter heater is determined by measuring the potential drop across the 10-ohm standard coil with a Wolff potentiometer. The same instrument can be used to check the constancy of the resistance of the heater and of the current by measuring the potential drop across it through the fine wire leads that are soldered to its ends.

By these means it is possible to keep the heating current constant with only negligible occasional fluctuations, to 1 part in 50,000 during any necessary interval of time: in the measurements here discussed it is customarily held constant to 1 part in 30,000. Since the calibration of 1 degree to ten-thousandths necessitates only about one-third this constancy, the calibration is quite unaffected by variability of the power transmitted. Within similar limits of fluctuation, also, the coil resistance remains constant during measurement; it follows, therefore, that all the significant errors of the calibration are calorimetric errors.¹³

Procedure

With these dispositions, a calibration is made by observing at any convenient intervals the temperatures indicated by the thermometer while the actual temperature of the calorimeter rises continuously and uniformly. To distinguish this type of measurement from those employed heretofore it may be called a calibration by continuous process, or, more briefly though inexactly, a *continuous calibration*. Since the thermal leakage of the system heated is negligible, and the influx of energy more than suf-

¹³ According to past experiences in this type of measurement, a safe and convenient rate of energy supply is about 5 calories a minute, or 0.35 watt, which in a calorimetric system of the usual heat capacity (approximately 1000 gram-calorie units) causes a temperature rise of about 0.01 degree in two minutes. If a rate somewhat less than this is established, the conduct of the measurement will be quite unhurried, and its duration not unduly prolonged.

ficiently uniform, and since the heat capacity of the system remains sensibly constant, or subject to slight and adequately determinable correction for change in its specific heat as the temperature rises, the only significant errors in actual measurement are those of thermometric registration and reading.

To reduce these errors, readings are made, not of temperatures, but of times. When the standardization is that of a mercury thermometer, the slowly rising meniscus of the thread is closely watched through a telescope while it is occasionally agitated by an attached electrical tapper of ordinary type, and as it approaches a graduation mark the vibration is made continuous. By this means capillary friction (which with a good instrument seldom significantly interferes with fairly correct reading on a rising thread) is reduced to its smallest probable magnitude for the instrument being tested, even if it is not actually eliminated from consideration.¹⁴ The times of the occultation of the meniscus with the graduation marks (which are usually very sharply defined) or those of its emergence from behind them, or both series of times, are taken by stop watches. These determinations may be made with such precision that, under favorable conditions of illumination and magnification after a little practise, and when the rate of energy supply is adjusted so as to cause a 0.01° rise of temperature in from two to three minutes,¹⁵ the temperature reading error is less than $\pm 0.0002^\circ$.¹⁶ At the end of the operation, the total time is taken with the same precision, that is, with quite negligible error; and from these data, after they have been corrected in the usual manner for the time equivalents of superimposed effects, the thermometric corrections are readily derived by any convenient method of calculation—which is not excessively laborious if multiplication tables of 60's are used, and is simple when calculating machines are available. These yield the relative values of the indicated 0.01° intervals, expressed as fractions of an indicated degree or other convenient range taken as an arbitrary standard temperature interval. The determination of the absolute value of this interval on a scale of equal energy increments is left for another similar operation—that of standardization. A fragment of an experimental record is here included, which explains the whole procedure very clearly, and illustrates a convenient form of tabulation (Table I).

¹⁴ The consistency of readings for identical repetitions of measurement indicates the maximal possible effect of capillary friction. In the calibration of the calorimetric thermometers used in this Laboratory it is usually not greater than ± 0.0003 degree; but there occur, even in these highly perfected instruments, points at which the discrepancies of reading are greater than this, although nothing indicates that for any imaginable reason the other experimental controls are less precise at these indicated temperatures. All experience still points to capillary friction as the most significant defect of mercury thermometers as instruments of precision.

¹⁵ Cf. above, footnote 13.

¹⁶ It is worth noting that the precision of such readings will depend very largely upon the fineness of the scale engraving, the importance of which is thus emphasized.

IMMEDIATE DATA OF A CALIBRATION^a
A. Data of Measurement

TABLE I

1	2	3	4	5	6	7	8	9	10	11	
Environment Thermometer C	Head of Thermometer [1 - 8]	Thermometer B, S. No. 8961 (twin of P. T. R. No. 54854)	Observed temp. and interpolated means	Apparent Observed [4 - 8]	head of bath At actual equilibrium	Actual head of bath [5 - 6]	P. T. R. No. 54854 Thermometer	Observed temp. of instrument being calibrated	Observed times in hours, minutes, seconds	In seconds from 6:0-0 p.m.	Criticism
Corrected Temp. °C.	[Envt.]										
21.50	+1.95	19.544	0.552	-0.002	-0.017	+0.015	19.55 (7 ₁)	6:33:28	2008	Good: ± < 3 secs.	
21.52	+1.96	0.560	.551	-.019	-.002	-.002	0.56	36:00	2160	Good: ± < 3 secs.	
	(+1.95)	.542	.547	-.023	-.006	-.006	.57	38:30	2310	Excellent: ± < 2 secs.	
	+1.94	.552	.561	-.019	-.002	-.002	.58	Missed	..	Capillary Friction!	
21.53	+1.94	.570	.575								
		.775	.777	-.013	(- .015)	+ .002	.79	7:34:00	5640	Cap. Frict. after: Good.	
21.76	+1.95	.780	.780	-.020	-.014	-.006	.80	36:30	5790	Cap. Frict. before: Fair.	
	(+1.90)	(.790)	.785	-.025	-.012	-.012	.81	39:13	5953	Fair: Etching defective.	
21.68	+1.85	19.800	.795	-.025	-.012	-.013	19.82 (7 ₂)	41:45	6105	Very good: ± < 2 secs.	

12	13	14	15	16	17	18	19	20	21	22	23	24
Corrections for superimposed effects in degrees	Exposure of thermometer stem	Imperfect isothermal conditions	Leakage to the bath	Punctation of heating current (reduced)	Sum of corrections in degrees	Computed from 6:0-0 p.m. observation in seconds [10 + 18]	Corrected times in seconds	From time of first observation interval, sec.	Value of 0.01° arbitrary summated intervals, sec.	Values of arbitrary intervals, [20 - 22] sec.	Calibration corrections in degrees	
	± 0 ^d	± 0	± 0	± 0	+0.0012	2026	0 (7 ₁)	152	152	152	± 0	± 0
19.55	± 0	+0.0012	± 0	± 0	+0.0012	2178	152	304	304	304	± 0	± 0
0.56	± 0	+0.0012	± 0	± 0	+0.0012	2329	303	456	456	456	± 0	± 0
.57	± 0	+0.0012	± 0	± 0	+0.0012	± 0	± 0
.58	+0.0001	+0.0012	± 0	+0.0001	+0.0014	± 0	± 0
.79	+0.0004	+0.0012	-0.0001	+0.0002	+0.0017	5665	3639	3648	3648	3648	- 9	- .0005
.80	+0.0004	+0.0012	-.0001	+0.0001	+0.0016	5814	3788	3800	3800	3800	- 12	- .0008
.81	+0.0005	+0.0012	-.0002	+0.0002	+0.0017	5978	3952	3952	3952	3952	± 0	± 0
.82	+0.0005	+0.0011	-.0002	+0.0001	+0.0015	6128	4102 (7 ₂)	4104	4104	4104	- 2	- .0001
Extreme values of corrections	+ .0005	± .00005	- .0002	± .0004	± 0							

^a B. & W.: Calibration No. 8, Part IV (March 27, 1922), in part. ^b By comparison with Baudin Standard Bur. P. et M. No. 18537. ^c From adiabatic comparison of P. T. R. No. 54854 with B. S. No. 8961. ^d ± 0 here means less than 0.00005°. ^e Drift, as shown by initial and final tests of the isothermal condition. ^f Mean within the range (19.55° to 19.82°) chosen for repeated tests: = (7₂ - 7₁) ÷ 27.

Facility in both measurement and calculation, and precision also perhaps (though certainly to a minor degree), is dependent upon the elimination of as many corrections for experimental error as possible. In the first measurements made by this method (Barry and Webb, 1923), the leakage corrections were far from negligible, and their application tedious; the results were accurate enough, but their determination, which required as a precautionary measure the simultaneous attention of two observers, was protracted, and the work lacked, in consequence, a certain persuasive elegance. In later measurements (Smith, 1925) advantage was taken of a close control of the temperature of the air surrounding the calorimeter, which was made possible by the installation of an enveloping chamber within which this temperature could be and was kept continuously within $\pm 0.02^\circ$ of that indicated by the thermometers, by a quickly adjustable thermostatic mechanism.¹⁷ This control made it necessary to carry out all observations and manipulations from the outside, without awkwardness, however, since the readings in any case were telescopic and since with this additional insulation all fluctuations of external temperatures were so slow and regular that they required much less attention. The consequently minute and uniformly periodic fluctuation of the bath, the minimal conduction of heat through projecting parts, and the very slight effects of thermometer-thread exposure made possible the reduction to negligible magnitude of all calorimetric errors, and therefore the elimination of all corrections whatever. It also facilitated measurement by making it safe for a complete calibration to be carried out by one observer. With a convenient disposition of telescope, galvanometer and mechanisms of control, the maintenance of adiabaticity and constancy of the development of heat required only occasional and momentary interruption of thermometric observations when the work was thus conducted; but the testing of the constancy of the coil resistance and of the constancy of the

¹⁷ This air thermostat was so constructed that the outer air, at a temperature a degree or more below that of measurement, drifted in slowly from below, was heated by lamps placed behind radiation screens and, ascending, was distributed by small fans before it found its way out from the top. Its temperature was regulated by a bimetallic strip suspended from light springs, one terminal of which was a screw adjustable through small gearing by a rod which pierced the wall. By means of a needle attached to this rod, which traversed a graduated dial on the outside of the wall, the position of the regulator terminal could be read with some precision, and adjusted nicely enough to make easy the stepwise regulation of the air temperature to within $\pm 0.02^\circ$ of that of the calorimeter. Telescopic readings were made through a window of plane plate glass, tested by a comparison of micrometer measurements of the thermometric intervals carried out with the window open and closed. Incidental manipulations were made through two elastic cloth sleeves set into apertures in the front wall. This apparatus improves both the facility and the precision of adiabatic measurements of all sorts so remarkably that it has been adopted as an essential part of all calorimetric installations here.

potentiometer system necessitated the omission of one or two 0.01° interval readings in the course of a determination.

There follow two records of calibration, by this method, of calorimetric thermometers of different types: the one, an instrument similar to the familiar Beckmann thermometer, with separate flat porcelain scale; the other, one of the normal thermometer type with scale etched upon the curved surface of the solid stem. Both scales had been made for convenience in reading with a hand lens to 0.001 or 0.0005° , and were, consequently, not as finely etched as that of a normal instrument; they were graduated in 0.01° intervals, which in each case were about 0.7 mm. apart. The first record shown (Table II) is that of a calibration of the flat-scale instrument, made in a constant-temperature closet with customary care,¹⁸ but without the accessory control of the air thermostat (Barry and Webb). The second (Table III) is taken from a later calibration of the solid-stem instrument in which this control was employed (Smith). It will be noted that the precision of these two calibrations is the same.

Criticism

The close consistency of the results obtained in repeated calibrations by this method indicates a very high precision of measurement, and thus justifies a critical examination of the errors which are characteristic of the procedures adopted. The results of a comprehensive survey of this sort, recently made, are typified by the data shown in Table IV, which apply to the particular calibrations here discussed. By exhibiting the relative magnitudes of all errors of control, these data yield the assurance that by nicer regulation of certain of these controls—an easily practicable matter—the precision of the method, which now closely approaches the present accepted limit of thermometric sensitivity for the usual calorimetric ranges ($\approx 0.0001^\circ$) may with certainty attain it, if the instruments tested are capable of a correspondingly precise consistency of registration.

In the effort to reach this precision, the inconstancy of the heating current need, obviously, cause no concern, since its constancy within one part in thirty thousand—as in these measurements—is adequate, and three or four times this constancy attainable, without excessive care. By use of the adjustable air thermostat, the influence of the external environment in causing leakage through the projecting parts of the calorimeter, and in affecting the temperature of the thermometer stem, may easily be made negligible also, when as here air temperatures are read to 0.01° . The control of the calorimeter bath, however, should be closer; for the error involved in the correction for its fluctuation when its thermal head is determined—as in these measurements—by a comparison of the corrected readings of twin mercury instruments read by estimation to $\approx 0.0005^\circ$,

¹⁸ THIS JOURNAL, 42, 1918-1920 (1920); 44, 900-902 (1922).

may be large enough to affect the evaluation of any whole temperature interval greater than half a degree, though it would probably not affect the ratios of the calibrated 0.01° intervals within ranges of less than two degrees. It is, however, by no means certain that the fluctuation of calorimeter temperature is more than approximately calculable from the

TABLE II
COMPARISON OF INDEPENDENT CALIBRATIONS OF A CALORIMETRIC THERMOMETER
WITH SEPARATE FLAT SCALE^a

1 Calorimeter temperatures indicated by P. T. R. No. 54854	2	3 Corrected times in seconds (Cf. Table I, Column 20)				6 Mean values	7 Calibration corrections ^b for P. T. R. No. 54854 in degrees	8 a. d. in sec.	9 Errors		10 A. D. in degrees $\times 10^4$
		I	II	III	IV				A. D. in sec.	A. D. in degrees $\times 10^4$	
19.55	0	0	0	0	0	= 0					
19.56	153	159	155	152	155	-0.0001	2.3	1.2	0.8		
19.57	304	308	302	303	304	= 0	1.8	0.9	0.6		
19.58 ^c	474	472	460	..	469	-0.0009 ^c	5.7	3.3	2.1		
19.59	..	612	613	..	613	- .0003	(0.5)	(0.4)	(0.3)		
19.60	752	753	752	751	752	+ .0006	0.5	0.3	0.2		
19.61	908	905	907	903	906	+ .0004	1.8	0.9	0.6		
19.62 ^c	(1076)	1057	1055	1052	1055 ^d	+ .0006	1.7 ^d	1.0 ^d	0.7 ^d		
19.63 ^c	1212	1216	(1227)	1207	1212 ^d	+ .0005	2.7 ^d	1.6 ^d	1.0 ^d		
19.64	1377	1386	1366	1369	1375	- .0001	7.0	3.5	2.3		
19.65	1514	1515	1518	1510	1514	+ .0004	2.0	1.0	0.7		
19.66	1666	1668	1670	1671	1669	+ .0002	1.8	0.9	0.6		
19.67	1825	1819	1823	1819	1822	+ .0001	3.3	1.7	1.1		
19.68	1968	1971	1971	1967	1969	+ .0005	1.8	0.9	0.6		
19.69	2111	2115	(2130)	2116	2114 ^e	+ .0009	2.0 ^e	1.2 ^e	0.8 ^e		
19.70	2268	2271	2278	2268	2271	+ .0006	3.3	1.7	1.1		
19.71	2421	2424	(2439)	2419	2421 ^e	+ .0006	1.7 ^e	1.0 ^e	0.7 ^e		
19.72	2571	2576	2576	2574	2574	+ .0007	1.8	0.9	0.6		
19.73	2733	2728	2730	2726	2729	+ .0005	2.3	1.2	0.8		
19.74	2884	2887	2881	2888	2885	+ .0002	2.5	1.3	0.8		
19.75	3028	3033	3024	3034	3030	+ .0007	3.8	1.9	1.2		
19.76	3204	3195	3189	3193	3195	- .0002	4.3	2.2	1.4		
19.77	3350	3358	3339	3344	3348	- .0003	6.2	3.1	2.0		
19.78	3500	3492	3490	3489	3493	- .0005	3.8	1.9	1.2		
19.79	3643	3635	..	3639	3639	+ .0006	2.7	1.6	1.0		
19.80 ^e	3793	(3818)	3788	3788	3790 ^e	+ .0007	2.3 ^d	1.4 ^d	0.9		
19.81	3950	..	3945	3952	3949	+ .0002	2.0	1.2	0.8		
19.82	4098	4103	4108	4102	4103	+ .0001	2.8	1.4	0.9		

^a B. & W.: Calibration of a Mueller calorimetric thermometer: Series VIII complete (1922). ^b The mean 0.01° interval of this range, taken as an arbitrary standard, is traversed in 152 seconds. Each mean value (column 6) is here subtracted from the proper multiple of 152 seconds and the difference converted into degrees $\times 10^4$ by the corresponding factor 0.658. The corrections are thus made independent of one another. ^c Capillary friction noted, undependable points (cf. Table I). ^d Single values (in parentheses) aberrant beyond twice the reading error, excluded for cause; these values alone were affected by noted uncertainties of reading due to capillary friction. ^e Arbitrary exclusion of grossly aberrant values (in parentheses): scale etching was obscured here, and the readings involved estimations.

TABLE III

COMPARISON OF INDEPENDENT CALIBRATIONS^a OF A THERMOMETER OF "NORMAL" TYPE WITH SCALE ETCHED ON SOLID STEM

Indicated Temp., °C.	Corrected times in seconds ^b (Cf. Table I, Column 20)					Arith. mean	Calib. corr. for C. U. No. 1 in degrees	Errors in seconds, or in degrees × 10 ⁴		Indicated Temp., °C.	Corrected times in seconds (continued)				Arith. mean	Calib. corr. for C. U. No. 1 in degrees	Errors in seconds, or in degrees × 10 ⁴	
	I	II	III	IV	a. d.			A. D.	I		II	III	IV	a. d.			A. D.	
20.50	0	0	0	0		# 0				20.76	..	2598	..	2589	2594	+0.0006	4.5	3.2
.51	99	..	97	..	98	+0.0002	(1.0)	(0.7)		.77	2694	2694	2691	2689	2692	+ .0008	2.0	1.0
.52	196	188	193	198	194	+ .0006	3.3	1.7		.78	..	2798	2796	2789	2794	+ .0006	3.7	2.2
.53	295	290	300	297	296	+ .0004	3.0	1.5		.79	2891	2893	2898	2892	2894	+ .0006	2.3	1.2
.54	397	385	402	..	395	+ .0005	6.3	3.7		.80	2995	2996	2996	2985	2993	+ .0007	4.0	2.0
.55	49481	3096	3082	3089	+ .0011	(7.0)	(5.0)
.56	594	584	..	591	590	+ .0010	3.8	2.2		.82	3194	3193	..	3185	3191	+ .0009	4.3	2.5
.57	699	690	695	+ .0005	(4.5)	(2.3)		.83	3295	3293	3291	3286	3291	+ .0009	2.8	1.4
.58	791	786	794	..	790	+ .0010	3.0	2.1		.84	3395	3399	3396	3388	3395	+ .0005	3.3	1.7
.59	891	887	898	890	892	+ .0008	3.3	1.7		.85	3496	3497	3496	..	3496	+ .0004	0.4	0.2
.60	..	991	..	992	992	+ .0008	(0.5)	(0.3)		.86	3596	..	3595	3592	3594	+ .0006	1.7	1.0
.61	1093	1090	1097	1094	1094	+ .0006	4.3	2.2		.87	3699	3692	3700	3697	3697	+ .0003	2.5	1.3
.62	..	1196	1201	1196	1198	+ .0002	2.3	1.6		.88	3796	3790	3796	3789	3793	+ .0007	3.3	1.7
.63	1302	..	1302	1294	1299	+ .0001	3.7	2.2		.89	3897	3894	3899	3891	3895	+ .0005	2.8	1.4
.64	1398	1394	1403	1396	1398	+ .0002	2.8	1.4		.90	3997	3995	4000	3993	3996	+ .0004	2.3	1.2
.65	..	1492	1504	..	1498	+ .0002	(6.0)	(4.3)		.91	4096	4092	4102	4095	4096	+ .0004	2.8	1.4
.66	1586	1595	1606	..	1596	+ .0004	7.0	4.1		.92	4195	4193	..	4195	4194	+ .0006	0.9	0.5
.67	..	1696	1707	1696	1700	# 0	5.0	2.9		.93	4293	4292	4295	4291	4293	+ .0007	1.3	0.6
.68	1801	1799	..	1795	1798	+ .0002	2.3	1.4		.94	4393	4393	4397	4391	4394	+ .0006	1.8	0.9
.69	1903	1896	1909	1892	1900	# 0	6.0	3.0		.95	4494	4494	..	4494	4494	+ .0006	0	0
.70	2001	2001	2007	1996	2001	+ .0001	2.8	1.4		.96	4595	4596	4594	4594	4595	+ .0005	0.8	0.4
.71	2102	2100	2104	2095	2100	# 0	2.8	1.4		.97	4698	4699	4701	..	4699	+ .0001	1.0	0.6
.72	2201	2200	2207	2196	2201	+ .0001	3.0	1.5		.98	..	4802	4799	4797	4799	+ .0001	1.7	1.0
.73	..	2297	2305	2297	2200	# 0	3.7	2.2		.99	4900	..	4899	4898	4899	+ .0001	1.0	0.6
.74	..	2406	2408	2396	2403	+ .0003	5.0	2.9		21.00	5000	5000	5000	5000		[≠0]		
.75	2499	..	2504	2492	2498	+ .0002	4.3	2.5										

Average divergence from the mean (a. d.) = 0.00031°.

Average dependability of a measurement (A. D.) = 0.00015.

^a Smith; Calibration of 0.5° on a Pfeuffer calorimetric thermometer. Series II, complete (1926). ^b Observed and corrected times are here proportionally adjusted to make 100 seconds correspond to the mean 0.01° interval for this range, taken as standard.

thermal leakage modulus on the assumption of its proportionality to the fluctuation of the bath; for, though this proportionality has been shown to hold for small bath heads when these are constant,¹⁹ it must be affected in opposite senses by the lag of the bath thermometer and that of the insulating air gap when the bath temperature fluctuates, and perhaps asymmetrically for its rise and fall. These lags, furthermore, make the calculation of corrections for imperfect adiabaticity inapplicable to calorimetric temperatures simultaneous with those of the bath from which they were derived; they must, therefore, be determined, if such corrections are to be correctly applied, to successive readings of a changing temperature. For these reasons it is highly desirable, if not imperative, that

TABLE IV
CORRECTIONS FOR DIVERGENCE FROM UNIFORM CONDITION^a
IN DEGREES $\times 10^4$, OR CALORIES $\times 10^1$

A. Total corrections for influx of heat in two hours							Precision ^e of the correction
Correction	Observer	I	II	III	IV		
1a Drift from initial equilibrium ^b	B. and W.	+19	+11	+5	+3	≈ 3.0	
	S.	-3	-3	≈ 0	...	≈ 1.7	
1b Direct leakage to environment ^{c,f}	B. and W.	-3.5	-3.9	-3.3	-4.7	≈ 0.00	
	S.	-0.17	+0.28	-0.11	+0.30		
1c Leakage to the bath ^d	B. and W.	+4.1	+2.1	-3.7	-1.1	$< \approx 0.6$	
	S.	+11.2	+21.9	-9.0	-60.6	$< \approx 0.5$	
1d Inconstancy of heating current	B. and W.	+0.17	Less than	0.20		≈ 0.02	
	S.	...	+0.15	+0.05	+0.17		
B. Maximal corrections for single determined 0.01° intervals							Precision of the correction
Correction	Observer	I	II	III	IV		
2a Drift from initial equilibrium	B. and W.	+0.4	+0.2	+0.96	+0.52	≈ 0.05	
	S.	-0.06	-0.06	≈ 0.00	...		
2b Direct leakage to environment	B. and W.	-0.07	-0.08	-0.07	-0.09	≈ 0.00	
	S.	≈ 0.00	+0.01	≈ 0.00	+0.01		
2c Leakage to bath	B. and W.	+2.4	-2.2	+1.1	+1.0	$< \approx 0.11$	
	S.	-3.0	-1.5	-2.0	-3.0		
2d Inconstancy of heating current	B. and W.	+0.004	Less than	0.004			
	S.	...	≈ 0.00	≈ 0.00	≈ 0.00		
2e Exposure of thermometer stem ^f	B. and W.	-8.58	-11.40	-9.60	-11.70	≈ 0.01	
	S.	+0.12	+0.19	-0.17	-0.14		

^a Applicable to the calibrations recorded in Tables II and III. ^b Determined from pre-period and post-period drift under thermostatic control, see p. 3797. ^c Conduction leakage through thermometer, stirrer-rods and electrical leads. ^d The bath fluctuates within a range of 0.05° or less: values here shown are maximal. The large corrections of observer S. are due to isodiabatic control. ^e Precision is discussed on p. 3793 ff. ^f The smaller corrections of observer S. are due to control of the temperature of the surrounding air.

¹⁹ Ref. 1, p. 918 ff.

corrections for imperfect adiabaticity be made quite negligible, and not only in operations of calibration or standardization like those here discussed, but in **all** measurements that involve the determinations of rates in the development or absorption of heat. The slight improvement of control which is necessary to ensure this result is easily attained by the use of a thermoelement to indicate the difference of temperature between bath and calorimeter; not in this case because of its greater sensitivity, but because of its small lag and the ease with which the bath temperature can be regulated so as to maintain a galvanometer reading close to the null point. Such installations, therefore, have now replaced that of twin mercury thermometers in all precision work in this Laboratory, with the result that corrections for imperfect adiabaticity are habitually reduced to negligible magnitude.

Finally, in this as in all protracted adiabatic measurements, the slow temperature drift that is usually detected when, under precise thermostatic control, the system should remain constant, causes the most serious uncertainties. This drift measures, of course, the aggregate effect of all disturbing influences either not yet identified or not yet brought under control: minute leakages, evaporations and condensations, adsorptions,²⁰ oxidations or other chemical changes, and so on. Inasmuch as it cannot be determined from accessory measurements in which its magnitude is proportionally exaggerated, but must be measured directly during pre-periods and post-periods the durations of which are at best of the same order of magnitude as that of the measurement itself, it is necessary that the utmost care be exercised to make it as small as possible by meticulous observance of all the precautions which minimize leakages, adsorptions and chemical changes in the system, and that it be measured with the highest precision.²¹ The data of Table IV show that the uncertainty of the total correction of this drift, which affects the definition of the whole temperature interval calibrated, may approach $\pm 0.0002^\circ$, but that it will not sensibly affect the determination of the relative values of 0.01° intervals.

It is perhaps worth remarking, in conclusion, that the efficacy of the precautions here discussed will be conditioned by a close observance of all the other niceties of technique which characterize measurements of like

²⁰ Ref. 1, pp. 931 *ff.* These observations have recently been amply confirmed, and the effects measured with precision under conditions that practically eliminate the possibility that they are due to chemical change. A paper descriptive of this work is now in press.

²¹ For this measurement, electrical thermometry is most efficacious; but since calorimetric mercury thermometers may, under carefully chosen conditions, be not only read to $\pm 0.0001^\circ$ but made to indicate chosen stationary temperatures with a consistency of $\pm 0.0002^\circ$, such measurements may be made by their means quite satisfactorily when the time which elapses between the observed isothermal periods does not exceed three or four hours—as is the case in calibrations like those here described.

sort: in particular, it will be important that the influence of external temperatures and pressures be exactly known. The air thermostat will, if properly controlled, eliminate corrections for stem exposure, but corrections for fluctuations of barometric pressure frequently cannot be avoided, and in work of this precision are likely to be significant, for changes in the registration of calorimetric mercury thermometers due to a change in external pressure of 1 millimeter of mercury usually approach 0.0002° , and with the most sensitive instruments may exceed this value.

Addendum

Those who are familiar with the techniques of the electrical calibration and precise adiabatic control of calorimeters will predict that, with the same exactitude that a calibration can be made by this method with reference to an arbitrary standard temperature interval, a complete standardization can be made with the same apparatus, with reference to that scale of equal energy increments which is defined by the electrical units. So far as can be told from a study of the estimated errors of one such standardization actually carried out, such is the fact. The experimental demonstration of this possibility, however, demands the comparison of two or more such standardizations of the same thermometer in which significantly different heat capacities and energy rates are involved, and such data are not at present available.

It will also be evident that, with mercury thermometers calibrated in the manner described, the actual heats of chemical reactions and other processes may be determined with the exceptional precision of calibration ($\pm 0.0002^\circ$) by working between fixed temperatures. After the usual isothermal period, the electric current, regulated as in calibration, is allowed to generate heat in a coil within the calorimeter. The times at which adjacent selected points on the thermometer are passed are then taken. The reaction is initiated and completed either while the current still flows, or after its interruption at another known time if the process is protracted. Finally, after its completion, the times are taken at which another previously selected group of points is passed—the current, if interrupted, having been started again at a known time. The precision with which the electrical heat can be measured will ordinarily be better than that of the experiment as a whole, so that no new systematic errors are introduced by the procedure. The advantages are: first, all readings are made with a rising meniscus and on exact scale divisions, the fractional temperatures determined by the reaction itself being calculated from the time measurement, and thus wholly without error. Second, the best portions of the thermometer capillary can be chosen for end-temperatures since the interval read may be of any range greater than that of the temperature change caused by the reaction. Third, since several different points are read as initial and

final temperatures, a number of different determinations with different accidental reading errors are obtained in one measurement, as with the slowly changing temperatures in non-adiabatic work, and yet with the advantages of adiabatic method. The maintenance of the adiabatic condition during the slow changes of end-temperatures is very easy if the calorimeter bath is also heated electrically. Finally, it will be noted that, if the heat capacity of the calorimeter has been accurately determined, this type of measurement yields the heat of reaction directly in units of energy, the thermometer acting as an indicating instrument only—or primarily.

Summary

This paper describes a procedure, dependent upon the precise maintenance of an adiabatic condition for a few hours, whereby the relative values of all the nominal 0.01° or other minute marked intervals of thermometers may be determined to $\pm 0.0002^\circ$ or less by a continuous process, that, namely, of the generation within the calorimeter of electrical heat at a constant rate, precision of reading being secured by observations of the intervals of time during which the scale intervals are traversed. The accuracy of the method is demonstrated by data on the calibration of calorimetric mercury thermometers, and on errors of measurement which are briefly discussed.

The method is presented as the essential basis of a procedure for the complete standardization of calorimetric mercury thermometers.

Its direct applicability to thermochemical measurement is briefly discussed.

NEW YORK CITY

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

LIGHT SCATTERING IN UNDERCOOLED BENZOPHENONE

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Introduction

The light scattering of pure liquids has been successfully described by von Smoluchowski and Einstein.¹ They have calculated from the fundamental postulate of the Boltzmann entropy-probability principle the fluctuations in density of a liquid at a given temperature, and applied to these the Clausius-Mosotti-Lorentz law which relates index of refraction n to density ρ

$$\frac{n^2 - 1}{n^2 + 2} \frac{1}{\rho} = \text{const.} \quad (1)$$

An expression emerges which gives quantitatively the relation between

¹ Von Smoluchowski, *Ann. Physik*, **25**, 205 (1908); Einstein, *ibid.*, **33**, 1275 (1910).