[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

A Direct Method of Calibration of a Copper–Constantan Thermel for Measurement of Temperature Differences at a Series of Temperatures

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The suitability of a thermel for differential temperature measurements has long been recognized,[2a] but heretofore the advantage of a differential method of calibration has been neglected. Because of inhomogeneity, the accuracy of an actual thermel is not, like that of an "ideal" thermel, independent of the method of calibration. The requirement for the highest accuracy—namely, that the temperature gradients be of the same order of magnitude and occur at the same places during calibration as during use—is approached most closely by the direct differential method of calibration described in the present paper.

A thermel that is to be used for the measurement of individual temperatures is calibrated regularly according to any one of several procedures[3] that permits the expression of the total e. m. f. as a function $E(t)$ of the temperature of one junction, when the other junction is kept at a fixed reference temperature. Inhomogeneity of a thermel calibrated in this way (to which we shall refer as "the integral method of calibration") introduces an error[2b] that is approximately a fixed proportion of the total e. m. f., because both vary directly as the temperature. Usually it is possible, however, to increase[4] the accuracy of temperature measurements with such a thermel by having the temperature gradients during calibration occur at the same places along the wires as during use.

A thermel that is to be used for the measurement of temperature differences also may be calibrated by the integral method; but the error from inhomogeneity will be considerably greater than if the same thermel were used for single temperature measurements. The error is magnified because, first, the e. m. f. that corresponds to the difference in temperature is the difference between two large e. m. f.'s with each of which is associated an error due to inhomogeneity; and, second, the temperature gradients during calibration are much steeper and occur along different portions of the wires than those during subsequent use.

This magnification of the error from inhomogeneity is particularly important with a copper–constantan thermel, for even the best constantan wire, especially in the smaller sizes,[5] is not completely homogeneous. An effect of this sort interfered with the calibration of a thermel of No. 40 copper and constantan wires intended for use in the piezo-thermometric method[6] of measuring the heat capacity of a small volume of liquid. It was overcome by the direct method of calibration that we describe in this paper.

A thermel is arranged during calibration by this method in a manner similar to that during subsequent use, which not only diminishes the error from inhomogeneity, but also often simplifies the experimental set-up. A further advantage of this method is that the e. m. f.'s measured during calibration approach in magnitude those during the later use of the thermel. Consequently the electrical measurements may be performed with greater convenience and accuracy. It was for this reason that a 26-junction thermel used recently for the measurement[7] of boiling point elevations was calibrated by the differential method.

Differential Method

The Function μ.—The direct differential method of calibration that we have used involves the measurement of the e. m. f. (ΔE) of a thermel whose junctions are at two temperatures (t_1 and t_2) and the simultaneous measurement of the temperature difference ($\Delta t = t_2 - t_1$). The results of the calibration are expressed conveniently in terms of a function that we call μ, which is the quotient of these two measured quantities. Provided that the temperature differences remain approximately constant, a series of μ's obtained during calibration can be expressed as a quadratic function of the mean temperature of the junctions

$$\mu \equiv \frac{\Delta E}{t_2 - t_1} = \alpha + \beta t_m + \gamma t_m^2 \left[t_m = \frac{t_1 + t_2}{2} \right] \quad (1)$$

in which α, β and γ are empirical parameters.

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(2) W. P. White, *Phys. Rev.*, **31**, 135–158 (1910): (a) p. 152; (b) p. 135; (c) p. 142.

(3) White, Dickinson and Mueller, *Phys. Rev.*, **31**, 163 (1910); Roeser and Wensel, *J. Research Natl. Bur. Standards*, **14**, 247 (1935).

(4) Holborn and Day, *Am. J. Sci.*, **10**, 202 (1900).

(5) Giauque, Buffington and Schulze, THIS JOURNAL, **49**, 2343 (1927).

(6) John S. Burlew, THIS JOURNAL, **62**, 681 (1940).

(7) Rodney P. Smith, THIS JOURNAL, **61**, 497 (1939).

The function μ is the slope of a secant that cuts the curve representing the function $E(t)$. The thermoelectric power ($\mathrm{d}E/\mathrm{d}t$) is the tangent to this same curve; but because of the shape of the curve for a copper–constantan thermel, the tangent at a particular temperature t_m is not quite parallel to the secant whose mid-abscissa is t_m. This curve is represented accurately over fairly large ranges of t by

$$E = at + bt^2 + ct^3 \qquad (2)$$

It can be shown algebraically by a combination of equations (1) and (2) that

$$\mu - \frac{\mathrm{d}E}{\mathrm{d}t} = c\left[\frac{t_2 - t_1}{2}\right]^2 = \frac{\gamma}{12}(\Delta t)^2 \qquad (3)$$

Hence a value of μ that applies to one temperature difference Δ_1 may be transformed into one to apply to any other temperature difference Δ_k by this equation

$$\mu_{\Delta_k} - \mu_{\Delta_1} = \frac{\gamma}{12}[(\Delta_k)^2 - (\Delta_1)^2] \qquad (4)$$

in which γ is the parameter in equation (1). For a copper–constantan thermel γ is about 1 (10^{-6}) (*cf.* equation (9)), and so this transformation term is not large. By the combination of equations (1) and (4), a temperature difference at any mean temperature within the range of the calibration may be computed directly from the measured e. m. f. of the differential thermel.

Relation of μ to the Integral Method.—Application of the function μ is not limited to a thermel calibrated by the differential method. If a homogeneous thermel that has been calibrated by the integral method is used for the measurement of a temperature difference, μ can be employed to compute that difference directly, which is simpler than the usual computation of the separate temperatures of the two junctions by a series of approximations. If the parameters in equation (2) have been evaluated as a result of the calibration by the integral method, it follows from equation (3) that the parameters in equation (1) can be derived from them as follows

$$\alpha = a + c\left[\frac{\Delta t}{2}\right]^2; \quad \beta = 2b; \quad \text{and } \gamma = 3c \qquad (5)$$

If the total e. m. f. has been expressed by the exponential equation[8]

$$E = At + B(1 - e^{Ct}) \qquad (6)$$

the parameters of equation (1) are given to a high degree of approximation by these relations

$$\alpha = (A - BC); \quad \beta = -BC^2; \quad \text{and } \gamma = -\frac{5}{6}BC^3 \qquad (7)$$

(8) L. H. Adams, *J. Wash. Acad. Sci.*, **3**, 469 (1913).

Experimental Procedure

In the calibration of a thermel by the differential method. we used a duplex oil thermostat having two similar halves mounted in a wooden cabinet (60 × 110 × 55 cm., supported on legs 40 cm. high) with a wooden partition between them. Each half was a separate thermostat that could be heated and stirred independently. Each thermostat tank, which was a cylinder of galvanized iron (45 × 45 cm.), had an overflow pipe 4 cm. from the top in order to keep the level of the automobile "flushing oil" constant. A stirrer-propeller that rotated in a tube about 10 cm. in diameter was directly driven by a high-speed motor mounted on the cabinet. Tap water could be circulated through a cooling coil of copper tubing in the upper part of each propeller tube. The oil-baths were heated electrically by commercial resistance units of the type that are used in radiant heaters, screwed into porcelain sockets mounted on the underside of a wooden cover resting on top of the tanks. The main heaters were controlled by lamp-banks, and an intermittent heater in each tank was controlled through a magnetic relay by a conventional mercury-in-glass thermoregulator immersed in the oil-bath.

A region of constant temperature in each oil-bath was provided by a well containing mercury, the top of which was 9 cm. below the surface of the oil. The well was constructed from iron pipe fittings (inside dimensions, about 4 × 25 cm.), the bottom part being a flanged nipple filled with lead.

Above the wooden cover resting on the oil tanks, the thermostat cabinet had a separate cover with a removable center. The thermel to be calibrated straddled the partition between the oil tanks, its mid-section clamped to a copper plate and its limbs immersed in the two mercury wells. The mid-portion of the constantan wire was kept at nearly the mean temperature of the junctions, both by having the mid-section of the case of the thermel constructed from a metal tube[9] that dipped into the oil in both halves of the thermostat, and by having this part placed beneath the upper cover of the thermostat. Then, by observing similar precautions during the use of the thermel, it could be assured that the temperature gradients along the constantan wire would be of approximately the same magnitude and would occur at about the same places as during calibration. The wires from the thermel passed through a shielded slot in the upper cover to a shielded copper connection box mounted on top of the thermostat cabinet. From there an all-copper circuit led through a shielded conduit to the potentiometer.

The temperature of each half of the duplex thermostat was measured in turn with a platinum resistance thermometer,[10] that dipped into the mercury well through holes in the covers. The thermometer was kept in each

(9) *Cf.* W. P. White, THIS JOURNAL, **36**, 2303 (1914). We have found that the assembly of a thermel is facilitated by the use of copper pipe and the copper solder-joint fittings that have come into use recently for household plumbing. These fittings enable one to enclose the thermel wires by easy stages without making the case undesirably bulky. A copper straight-coupling makes an especially good socket in which to cement the glass tube that forms the lower end of a limb of the thermel.

(10) An alternative arrangement would be the use of a pair of resistance thermometers connected differentially, as described by Laby and Hercus, *Trans. Roy. Soc.* (*London*), **227**, 63 (1928).

side long enough to show that the temperature there was constant, after which it was returned to the first side to make certain that its temperature had not changed. During all three sets of observations the e. m. f. of the thermel was measured at regular intervals.

The temperature within either well of the thermostat in the temperature range 20 to 140° had a maximum variation of ±0.005° over a period of about one-half hour—although often the variation was only ±0.001°. The observed variation in the e. m. f. of the thermel gave a direct measure of the constancy of the temperature difference between the two halves of the thermostat. In a series of measurements during the calibration of a particular thermel at five mean temperatures from 20 to 65°, the average maximum fluctuation in the temperature difference of 10° was ±0.002°. At higher temperatures (up to 125°) the maximum fluctuation was about twice this amount. The latter variation represented an uncertainty of ±0.05% in the measured e. m. f., which was about the same magnitude as the uncertainty in the temperature difference as measured with the resistance thermometer.

The quotient of the e. m. f. divided by the temperature difference was a value of μ at a particular mean temperature t_m. A series of eight or ten such measurements was made, using a temperature difference between the junctions of approximately 10° at different mean temperatures. From the resulting μ's and t_m's the parameters in equation (1) were evaluated by the method of least squares.

Experimental Comparison of Methods

The differential and integral methods of calibration were compared by direct experiment using two copper–constantan thermels that had been constructed from No. 30 constantan and No. 36 copper wires. The maximum inhomogeneity of the constantan was less than 0.05% of its thermoelectric power against copper, as determined by the method described by White.[2c]

Calibration of Thermel A.—Thermel A was calibrated according to the integral method by measurement of the e. m. f. produced when one junction was kept at 0° and the other was heated to different temperatures between 40 and 130°. Temperatures were measured with a platinum resistance thermometer (Leeds and Northrup), the fundamental interval of which we redetermined prior to the calibration, measuring the resistance with the same Mueller-type bridge (Leeds and Northrup) that we used during the temperature measurements. The calibration measurements were made at 10° intervals with first one junction at 0° and then the other. Each value of the e. m. f. was divided by the corresponding temperature; and then the two sets of values of E/t were fitted to separate quadratic equations in t by the method of least squares,[11] with equal weight assigned to each variable. Residuals were computed for each set of data with respect to the equation derived from it and also with respect to the equation obtained by taking the mean values of the respective parameters of the two equations. The probable error (P. E.) of a single observation corresponding to the residuals of the mean equation was only slightly larger than that corresponding to the residuals of each individual equation—4% larger in one case and 16% in the other. For as few as ten observations these differences are without practical significance; and so the mean equation is used to represent the e. m. f. of the thermel

$$E = 38.3162\,t + 4.56212\,(10^{-2})t^2 - 3.3208\,(10^{-5})\,t^3 \quad (8)$$

The P. E. of this function,[12] based on the residuals, is 0.003% or less in the range 40 to 130°. This low P. E. and the agreement between the reversed calibrations indicate that the inhomogeneity of this thermel was very small.

Calibration of Thermel B.—Thermel B was calibrated according to the differential method in the duplex thermostat already described by measuring the e. m. f. that was produced by at emperature difference of about 10° at different mean temperatures at 15° intervals from 5 to 125°. Each junction of the thermel was the cold junction during half the measurements. The temperature differences were measured with the same resistance thermometer used in the calibration of Thermel A. The separate values of μ were fitted to a quadratic equation in t_m by the method of least squares,[11] with infinite weight assigned to the values of the mean temperature. The resulting function

$$\mu_{10} = 42.6744 + 7.6183\,(10^{-2})\,(t_m - 65) - 9.745\,(10^{-5})\,(t_m - 65)^2 \quad (9)$$

has a P. E.[12] of 0.03% or less in the range 10 to 110°.

Mode of Comparison.—For the comparison of the two methods of calibration, both thermels were placed in the duplex thermostat at the same time. The temperatures of the two sides of the thermostat were maintained 10° apart at each of six mean temperatures from 30 to 105°. The temperature of the colder side was measured with the platinum resistance thermometer that had been used in the calibrations. The same ends of the thermels were always on this side. Two sets of observations at each temperature were made twenty minutes to an hour apart.

(11) W. E. Deming, *Phil. Mag.*, **11**, 146 (1931).

(12) H. Schultz, *J. Am. Stat. Assoc.*, **25**, 139 (1930).

TABLE I

MEASUREMENT OF TEMPERATURE DIFFERENCES WITH THERMEL A

Nominal mean temp., °C.	t_1, °C.	E_A μv.	E_1 μv.	E_2 μv.	t_2, °C.	$(\Delta t)_A = (t_2 - t_1)$, °C.
30	25.009	405.62	986.26	1391.88	34.911	9.902
	25.011	405.66	986.35	1392.01	34.915	9.904
45	40.106	412.64	1607.95	2020.59	49.880	9.774
	40.102	413.37	1607.79	2021.16	49.893	9.791
60	55.100	435.30	2244.17	2679.47	65.121	10.021
	55.099	434.47	2244.13	2678.60	65.101	10.002
75	69.917	446.48	2890.61	3337.09	79.930	10.013
	69.919	446.48	2890.71	3337.19	79.932	10.013
90	85.292	462.41	3579.34	4041.75	95.400	10.108
	85.291	462.76	3579.30	4042.06	95.407	10.116
105	100.088	509.31	4258.71	4768.02	110.963	10.875
	100.078	509.51	4258.24	4767.75	110.957	10.879

Data.—In Table I under "t_1" is listed the cold temperature measured with the resistance thermometer, and under "E_A" is listed the e. m. f. of Thermel A. The temperature difference corresponding to this e. m. f. difference was found by computing the temperature (t_2) of the hot side of the thermel in the following manner. First the e. m. f. (E_1) corresponding to t_1 was computed from equation (8). To it was added E_A to give E_2. Then the temperature (t_2) corresponding to E_A was computed from equation (8) by successive approximations.

TABLE II

MEASUREMENT OF TEMPERATURE DIFFERENCES WITH THERMEL B

Nominal mean temp., °C.	t_1, °C.	E_B μv.	t_m, °C.	μ μv./°C.	$(\Delta t)_B = E_B/\mu$, °C.	Difference $(\Delta t)_A - (\Delta t)_B$, °C.
30	25.009	394.87	29.959	39.885	9.900	+0.002
	25.011	394.87	29.961	39.885	9.900	+ .004
45	40.106	401.76	44.993	41.111	9.773	+ .001
	40.102	402.50	44.998	41.112	9.791	± .000
60	55.100	423.85	60.110	42.300	10.020	+ .001
	55.099	423.07	60.100	42.299	10.002	± .000
75	69.917	434.81	74.924	43.421	10.014	− .001
	69.919	434.81	74.926	43.421	10.014	− .001
90	85.292	450.47	90.349	44.543	10.113	− .005
	85.291	450.74	90.351	44.543	10.119	− .003
105	100.088	496.03	105.527	45.602	10.877	− .002
	100.078	496.25	105.519	45.601	10.882	− .003

In Table II under "E_B" is listed the e. m. f. of Thermel B. The temperature difference was found by a series of approximations, usually three. First a value was assumed for the mean temperature, and the corresponding value of μ was computed from equation (9). The first approximation to the temperature difference was found by dividing E_B by μ. Half of this difference was added to the measured cold temperature to obtain a second approximation for the mean temperature. The cycle was repeated until the same value of the mean temperature was obtained twice in succession. It is this final value of "t_m" together with the corresponding "μ" that is listed in Table II.

Conclusion.—The agreement between the values of Δt that were obtained with the two thermels is excellent, inasmuch as the estimated relative probable error of a single measurement of the temperature difference with either thermel was ±0.008°. The maximum difference between the two sets of values, as shown in the last column of Table II, is 0.005°, and the average difference without regard to sign is 0.002°.

Summary

The computations involved in the measurement with a thermel of temperature differences at a series of mean temperatures (t_m) are simplified by the introduction of the function

$$\mu \equiv \Delta E/(t_2 - t_1) = \alpha + \beta t_m + \gamma t_m^2$$

A direct differential method of calibration, whereby the parameters of this equation are evaluated, minimizes the error from inhomogeneity. For the demonstration of the experimental validity of this method, a copper–constantan thermel that had been calibrated by it was compared with one that had been calibrated by the ordinary integral method: in a series of temperature differences measured with the two thermels the maximum divergence was 0.005°, which was less than the experimental uncertainty.

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