SOME CALORIMETRIC METHODS.

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THE calorimetric method of mixtures has recently undergone a marked development. New methods have been introduced, and the standard of accuracy has been greatly advanced. The significance of this development is not yet wholly clear; considerable disagreement is manifest as to the exact relation between the methods and the accuracy, so that the value of the methods and the relative importance of the remaining sources of error are still uncertain.

The present series of papers makes some contribution toward a further knowledge of the different calorimetric errors and of the advantages of different methods. It also describes some apparatus and methods now in use at the Geophysical Laboratory, of which some account has already been given.¹

I. A SHORT METHOD FOR GETTING THE COOLING CORRECTION.

The cooling correction is often discussed with the aid of a figure² similar to Fig. 1, where the heavy curve represents the calorimeter temperature, plotted against time. If heat is communicated to the calorimeter during the *transfer period*, t , raising the temperature from ϑ_0 to ϑ_2 , some heat will (usually) at the same time be lost by convection, etc. The heat transferred will thus be measured by the temperature difference, $\vartheta_2 - \vartheta_0$, plus the loss of temperature due to the heat which has escaped. This loss is the cooling correction. It has to be calculated, and the data required are, first, the temperatures of the calorimeter during the transfer period, and second, the relation between these temperatures and the cooling

¹Walter P. White, *PHYS. REV.*, 25, 137, 1907; 26, 536, 1908; 28, 461, 1909; *Amer. Journ. Sci.* (4), 28, 334, 1909.

²The essentials of which, as well as some other features of the present discussion were suggested by the paper of Jaeger and von Steinwehr, *Ann. d. Phys.*, 27, 23, 1906,

rate. This relation varies from time to time, and is usually re-determined for each experiment.¹

Fig. 1.

Temperature-time diagram of a typical calorimetric determination.

The most advantageous method of getting the cooling correction will depend somewhat upon the experimental conditions. A very simple (and probably new) procedure is possible if the environmenting temperature can be measured, and if the heat change due to stirring and evaporation is known to a rough approximation. In deriving the formula, it will² be convenient to put:

ϕ_n for the temperature difference of calorimeter and jacket at the time, t_n ,

$\Phi_m = \int_m \phi$, for the total value of ϕ for the interval T_m ,

w , for the temperature fall per minute due to the combined effect of evaporation and stirring.

The value of the cooling rate for any particular experiment is found by running a cooling period immediately after the transfer period. During this period the temperature falls from ϑ_2 to ϑ_4 . The value of Φ is then Φ_3 , for which T_3 times the mean value of

¹Some observers have also redetermined it for several different temperatures in each case, as if by so doing greater accuracy could be obtained. This does not appear to be true for the experimental conditions contemplated in the present paper. The change of the cooling rate with temperature is so nearly linear that its deviation from proportionality is commonly neglected (data on this point are given on p. 556); the variation of this negligible variation can hardly compare with the changes which may result from the manipulation and delay of the supposedly more accurate procedure. See further, p. 550, footnote 2.

²Notation. The notation here used agrees with that of most writers on this subject in using V for rate of cooling. It agrees with Jaeger and von Steinwehr in taking t for time, with Pfaundler and with Louguinine and Schukarew in using ϑ for temperature, though it differs from them in doing so consistently. Primes indicate corrected quantities; subscripts refer only to time, odd numbers for the periods, even, for their terminations. The additional symbol, ϕ , is introduced for the temperature difference of calorimeter and jacket, with Φ for its integral. w indicates that part of the rate due to stirring and evaporation.

ϕ can always be taken. The experimental data required, then, are (besides the time intervals, T_1 and T_3) the temperatures, ϑ_0 , ϑ_2 , ϑ_4 , the integrated differential temperatures Φ_1 , and Φ_3 , and, approximately, the rate w . It will be convenient to begin by assuming that the heat *directly* lost is proportional to ϕ ; that is, that Newton's law of cooling holds. This assumption underlies most cooling correction methods. Here it is made merely to simplify the presentation, and will be dispensed with presently. In accordance with this assumption, since

$$\vartheta_2 - \vartheta_4 - wT_3 \quad (1)$$

is the *direct* loss of temperature in period 3,

$$(\vartheta_2 - \vartheta_4 - wT_3) \frac{\Phi_1}{\Phi_3} \quad (2)$$

is that in period 1, and

$$(\vartheta_2 - \vartheta_4 - wT_3) \frac{\Phi_1}{\Phi_3} + wT_1 \quad (3)$$

is the cooling correction. The advantage of this formula is gained by transforming it through

$$(\vartheta_2 - \vartheta_4 - wT_3) \left(1 + \frac{\Phi_1 - \Phi_3}{\Phi_3} \right) + wT_1 \quad (4)$$

to

$$\vartheta_2 - \vartheta_4 + (\vartheta_2 - \vartheta_4 - wT_3) \frac{\Phi_1 - \Phi_3}{\Phi_3} + w(T_1 - T_3). \quad (5)$$

Here the first two terms are directly observed; the fourth vanishes if $T_1 = T_3$, that is, if the two periods are taken of equal length; the third becomes very small if Φ_1 is nearly equal to Φ_3 . Now in many cases Φ_1 can be nearly equal to Φ_3 when T_1 equals T_3 . Hence in such cases a very imperfect knowledge of w suffices, and the computation of the second term can always be done by the slide rule, and often by inspection. Another advantage of the method lies in the fact that it is wholly independent of all conditions previous to the time, t , the beginning of the transfer period. Hence the method is of value whenever it is desirable to alter the constants of either calorimeter or jacket at that time (as by dropping bodies in, putting on a cover previously left off for convenience, etc.), since it

imposes no restrictions whatever on such operations, and requires no correction or allowance for the change produced.

2. THE CUSTOMARY METHOD.

The fundamental requirement of the previous method, that the temperature of the environment shall be measured, is incompatible with most existing apparatus, where the jacket does not cover the calorimeter, and the environment consists of various bodies, at different temperatures. For this state of affairs the ordinary Regnault-Pfaundler method is adapted, in which observations on an additional cooling period give data enough for eliminating not only the effect of the environing temperature, but also that of the stirring, etc. This method, however, does require that the environing temperature be assumed to be constant, that no changes take place in the calorimeter constants,¹ and that Newton's law holds.² In order to make this last assumption true, it is customary to limit the temperature range used, often to less than 2°.

The formula for this method seems to admit of a simpler derivation than has yet been offered. To obtain it, let V be put, as usual, for the *observed* cooling rate, $= d\vartheta/dt$. Let K be the cooling constant of the calorimeter, let ϑ_e be the mean effective temperature of the environment, and let the subscript -1 indicate the quantities belonging to the extra cooling period (which comes before the time denoted by zero in Fig. 1). Then $V - w$, the direct cooling,

$$= K(\vartheta - \vartheta_e),$$

or

$$K = \frac{V - w}{\vartheta - \vartheta_e} \quad (6)$$

W and ϑ_e are, of course, unknown. The extra cooling period renders it possible to eliminate them, for, by composition of ratios,

$$K = \frac{V_3 - V_{-1}}{\vartheta_3 - \vartheta_{-1}}, = \frac{V_x - V_{-1}}{\vartheta_x - \vartheta_{-1}}, \text{ etc.}, \quad (7)$$

and therefore

$$V_x = V_{-1} + K(\vartheta_x - \vartheta_{-1}), = V_{-1} + \frac{V_3 - V_{-1}}{\vartheta_3 - \vartheta_{-1}}(\vartheta_x - \vartheta_{-1}), \quad (8)$$

¹Such as are produced by dropping bodies in, etc. When they occur, further corrections are necessary.

²For data on the importance of this assumption, see p. 556.

where V_x is the unknown rate corresponding to any observed temperature, ϑ_x , and the other ϑ 's are the *mean* temperatures of the intervals indicated by their subscripts. In this formula, ϑ_{-1} replaces ϑ_e as the temperature of reference, the difference between V_{-1} and any rate being proportional to the difference between ϑ_{-1} and the corresponding temperature. The cooling correction can now be expressed at once. It is merely the integral of V_x for the transfer period, or

$$V_{-1}T_1 + \frac{V_3 - V_{-1}}{\vartheta_3 - \vartheta_{-1}} \left[\int \vartheta dt - \vartheta_{-1}T_1 \right]. \quad (9)$$

This is essentially Pfaundler's formula.¹

3. THE SURROUNDING TEMPERATURE.

The two methods just presented are alike in requiring that the heat of stirring and evaporation shall be constant.² The environmenting temperature must be known for the first, but need not be constant; for the second it must be constant, but need not be known. The probable amount of error from a failure of constancy (in case the second or Regnault method is used) can be easily estimated by considering a simple case. Suppose the calorimeter temperature rises suddenly at first and then remains sensibly constant through both the transfer and the cooling period. Suppose the two periods

¹Jaeger and von Steinwehr's final formula (4) differs from this only in leaving the whole bracketed term for graphic integration, and in substituting

$$\frac{\vartheta_4 - \vartheta_0}{2} + \frac{1}{2K} (V_0 + V_2)$$

(afterward multiplied by K) for V_{-1} in the first term. In copying Pfaundler's formula, however, and in stating their own, Jaeger and von Steinwehr, though using values of V taken over the two cooling periods (*i. e.*, V_{-1} and V_3), number these as if they applied to the end temperatures (*i. e.*, V_0 and V_2 in the present notation), and hence are led to insert, instead of ϑ_{-1} and ϑ_3 , the end temperatures ϑ_0 and ϑ_2 , which do not correspond to the V 's as actually determined. But $\vartheta_2 - \vartheta_0$ may differ from $\vartheta_3 - \vartheta_{-1}$ by $KT_2/2$ of itself, and this error will affect the cooling correction proportionately. The resulting final error, while safely negligible in their case, will often exceed .0005 of the whole temperature rise, or about the usual magnitude of the thermometer lag error (pointed out by Jaeger and von Steinwehr) which has in two instances been accounted an important reason for the introduction of new calorimetric methods. Of course, it is just as easy to use the correct values, ϑ_{-1} and ϑ_3 .

²That it must also be approximately known for the first method practically adds nothing to the difficulty of the method.

are equal in length. The Regnault method will then make the cooling correction, that is, the loss in the transfer period, equal to the loss in the cooling period, because the temperatures of the two are equal. But if the environing temperature changes, the temperature difference, on which the cooling depends, will not be the same, and the error will be proportional to the change in the environment from one period to the other. For instance, a fair value of the cooling correction is 25 per mille of the total rise, so that for an accuracy of 1 per mille the correction must be known to one twenty-fifth. If, then, the rise is 2.5° , an accuracy of 1 per mille requires an environment constant to 0.1° , while to reach 0.1 per mille, an accuracy already attained in this type of calorimetry,¹ an environment constant to $.01^{\circ}$ is needed.² With a more gradual rise of the calorimeter temperature, the error becomes less, but in very many cases it will be at least half that just given. It is clear that the simplest solution of the difficulty will often be to provide an environing temperature which can be measured, and which, therefore, does not need to be constant. This will usually call for: (1) a stirred water jacket, completely inclosing the calorimeter; (2) the absence inside it of all bodies at indefinite temperatures, such as calorimeter covers not touching the water of the calorimeter. The fulfillment of these two requirements gives a system in which practically everything is at one of two measured temperatures, where the direct heat loss from the calorimeter, the cooling proper, is so regular as to be practically negligible as a source of error.

The complete jacket has sometimes been condemned³ on account of the irregularity it may introduce into the evaporation, which will vary as the confined space approaches saturation. Irregular evaporation is a serious source of error, but the remedy thus suggested, of exposing the calorimeter to the whole room, and then, perhaps, restricting ventilation, burners and lights, in order to keep the room in a constant condition,⁴ seems rather crude, and suggests the early

¹See the fourth article of this series.

²The change in temperature will generally increase with the time. The bearing of this fact upon the accuracy of the protracted methods, sometimes counted superior, is clear (see footnote, p. 546).

³E. g., by Louguinine and Schukarew, *loc. cit.*, pp. 60, 61.

⁴Louguinine and Schukarew, *loc. cit.*, p. 46.

method, celebrated by Charles Lamb, of roasting pigs by burning down the house. A jacket large enough to steady a rather copious evaporation is easier to control than a room. The evaporation, however, can and generally should be reduced to a small value. An air space of two or three liters inside the jacket is then sufficient and this is open to no objection.¹ If the heat produced by stirring is also kept constant, the three effects included in the usual cooling correction are all very regular.²

4. VARIATIONS IN PROCEDURE.

1. *Choice between the new and the Regnault-Pfaundler methods.*—With a complete jacket the calorimeter temperatures used for the determination of the cooling correction can most simply be referred directly to those of the jacket, if a differential (electrical) method of reading is convenient, or else a correction for the slight variation of the jacket is easily applied. In either case the use of the Regnault-Pfaundler method is not at all interfered with, but the chief reason for using that method is removed and the more direct method of section 1 can often be substituted. The most important difference in the two methods is in the matter of time. With the classical method a correction can usually be applied for changes in the calorimeter constants, while the newer method becomes practically equivalent to the older if extra observations are made so as to determine the value of w (p. 546). Such observations, however, will be needed only occasionally; ordinarily the new method saves nearly ten minutes, or over a third of the whole time demanded by the cooling correction for both observations and computation. This would mean several days in an ordinary series of from 50 to 100 determinations. The new method is at its best when the older method is at its worst, *i. e.*, when the bodies are dropped into the calorimeter, for the rapid temperature rise favors the adjustment of T and φ described on p. 547. Whenever the calorimeter starts at a temperature much below that of the jacket, or the temperature rise is relatively slow, as often in electrical calibration, the older method will often be preferable.

2. *Methods of Computation.*—In Pfaundler's formula, as usually

¹See p. 581.

²See p. 576.

given, a specific method is indicated for obtaining the $\int \vartheta dt$ of formula (9), namely, to add the readings made at equal intervals through the transfer period. If the temperature rise is rapid at first, readings should be taken more often at first than it is desirable to make them later on. In that case, the general method used in this laboratory has some advantages. Readings are made for the first few minutes at the rate of four to the minute. These are added separately and divided by four, and this sum is then added with the other readings, which are taken at one minute intervals. If the observations are first recorded in columns the necessary additions may, without any copying, be performed during the spare time in the last cooling period. The end of the observing thus finds the computation of the cooling correction also practically done, *less than a minute more being required* if the newer method is used.

This method of adding is probably superior in quickness, and certainly in ease, to any graphical method of comparable accuracy. In fact, the only place where graphical methods seem appropriate is in connection with electrical temperature measurement where a null method is used, and where it is therefore necessary to observe the irregular intervals required for equal changes in temperature. There is reason for thinking that even on the score of convenience in reading, this method is inferior to that in which readings are made at regular intervals, a method easily secured by a little attention to the sensitiveness of the galvanometer. That, however, is a question whose consideration belongs elsewhere; as far as the computing is concerned, regular intervals and arithmetical methods seem preferable.

5. VARIATIONS IN THE TEMPERATURE MEASUREMENT.

If the temperature is measured with a resistance thermometer, a change in the temperature of the auxiliary coils will usually cause a change, that is, an error, in the temperature reading, and similar effects may arise from other causes. These changes are ordinarily gradual and small, and hence their rate may be taken as uniform. Their effect on the final result is then the same as that of the factor w , that is, it is a steady variation in the temperature reading, which is independent of the calorimeter temperature. It therefore enters as part of the w correction.

6. METHOD FOR LARGE TEMPERATURE INTERVALS, WHERE K
IS VARIABLE.

If a given quantity of heat is to be measured, the resulting temperature change can of course be made larger or smaller according to the mass of water heated in the calorimeter. Each procedure has its advantages (see p. 580), but if much of the total error comes in the temperature measurement, as it usually does, an increase in the interval, often to 10° , is altogether preferable. The principal argument against so large an interval is that for it Newton's law of cooling no longer holds. But Newton's law of cooling is no more exact than the similar laws which hold for larger intervals; its only advantage is in simplifying calculation, and this is of little importance in comparison with an increase in accuracy. Moreover, the extra labor needed in computing for larger intervals may be made surprisingly small, and often disappears altogether, even for intervals of 20° .

This ease of computation arises from the fact that for all probable experimental conditions, and with all needful accuracy, the cooling is dependent solely on φ , the temperature difference between calorimeter and jacket.¹

That is, if V' is the true cooling rate (equal to V , the observed rate, minus w , the small effect due to evaporation and stirring) then

$$V' = f(\varphi), \quad (10)$$

which may be put,

$$V' = K \varphi',$$

where φ' is another function of φ . But if Newton's law held, we should have had $V' = K \varphi$. Hence if for the observed values of φ corresponding values of φ' are substituted, the resulting quantities bear to each other the same relation as obtains where Newton's law holds, and can therefore be treated by any formula based on that law. In other words, since V' is not proportional to φ , we make φ proportional to V' and proceed as before. The labor required is: (1) $f(\varphi)$ is observed directly, which requires single observations of cooling, and can be done for a wide temperature range, in duplicate,

¹Theory of Heat, Preston, 2d ed., 1904, p. 539.

in a day; and (2) values of $\varphi' - \varphi$ are plotted or tabulated against φ . So much is done once for all. Then (3) in each determination the corrections (seldom over eight in number¹) are looked up for each value of φ and their sum added to the value of Φ . This takes from one to three minutes, which is the maximum increase in time ever demanded by this method of using larger temperature intervals.²

To find the error which may result, it will be convenient to begin with the error due to neglecting altogether the variation from Newton's law. It will also be convenient to take first an artificially simple case in which the temperature rises at a uniform rate throughout the transfer period, and the values of the cooling rate, V_0 and V_2 , are determined for the end temperatures, t_1 and t_2 . (See Fig. 2, where cooling rate, and not temperature, is plotted against time.) Then the cooling correction, computed by any accurate method which assumes Newton's law, will be simply

$$\frac{V_0 + V_2}{2} T_1$$

represented by the area $OPQRN$. But if the true values of V' at the intermediate temperatures lie along the curve XYZ , the true correction is represented by $OPXYZRN$. The error is the difference of these two, represented by the narrow area.

Let V' be given by:

$$V' = A\varphi + B\varphi^2 + C\varphi^3 + \dots, \quad (11)$$

of which it will be sufficient here to consider the first three terms. Now, in this special case, since the temperature rise is linear,

$$\varphi = \varphi_0 + \alpha t$$

Hence, V' can be expressed as a function of constants and t , and the $\int V' dt$ can easily be found. It will be

$$\int_{t_0}^{t_2} \{A(\varphi_0 + \alpha t) + B(\varphi_0 + \alpha t)^2 + C(\varphi_0 + \alpha t)^3\} dt. \quad (12)$$

¹For temperatures within a degree of each other, the correction to the average does not differ appreciably from the average correction. Hence a few corrections can be made to answer for a much larger number of observed temperatures.

²See, further, footnote, p. 556.

The simply computed correction,

$$\frac{V_0 + V_2}{2} T_1,$$

equals

$$T_1 \left\{ A \frac{\varphi_0 + \varphi_0 + \alpha T_1}{2} + B \frac{\varphi_0 + (\varphi_0 + \alpha T_1)^2}{2} + C \dots \right\}. \quad (13)$$

On subtracting this from the evaluated integral, and dividing by the temperature rise, $\Delta\vartheta$, the proportional error is obtained, equal to:

$$-\frac{T_1}{6} \Delta\vartheta \left\{ B + 3C \left(\varphi_0 + \frac{\Delta\vartheta}{2} \right) \right\}. \quad (14)$$

In one calorimeter, which holds about 1400 cc. of water, the value of V' up to $\varphi = 20^\circ$ was given by:

$$V' = .00312\varphi + .000083\varphi^2 - .000001\varphi^3 \quad (15)$$

This result can not be assumed to hold for other calorimeters, but it gives a sufficient idea of order of magnitude. In accordance with it and (14) the error in a 10-minute period from improperly assuming Newton's law is only about 1 per mille for a 10-degree interval.

This value, however, is merely an upper limit of the error, which is always less than that just given, for two reasons: (1) The largest contribution to the error comes from the temperatures midway

Fig. 2.

Fig. 3.

between those where the rates are observed. In any actual case these temperatures would prevail for a smaller part of the time. (2) In any actual case, the temperature, after rising, will also fall before the final reading is made. Hence for part of the time there

will be temperatures above the final, as indicated in Fig. 3, whose effect will tend to neutralize that of the lower temperatures. (The error is indicated by the *difference* of the two shaded areas.) As a result, it will nearly always be possible to neglect entirely the variations from Newton's law (for periods of ten minutes or less) for any interval less than 8° , if the accuracy desired is not over .5 per mille, and frequently there will be no error amounting to .1 per mille for any interval up to 20° . The latter has actually been the case in nearly all our own work.¹

The above formula, (14), supposes two determinations of V as in Pfaundler's formula (9) for the cooling correction. With the simpler formula (5) the expression for the error is more complicated, but its values are not necessarily larger, unless ϕ_0 is relatively large.²

It remains to consider the errors which may arise when the correction is applied. Such an error cannot come from a change in *total magnitude* of the cooling factor, since this is (usually) re-determined for each determination, just as with other methods. The error can only come from the use of a wrong value for the *form* of the curve given in expression (15), that is, a wrong value for the ratio B/A or C/A in that expression. That will of course amount to a wrong value of one or both of the constants B and C . Now, a ten-degree interval is the largest likely to be often needed in practice, and for that the error from neglecting the correction entirely is practically never more than 0.6 per mille; hence not until the variation in B/A had reached the highly improbable value of 16 per cent. would the resulting error be 0.1 per mille.

This conclusion, however, applies only to the case of a consistent error in the correction curve as a whole. It holds because such an error, as shown in Fig. 3, is not very effective except in a small

¹In repetitions of the same determination, or in similar determinations, the chance variations in these small corrections will be negligible in almost any case. The correction found for the first determination can then be applied to other similar ones without any further computation. Hence the three minutes given on p. 554 as the time for computing a large-interval correction is not the time per determination, but rather the time for a whole series.

²The full formula in this case is:

$$-T_1\{B(\frac{1}{2}\phi_0 + \frac{1}{8}\Delta^2) + C(\phi_0^2 + \phi_0\Delta^2 + \frac{1}{2}\Delta^2)\}$$

This corresponds to (14), that is, it gives the upper limit of the error.

part of the whole cooling correction. For accidental irregularities in the values of the different corrections the case is quite different; these corrections evidently must not deviate from a smooth curve by more than the permissible errors in the individual observed values of ϕ . This requirement is easily met by aid of the following device.

First, let the correction, $\phi - \phi_1$ be denoted by M . Then, according to equations (10) and (11), M equals $V'/A - \phi$, and gives, on addition of ϕ , V'/A as the corrected value of ϕ . But the only requirement for the corrected value of ϕ is that it shall be proportional to V' . It may as well be V'/R , where R is any number; M then equals $V'/R - \phi$ or $(V'/\phi R - 1)\phi$, and there is a range of values of R , easily found by inspection or after a few trials, for which $dM/d\phi$ is in the neighborhood of zero for part of the curve, and small for the rest of it. Precision in the determination of M can thus be easily attained.

7. PROCEDURE WITH ELECTRICAL THERMOMETERS.

The choice of temperature scales is always more or less arbitrary, and the scale furnished by any electrical thermometer is suitable to use directly in determining the cooling correction, even where the method of the preceding section is used. Considerable time is thereby saved, for all preliminary computations are done in microvolts or fractions of an ohm (according to the type of thermometer), and the two final corrected temperatures are the only ones that need be reduced to degrees. This procedure, however, involves an error which is sometimes a little too large to be neglected. It arises as follows: The heat losses during the transfer period are inferred from the temperatures of the calorimeter at that time. Thus, for, instance, a temperature of, say, A microvolts in the second minute of the period indicates a temperature loss of B microvolts during that minute; which corresponds to b degrees. But in the computation the B microvolts are (in effect) added to the similar values for the other minutes, and the sum then added to the observed final temperature, C , to get the corrected final temperature, D , and this corrected temperature is translated from microvolts into degrees. B is therefore really reduced to degrees at the temperature $\frac{1}{2}(C+D)$ microvolts, which is much higher than A , for which B was actually derived, and at this higher temperature B corresponds no longer to b , but to b' , degrees. Hence the error. It is proportional to the value of B , to the interval between the temperature at which the cooling, B microvolts, actually occurred, and that for which it is evaluated (that is, to the interval, $\frac{1}{2}(C+D)-A$) and to the rate at which the ratio, microvolts $\div$ degrees, changes with temperature. This rate can be taken as constant for copper-constantan thermoelements over intervals of 20° , hence the computation of the error is not laborious. For a fifteen-degree interval the error is only about .1 per mille, unless the calorimeter is already cooling rapidly at the beginning of the transfer period. It is therefore quite negligible in most cases. For the resistance thermometer it is considerably smaller than with the thermoelement.

8. REDUCTION OF THE THERMOMETRIC INTERVAL.

Although the use of large temperature intervals diminishes the effect of thermometric errors, and is therefore generally to be pre-

ferred, yet there are often occasions where a small interval is desirable or necessary. In such cases, of course, greater thermometric accuracy is needed. This does not necessarily involve any higher proportional accuracy in the temperature interval measured, but rather the extension of ordinary *proportional* accuracy to an extraordinarily small interval, as, for instance, the measurement of a one degree interval to .01 per cent., that is, to .0001°. For this increase in *absolute* accuracy, the mercury thermometer is inadequate. The resistance thermometer and the thermoelement have sufficient precision. The auxiliary electrical measurements with these, however, are somewhat exacting. At ordinary temperatures, .0001° corresponds to a change of only one three-millionth in the resistance of a platinum resistance thermometer; an oil-filled thermostat, surrounding the auxiliary resistance coils, is probably the easiest and simplest means of avoiding the chief resulting difficulties. With the thermoelement a corresponding temperature measurement requires a precision only one tenth as great in the electrical measurements,¹ and the thermostat is usually not necessary, but the precision required is still many times that attained in measuring the temperature interval.

This disadvantage can be almost entirely obviated as follows: The thermoelement is essentially a differential instrument; hence in reading single temperatures with it a comparison temperature is always necessary. For this the ice-bath is commonly chosen on account of its constancy, but it is so far below the ordinary room in temperature that its use commonly necessitates the measurement of intervals considerably greater than those actually employed in the calorimeter. If the comparison temperature is near that of the calorimeter, the temperature differences diminish accordingly, and most of the instrumental errors diminish with them; the maximum precision required anywhere is then comparable with that of the calorimetric observation itself—one ten-thousandth, or less. Such a comparison temperature can be obtained by a suitable comparison body, jacketed like a calorimeter. The temperature of such a body, in general, will not be strictly constant, but the small correction required on account of its variations is a cooling correc-

¹See The Thermoelement as a Precision Thermometer, *PHYS. REV.*, 31, 154, 1910.

tion, smaller and more certain than the cooling correction for the main calorimeter, and hence it introduces practically no error and almost no inconvenience. For the body can easily be given a cooling factor, K_B , as small as .002. In a 30-minute interval the body will then change only .06 of the mean temperature difference between it and its jacket. Hence for an accuracy of $.0001^\circ$ this difference need be known only to $.001^\circ$ —which is an accuracy far less than that attainable with ease by a differential thermoelement under the given conditions. Again, the jacket will ordinarily have a cooling factor well under .002. A difference of 5° between it and the room for 30 minutes would then cause a change of only 0.3° in its temperature. And with a jacket as constant as this, it is easy to show that a solid block of copper weighing, say, 8 kg, could be used for the comparison body without any error from internal irregularity of temperature. In that case all trouble from evaporation, etc., would disappear, and K_B would always be the same.¹ The comparison body thus requires almost no attention, the calculation required for correcting for its temperature change becomes very simple and easy, while the necessary observations are few, two in a ten-minute interval at most.²

The comparison body thus causes less trouble than it saves. Its possibilities in the direction of accuracy are evident. Furthermore, the correction which it introduces is simple, usually familiar, and easily controlled by simple tests, while the errors which are avoided depend upon the quality or constancy of electrical apparatus, etc., and are especially hard to detect. The comparison body, therefore, particularly increases the certainty and ease of the measurements, and therein, perhaps, lies its greatest value.

The only uncertainty worthy of mention concerning the comparison body just described relates to the magnitude of the effect which the room temperature may produce through conduction along the thermoelement. There is no question that such effect can be abso-

¹An uncertainty of several per cent. in K_B , however, would ordinarily be permissible. The use of such a block, though perhaps the best and simplest way, is, of course, not the only satisfactory way of obtaining a comparison temperature.

²The jacket, with its stirrer, is easily made into a thermostat, in which case no correction at all is needed, but, in view of the ease with which the correction can be made, it is perhaps more advantageous to apply it.

lutely prevented, if necessary—for instance, by leading the thermoelement in through the water of the jacket. If such an effect is present, however, it will probably affect the calorimeter also, in which case the effect on the body will tend to act as a compensation, and may be a positive advantage.

SUMMARY.

1. The oft-noted uncertainties in the calorimetric cooling correction are usually due to changes in room temperature and to evaporation. For the greatest accuracy, and usually for convenience also, it is well to have: (1) A jacket whose temperature is measured directly, completely surrounding the calorimeter; (2) the calorimeter cover in contact with the water so that all bodies at uncertain temperatures are avoided; and (3) evaporation made very small. The difficulties of the cooling correction then largely disappear.

2. This system facilitates a method of computing the cooling correction which requires but one cooling period, and but one minute's arithmetical work after observations are finished. The method is especially advantageous where bodies are dropped into the calorimeter.

3. Ordinarily, in accurate calorimetry, a very small temperature interval is used, in order that the observer may have the advantage of assuming Newton's Law of cooling in his computations. This magnifies the effect of thermometric errors. To make a correction for the variation from Newton's Law not only increases accuracy in most cases, but does not increase appreciably the labor of computation. The procedure is this: Since the cooling rates are not proportional to the temperatures, the temperatures are simply corrected so as to be proportional to the rates; all the ordinary formulæ can then be applied. For ordinary accuracies, the correction can be disregarded up to 8° . With the correction, deviations from Newton's Law cause no error in 20° intervals.

4. If a small interval is necessary, the preceding method can not be applied. The required absolute accuracy in temperature measurement can then usually be obtained by electrical methods, but with these, as usually conducted, the electrical quantity measured

corresponds to a relatively large temperature interval (20° to 300°), so that great precision is required. This difficulty is avoided if, with the thermoelement, the customary ice bath is replaced by a comparison body in a water jacket. The correction for its change is only a cooling correction, and does not materially affect the total error, since the regular calorimeter necessarily has a larger and more uncertain correction of the same kind, or something equivalent. The net gain is a considerable simplification of the problem of accurate temperature measurement, where intervals and not absolute temperatures are required.

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WASHINGTON, D. C., July 15, 1910.