Constantan wire for thermoelements has been so far improved that continuous lengths are frequently obtainable which vary (in electromotive force against copper) less than 0.0002, making sensitive thermoelements with errors usually less than 20 per million.

The testing of wire enough for a thermoelement of maximum sensitiveness takes but an hour or two, with simple apparatus.

On account of the ease with which thermoelements can be constructed, the more sensitive combination of several couples is generally preferable to a single couple, even for cruder measurements.

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EASY CALORIMETRIC METHODS OF HIGH PRECISION.

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In calorimetry by the "Method of Mixtures" a precision of 1 per mille appears to be generally counted excellent. It scarcely deserves, however, to be considered high at the present time. Calorimetric precision depends more on the adequacy of the apparatus than on any special skill exercised by the observer, and it has been found that appropriate apparatus and methods are easily attainable which will yield a precision approaching 0.1 per mille with little more labor than is needed to get 1 per mille with some customary arrangements.[1] It is true that 1 per mille appears in most cases to be quite sufficient. Errors in associated temperatures or defects in chemical purity are often such that a higher calorimetric precision would be of comparatively little value. Nevertheless, there are cases where a higher precision is desired, and these will doubtless increase with the general progress of science; often, too, the associated measurements or the chemical purity attained have probably really been governed by the limitations of the calorimeter, and would readily be improved if greater calorimetric precision should appear less difficult to get; finally, there are many determinations where, though high relative precision may not be desired, yet high absolute precision is necessary on account of an unavoidable small temperature interval (in measuring heats of dilution, for instance). A relative precision of from 1 to 0.1 per mille, and an absolute precision of from 0.001° to 0.0001° are therefore of interest, and these are in view in the present paper.

Precision in calorimetry depends first upon the temperature measurement, and second upon the determination of the heat which escapes and is determined indirectly. The control of the heat losses has been made not only sufficient for the highest precision but convenient, owing mainly

[1] One-fiftieth per mille has been reached, under specially favorable conditions.

to the introduction of convenient and simple arrangements for complete inclosure of the calorimeter by the jacket. With this complete inclosure given, the other essentials of effective control, namely, accurate measurement of the jacket temperature and control of evaporation and heat of stirring, are easily added. In the temperature measurement electric thermometers give high precision, but their relative convenience is not so evident. This convenience, however, has been increased in the case of the resistance thermometer by the work of recent years, and especially by the improvements of Dickinson and Mueller, who have produced instruments convenient enough for commercial work, and also capable of more than commercial precision under proper conditions.

The differential thermoelement is inherently free from the most serious sources of error affecting the resistance thermometer, and hence affords methods which, on account of the extraordinarily few precautions needed in them, are highly convenient as well as certain. The electrical arrangements and their advantages have been described in detail in previous papers of the present series.[1] Some of these advantages are obtained at the expense of a slight complication on the calorimetric side. The present paper deals with various arrangements by which this disadvantage can be minimized.

The complication is the addition of a second calorimeter, the comparison or "cold" calorimeter, in place of the more familiar ice bath around the "cold" end of the thermoelement. The advantages thereby secured are, first, avoiding the ice bath and its small errors, and second, gaining the power to make the measured temperature difference as small as the change in the working calorimeter, and hence securing a precision which, up to a certain point, becomes greater as the measurement becomes more delicate, and thus tends to increase in proportion to the need for it. The exact temperatures of the two calorimeters are of no importance. The changes in the temperature of the added, or comparison, calorimeter are determined along with those unavoidable in the working calorimeter, and therefore add practically nothing either to the error or to the number of observations required.

One method of this sort has already been employed,[2] especially in Germany, with the second calorimeter an exact duplicate of the first. The differences, however, between that earlier method and those here described are rather important. First, the thermoelements and the auxiliary ap-

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[1] "Thermoelement Installation, Especially for Calorimetry," THIS JOURNAL, 36, 1856 (1914); "Potentiometers for Thermoelectric Work, Especially in Calorimetry," *Ibid.*, 36, 1868; "Leakage Prevention by Shielding, Especially in Potentiometer Systems," *Ibid.*, 36, 2011; "Thermoelements of Precision," *Ibid.*, 36, 2292.

[2] H. von Steinwehr, *Z. physik. Chem.*, 38, 185 (1901); H. Hausrath, *Ann. Physik*, 9, 522 (1902); G. Rümelin, *Diss. Gött.*, 1905; *Z. Physik. Chem.*, 58, 449 (1907); H. Magnus, *Ann. Physik*, 31, 597 (1910); *Z. Instrumentukunde*, 32, 127 (1912).

paratus of the German investigators were less developed; and therefore, while admirably adapted to their object, the securing of great delicacy with a very simple installation, they were not very flexible nor favorable to high relative precision. Second, the German investigators attached far greater importance to the strictly calorimetric advantages of the twin calorimeters—that is, to the partial compensation of heat losses which resulted from the similarity of the two. In the present methods a still better control of heat losses had already been attained by thorough jacketing; the second calorimeter thus became of value solely as an aid in temperature measurement, and arrangements more accurate and much more convenient than the twin became possible.

The validity of our methods of treating the second or "cold" calorimeter can perhaps be most directly shown by means of the very simple mathematical analysis of the thermal actions involved, which at the outset convinced us of the relative inferiority of the twin arrangement. This analysis is the more worth while since the notion is very plausible, and is probably widely held, that similarity in a pair of calorimeters, by providing an automatic compensation of certain thermal actions, is able to remove serious sources of error.

1. Thermal Relations of the Calorimeters.

Consider two calorimeters, or other bodies, the active one a, and the blank, or comparison body b. Let

Θ_a, Θ_b be their temperatures.

C_a, C_b the temperature of the chamber (jacket) in which each is;

K_a, K_b their cooling factors, as dependent on the chamber, that is, as defined by (*e. g.*),

$$d\Theta_a/dt = (C_a - \Theta_a)K_a$$

k_a, k_b their cooling factors toward each other, defined by (*e. g.*),

$$d\Theta_a/dt = (\Theta_b - \Theta_a)k_a$$

w_a, w_b temperature change due to evaporation and stirring.

$d/dt\ (\Theta_a - \Theta_b)$ is then the rate of change of the differential temperature, that is, of the temperature which is observed with the highest precision and which, when corrected, gives the calorimetric interval.

Then, in the most general case, considering only the heat passing to or from the environment,

$$d/dt\ (\Theta_a - \Theta_b) = K_a(C_a - \Theta_a) - K_b(C_b - \Theta_b) + k_a(\Theta_b - \Theta_a) + k_b(\Theta_b - \Theta_a) + w_a - w_b. \quad (1)$$

If the bodies are in the same jacket, this becomes

$$d/dt\ (\Theta_a - \Theta_b) = K_a(C - \Theta_a) - K_b(C - \Theta_b) + (k_a + k_b)(\Theta_b - \Theta_a) + w_a - w_b, \quad (2)$$

which may also be written:

$$d/dt\,(\Theta_a-\Theta_b) = (K_a+k_a+k_b)(\Theta_b-\Theta_a) + (K_a-K_b)(C-\Theta_b)+w_a-w_b. \quad (3)$$

If the calorimeters can be treated as equal the last two terms vanish, and we have the very simple expression:

$$d/dt\,(\Theta_a-\Theta_b) = (K+2k)(\Theta_b-\Theta_a) \quad (4)$$

Equations 1, 3 and 4 are, of course, the formulae for finding the cooling corrections under the different conditions described.

2. The Twin Calorimeter Method.

From these equations the limitations of the twin calorimeter methods are easily seen. Equation 4, to be sure, is exceedingly simple, and the external temperature does not appear in it at all, so that complete independence of the environment and its changes appears to have been gained. But Equation 4 applies only to the ideal case of the twin method, the case where the calorimeters are identical twins in a perfectly uniform environment. In practise, there will be differences in the cooling rates K_a and K_b, and irregularities in the exterior temperature distribution, so that (3) or even (1) will be the correct equation. But these equations are not practically usable, and yet a neglect of the extra terms they contain can easily be shown to involve a danger of error. For instance, if K_a and K_b differ by only 5%, and external temperatures are so uniform that (3) holds, then $C-\Theta_b$, the temperature difference of jacket and cold calorimeter, must ordinarily be *and remain* less than the change in the working calorimeter, in order that (4) may be used without an error of 1 per mille, and less than 0.1 of that change for a precision of 0.1 per mille.

There are three methods of diminishing this difficulty, but, even so, the twin arrangement remains less advantageous than that described below. These three methods are:

(1) By a very careful adjustment of the equality of the calorimeters and of the uniformity of their immediate environment. This is, in general, decidedly troublesome.

(2) By running a "fore" and an "after" cooling period, as in the Pfaundler method with single calorimeters. The errors from the extra terms in (1) and (3) are then considerably diminished, as can easily be shown. This requires 3 observation periods, and is thus more laborious than the other methods given later (which require but 2) besides being less accurate.[1]

(3) By using a completely-inclosing jacket, so that the total effective temperature around the calorimeters can be definitely known, and then taking advantage of this knowledge to make $C-\Theta_b$, the jacket-cold-

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[1] It is, however, more accurate than the same three-period method with a single calorimeter.

calorimeter temperature difference of Equation 3, negligibly small, so that the term containing it vanishes and Equation 4 *practically* applies.[1] Since approximate temperature adjustments are easily made, and since a very rough approximation to equality between the two cooling rates, K_a and K_b, is now sufficient, this method is not laborious. The working calorimeter alone, however, is now quite as effective as the twin arrangement, since (1) the jacket-calorimeter temperature difference, which must be measured to get the cooling correction of the single calorimeter, is numerically almost the same as the temperature difference between the two calorimeters, which plays a corresponding part in work with them, and (2) the effect of irregularities in the jacket temperature is similar and rather larger with the twin arrangement.[2]

The duplicate calorimeter, then, is as a rule of no advantage thermally

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[1] The German investigators who have worked with the twin calorimeters have, in general, used the first two of these methods, and also got some of the benefits of the third by initially adjusting to equality the four temperatures of the room, of the (incomplete) jacket, and of the two calorimeters. Their methods were thus effective but laborious, and need not be further treated here. Two special features of their procedure, however, appear to deserve comment, since they have to do with principles of general application in calorimetry.

One of these features occurs in A. Magnus' very interesting and ingenious installation (*Loc. cit.*). Magnus used calorimeters holding 60 liters, and did so for the purpose of diminishing the cooling correction. If his intention was to increase also the quantity of heat measured, keeping the temperature interval the same, the procedure was correct. In comparison with calorimeters of one twenty-seventh the size, or 2.2 liters, the heat losses would be only one-third as great, since the surface, though nine times as great, is smaller in proportion to the amount of heat measured. If, however, the intention was to measure the same amount of heat with the larger calorimeters, the ninefold surface would mean a ninefold increase in the effect of irregularities and uncertainties in the external temperature, to which in most installations (including, probably, that of Magnus) nearly all the heat loss errors are due. In such a case, then, these errors not only fail to be decreased, but are largely increased by the use of such Gargantuan calorimeters.

Another notable feature of some previous work is the use of insulating layers, as of cork, between the twin calorimeters. As to that, all methods based on (3) or (4) have one advantage which deserves mention. The direct heat flow from one calorimeter to the other (terms containing small k_a and k_b) does not complicate the case at all, not even if K_a and K_b are unequal, as is evident from (3) and (4). To bring the jacket in between, so as to prevent a direct heat flow, is a superfluous complication; to put between any heat insulating material (as has often been done) is an unmitigated disadvantage, since any such layer will have a lagging temperature, and its insertion therefore means the introduction of a real error in order to avoid a purely imaginary one.

[2] The jacket temperature is more changeable than that of the cold calorimeter, and hence might need to be measured more frequently, but this fact is of no practical importance in most cases, especially since the working calorimeter temperature is usually more changeable than that of the jacket, so that it governs the number of observations needed.

when a complete jacket is used, and is comparatively unsatisfactory whenever a complete jacket is not used. Its real advantage, therefore, is not calorimetric but thermometric; its usefulness lies almost entirely in securing the simplicity and the high precision of the differential thermoelectric measurement.

3. The Compensated Cold Calorimeter.

Two features distinguish our present method, the "Compensated Calorimeter Method." First, the second calorimeter is simply a vacuum-jacketed vessel, whose cooling factor (lag constant) is from one-fifth to one-tenth as great as that of most duplicate calorimeters would be. Thereby all adjustments of the temperature of the second calorimeter, or of the amount of water in it, as well as all temperature measurements or distributions affecting it, need but one-fifth, or less, of the precision needed in a twin installation. Indeed, as we shall see presently, the use of such a vessel as cold calorimeter reduces to one-fifth, or less, the precision needed in adjustments affecting the cooling constant of the working calorimeter also. This arrangement, considering the heat losses alone, is still not quite so good as a properly jacketed single calorimeter, but its errors are a little less, and its convenience much greater, than with the twin method.

The second feature is a specially arranged thermoelement combination, used for the cooling correction determination, and made necessary by the fact that Equation 4 does not apply unless the cooling corrections of the two calorimeters are equal. The combination consists of two auxiliary thermoelements, each running from the jacket to one of the calorimeters. These thermoelements are connected in series, so that their combined E. M. F. is obtained by a single reading. One of the thermoelements is compensated for the difference in the cooling constants of the calorimeters, that is, it is adjusted so that its sensitiveness is to that of the other thermoelement in the same ratio as the cooling constants of the respective calorimeters. Each reading will then be proportional to the temperature rate of its particular calorimeter. and the combined reading to the resultant change in both. For instance, one of our comparison calorimeters has a cooling factor which is one-sixth that of the working calorimeter, and its auxiliary thermoelement is accordingly made one-sixth as sensitive as that of the other. A given electromotive force in this auxiliary, therefore, accompanies six times as large a temperature interval as with the working calorimeter auxiliary. But this six-fold temperature difference, acting upon the six times smaller cooling factor, produces the same rate of temperature change, and therefore the same magnitude of effect on the main differential thermoelement, as would accompany the same electromotive force in the working calorimeter auxiliary. The change in the main thermoelement will therefore be proportional to the reading of the combined auxiliary elements, whatever their individual electromotive forces may be, and hence that combined reading may be used like $\Theta_b - \Theta_a$ in the *second* member of Equation 3 or 4, giving a cooling correction formula as simple as that of the twin arrangement, or as that of a completely jacketed single calorimeter.[1]

Of course this compensated arrangement demands a complete and uniform jacket. But since such a jacket is easy to make (see Fig. 3 in Section 9*b*), saves many uncertainties and precautions, and is necessary for very high precision with other methods, this requirement cannot be considered a real drawback.

The lower sensitiveness of the auxiliary thermoelement of the cold calorimeter is obtained, in part, by using fewer couples, but also, as a rule, by the use of a shunt. By providing several interchangeable shunts, several working calorimeters can be used with the same cold calorimeter and auxiliary thermoelement. The adjustment of the shunt demands a determination of K_a and K_b (the two cooling rates) at the time the calorimeters are first put in commission. A very approximate determination suffices, however. This is because K_a, the cooling factor of the working calorimeter, will seldom be strictly constant, hence there is no advantage in maintaining or measuring K_b with great precision; instead, the temperature difference $C - \Theta_b$ of Equation 3 is kept small, as suggested above (Section 2), in order to make negligible the term containing $C - \Theta_b$. For the same reason, the shunt need not be very *constant;* a copper shunt,

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[1] The equation for this arrangement, corresponding to Equation 3, is obtained as follows:

Let n be the ratio of the two cooling rates K_a and K_b. Then the reading of the cold calorimeter auxiliary will be made proportionate to $\frac{\Theta_b - C}{n}$. Since Equation 2, omitting the small k's, may be written:

$$d/dt\ (\Theta_a - \Theta_b) = K_a\ (\Theta_a - C) - n\ K_b \frac{\Theta_b - C}{n} + w_a - w_b$$

we may have instead of (3):

$$\begin{aligned} d/dt\ (\Theta_a - \Theta_b) &= K_a\left(\Theta_a - C - \frac{\Theta_b - C}{n}\right) \\ &\quad + (K_a - nK_b)\frac{\Theta_b - C}{n} + w_a - w_b \\ &= K_a\left(\Theta_a - C - \frac{\Theta_b - C}{n}\right) \\ &\quad + \left(\frac{K_a}{n} - K_b\right)(\Theta_b - C) + w_a - w_b \qquad (3a) \end{aligned}$$

where $(\Theta_a - C - (\Theta_b - C)/n)$ is the combination auxiliary reading, and $K_{a/n} - K_b$, like $K_a - K_b$ of (3), is the difference of two nearly equal quantities. In this, the error term, here, K_a appears divided by n—that is, every error due to variation in the cooling rate of the working calorimeter is diminished by reducing the cooling rate of the other.

which may possibly vary nearly 5% as a result of temperature changes, is admissible, though a shunt mainly of manganin, constructed so as to be thermoelectrically neutral, is usually more convenient. The temperature difference of jacket and cold calorimeter, $C - \Theta_b$, can be as large as 0.2°, and a simultaneous variation of 5%, both in K_a and in the resistance of a copper shunt, will not cause an error of 0.0001° in a period of 10 minutes. If K_a is likely to be constant to 2%, as will often be the case, and the shunt is of manganin, adjusted to 2%, $C - \Theta_b$ may vary 0.5°. For longer intervals, of course, the tolerance is correspondingly less.

If the working calorimeter is also a vacuum-jacketed vessel, the cold calorimeter can profitably be made like it, and then there will usually be little to choose in efficiency between the compensated and the twin method.

4. Divided Installations.

All the important advantages of the above method can be secured if the two calorimeters are in separate jackets which are at different temperatures. The only requirement is to let each section of the combined auxiliary thermoelement run to the jacket surrounding its own calorimeter. The two can be as easily connected and read in series as if they ran to the same jacket.

The comparison calorimeter and its jacket must have the same equality of temperature as is necessary with a single jacket, and departure from this brings errors of the same amount;[1] the jacket around the working calorimeter may have any varying value, just as in work with a single calorimeter.

This method is more adaptable than the single jacket method, and is, of course, essential if adiabatic methods are to be used. It is a little more expensive if constructed from the start, but less so where a jacketed single calorimeter is already at hand.

5. Thermostats.

With a single calorimeter it is often convenient to make the jacket a thermostat. This may save considerable tiresome preliminary adjusting of temperatures, renders the subsequent observations more uniform, enables determinations to be more readily compared, since all have the same initial temperatures,[2] and reduces the necessity of dealing with troublesome temperature coefficients in thermochemical work. With a comparison calorimeter still further advantages of the thermostat appear; the equality of temperature between the jacket and the comparison calorimeter may be made more exact with less trouble, and hence greater

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[1] That is, errors depending only on the difference $\left(\frac{K_a}{n} - K_b\right)$ of Equation 3*a*.

[2] The supply of water for the working calorimeter can conventiently be kept in a bottle immersed in the thermostat jacket.

latitude is allowed in the permanent adjustment of the compensating shunt (of the auxiliary thermoelement), and also in the temporary values of the cooling factor of the working calorimeter, all of which makes for ease and precision. With the high precision appropriate to the differential calorimetric methods, however, there arises a difficulty in using a thermostat with an *ordinary* calorimeter. With such a calorimeter a precision approaching 0.0001° usually demands that the differential temperature, in which the jacket enters, be measured to better than 0.003°. But if the jacket temperature is oscillating through 0.01° or so, any one measurement of it may be 0.005° from the mean, so that there may be an error of 0.005°, unless an unusually and objectionably large number of observations is made. The difficulty can be avoided: (*a*) by using a thermostat accurate to 0.001°, methods of doing which will probably be discussed later on. (*b*) By putting within the thermostat only the vacuum-jacketed calorimeter, whose low cooling factor renders a constancy of 0.01° sufficient; foregoing, of course, the advantages of a thermostat around the working calorimeter. (*c*) By working the thermostat with the heater very near the regulator bulb, which makes the oscillations shorter, and therefore smaller; the resulting increased influence of room temperature upon the bath will act too slowly to be troublesome. (*d*) By increasing the lag of the jacket ends of the auxiliary thermoelements, so that the reading depends on the *mean* temperature of the jacket. This can be done by pulling over a rubber tube. There need be no fear for the accuracy of this method, since the only objection to the thermostat is that a single reading of an oscillating temperature is usually not representative.[1]

In a thermostat used as here indicated, if the heater is put near the bottom, there is no need whatever to have the stirrer in operation except during the determinations and for a few minutes before.

If the thermostat is constant to 0.01°, the cold calorimeter can (ordinarily) be made to have quite negligible temperature fluctuations, and so can be used simply as a body of constant temperature, constituting a frequently advantageous substitute for an ice bath.[2] The addition of the compensated (*i. e.*, shunted) auxiliary thermoelement (not yet devised in 1910) improves this method, so that its original form may be said to have been superseded. Used with the shunted auxiliary, of course, it is nothing but the regular compensated calorimeter method as used with a thermostat.

The copper block formerly suggested for the comparison calorimeter also seems less desirable than the present arrangement. Although such a block has been used (independently) in other laboratories as a *working* calorimeter, as a comparison calorimeter it is less effective, and probably less simple to instal, than a vacuum-jacketed bottle with a simple stirrer.

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[1] If the oscillations of the thermostat temperature are too slow, however (a minute or more) they may make a more than negligible unevenness in the variation of the calorimeter temperature.

[2] Described from this laboratory in: "Some Calorimetric Methods" (*Phys. Rev.*, 31, 557 (1910)) under the name of "comparison body."

6. Compensation of the Stirring.

With twin calorimeters the heat of stirring in each is naturally compensated by that in the other, and the same compensation can easily be obtained by a little adjustment, where the two calorimeters are unlike. This is a possibility belonging only to two-calorimeter systems. There will usually be considerable doubt, however, as to whether the compensation is better than the alternative procedure, which is to make the stirring of the working calorimeter so constant that variations in the heat produced are negligible, at the same time simply making the stirring very slow in the cold calorimeter, which will always be admissible. The constant stirring may perhaps call for a governor; the compensation demands that the stirrers of the two calorimeters be somehow geared together, and that with each of them pains be taken to see that no change in conditions is allowed to occur which may affect the relation of heat produced to speed of stirring. Experience of the relative merits of the two procedures appears to be wholly lacking; a brief discussion of calorimeter stirring in general has been published elsewhere.[1]

7. Experience with the New Methods.

The "Comparison Body" method, and, subsequently, the "Compensated Calorimeter" method. have been used in the Geophysical Laboratory for the last two years. Their *convenience* has been clearly shown. The work thus far done with them, and the auxiliary apparatus used, have not been adequate to show the *precision* of which they are probably capable, but some indication of it has been obtained in the following case: Eight regular calorimetric determinations were extended to occupy an hour, when it was found that for successive ten-minute intervals the temperature observations were concordant to 0.000070° on the average. Even with absolutely perfect apparatus an average variation of 0.000035° would, in accordance with the laws of chance, have resulted from the fact that the record was only made to 0.000100°; the average *error*, therefore, was considerably less than 0.000070°, and this includes, besides the errors of the electrical system, the effects of uncertainties in jacket temperature and in measuring it, of variations in stirring, and of the observer's possible failure always to estimate tenths correctly. This result was reached without using a thermostat, and in a room of very changeable temperature.

8. Experimental Details.

(*a*) *The Comparison, or "Cold" Calorimeter.*—Where a single jacket is used, the vacuum-jacketed comparison calorimeter can be immersed in it, just outside the chamber holding the working calorimeter, and can be covered with the same cover, as is partly shown in Fig. 3. In our own

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[1] "Lag Effects and Other Errors in Calorimetry." Walter P. White, *Phys. Rev.*, 31, 575 (1910).

work the comparison calorimeter was in a separate jacket. An attempt was made to secure complete uniformity of temperature around the calorimeter by means of a cover of very thick copper, but a more certain, more effective, and easier way of accomplishing this result afterward seemed to be by means of the double walled "water cap" shown in Fig. 1. This was made by a tinner for about $4.00, and was at once ready for use. Filled with water, and with one opening placed over the jacket stirrer, it provides abundant circulation above the calorimeter, and, touching the open water on all sides, it absolutely excludes air currents from the inclosed space. The thermoelement, as it runs to the calorimeter, dips down under this cover, and thus passes for some distance through the water. This arrangement can be made to prevent any influence of the room temperature upon the calorimeter. A reciprocating "bucket" stirrer is used (that is, a long tube with a light hinged valve), which can be operated by rods passing up from below through the water, and therefore without complicating the cover.

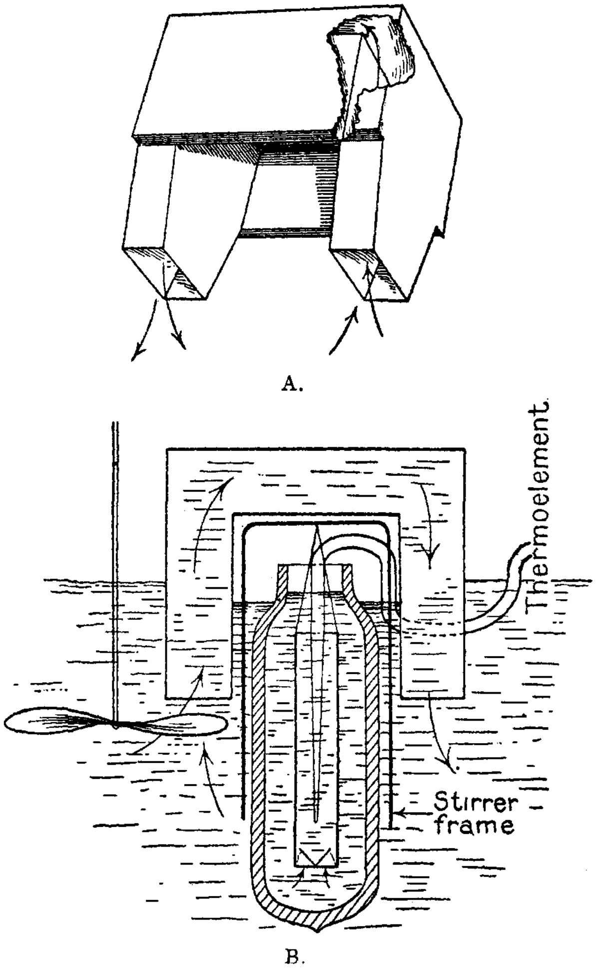

Fig. 1.—Copper "water cap," which helps secure a uniform temperature completely surrounding the cold calorimeter. A, Perspective; B, Sectional View, with a calorimeter, etc. An auxiliary thermoelement is omitted to simplify the drawing.

Evaporation under the water cap can be prevented by pouring a layer of heavy oil on the water in the calorimeter, and then keeping the calorimeter always a little warmer than the jacket. When evaporation was permitted, however, it only increased the cooling rate 20%, and it must become constant very quickly in the small inclosed body of saturated air, so it is allowed to occur unhindered.

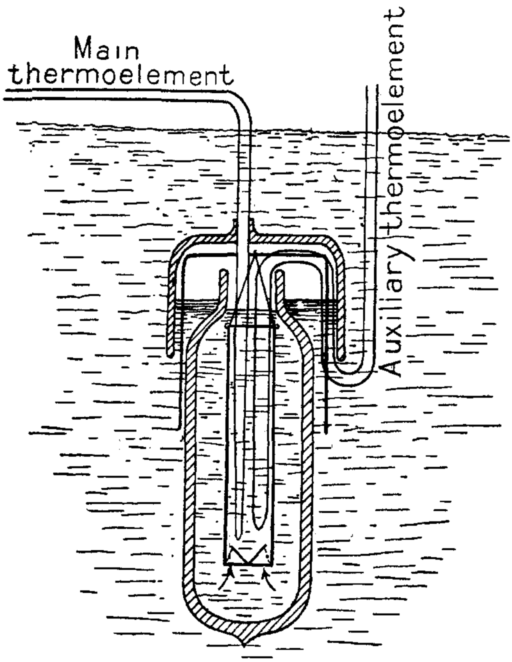

Fig. 2.—"Submarine" arrangement of cold calorimeter, accomplishing the same object as the water cap.

Another arrangement of the comparison calorimeter was tried, and is shown, somewhat improved, in Fig. 2. The cover, a sort of diving bell, is borne by the thermoelement case. The insertion of the thermoelement carries down the air which fills this bell and surrounds the neck of the calorimeter.

Here the calorimeter temperature automatically becomes equal to that of the jacket whenever the thermoelement is removed.[1]

(*b*) *An Inexpensive Complete Jacket.*—The water cap just described serves, with a little modification, as the most characteristic part of a completely inclosing jacket for working calorimeters, and this deserves description here, since the value of the "Compensated Calorimeter Method" is somewhat dependent on the ease with which complete inclosure can be attained. An installation now in process of construction has the following essentials (Fig. 3): (1) For the outer vessel a commercial paper tub is used, which of course reduces expense. (2) Two metal bars crossing this tub at the top serve to support the inclosure of the calorimeter chamber. (3) This inclosure consists of two parts. The lower part is a nearly plain pot of suitable shape, which ordinarily remains fixed in position, though it can be changed, if desired, when a change is made in the working calorimeter. (4) The upper part, or jacket cover, is a parallelipipedal box,

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[1] This of course supposes that the stirrer is operated when the calorimeter has become colder than the jacket. In this case it may be desirable or necessary to insert a wide, short tube temporarily in the mouth of the bottle. to assist the stirrer in bringing the colder water well out of the bottle.

closed except for two large pipes, projecting downward like the horns in the water cap of Fig. 1, and of similar function. This cover can be slid about at will upon the cross bars, and will ordinarily serve for all the different calorimeters used.[1] (5) The power for the stirring may be brought into the chamber in various ways, according to circumstances. In our case the cover is in two parts, one of which is clamped fast during a determination, and carries the stirrer pulley and connection, while the other part is at all times freely movable.[2] (6) For a thoroughly complete inclosure the jacket water temperature must prevail up to the very

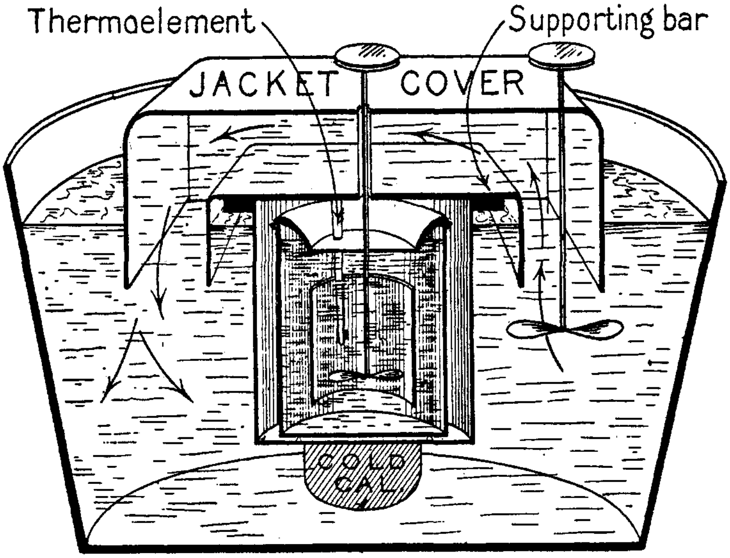

Fig. 3.—Complete inclosure of uniform temperature surrounding an ordinary calorimeter. Here the cold calorimeter, situated beyond the calorimeter-chamber shown, is covered by the same cover.

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[1] With a tub as small as that shown in Fig. 3 there would not be room to move the covers back far enough to expose the calorimeter. In general, a larger tub can be used, with advantages in several directions. In adiabatic work a small tub will usually be much more desirable. With it the covers are emptied and lifted off, and then refilled when replaced. The filling and emptying are done by sucking or blowing air through an inverted siphon; the procedure is thus not at all troublesome. If the resulting rise in the water level in the tub is objectionable, it can be avoided by removing water before the emptying of the cover, returning the same after filling. The level thus remains the same except during the filling or emptying, when it is low. A convenient way of removing the water is to transfer it into an inverted vessel (not here shown) somewhere inside the tub, making the transfer, again, by means of an inverted air siphon. The siphon tubes should be about a centimeter in diameter; the transfers are then almost instantaneous.

[2] An arrangement of this sort, applied to a more elaborate, but no more effective, jacket installation, has already been described, in "Some Calorimetric Apparatus," Walter P. White, *Phys. Rev.*, 31, 673 (1910).

top of the side wall of the calorimeter chamber. This has generally been secured by bringing the water up to the top of the side wall, which is a little troublesome, but is a slight price to pay for absence of all uncertainty as to the jacket wall temperature. Fortunately, however, a sufficient and very certain uniformity of temperature in the jacket wall can be attained as follows: (Fig. 4): The upper 4 cm. or more of the wall is of (or is reinforced with) copper, about 1.5 mm. thick, and does not project more than 3 cm. above the water surface; outside of this and 4 or 5 mm. from it is a shielding rim whose lower edges turn outward 2 cm. or so in the water, so as to touch the water abundantly without keeping it from the true rim. This shielding rim, coming nearly to the temperature of the water, prevents the true rim from being sensibly affected by the room temperature, whose changes will cause not over 0.0005 as much change in the true rim. The lag of the very top of the rim will not be over 4 seconds, which is negligible even in the most accurate work, since it affects only a small part of the whole calorimeter chamber wall. The shielding rim does not appear in Fig. 3 because it is not needed under the ends of the jacket cover.

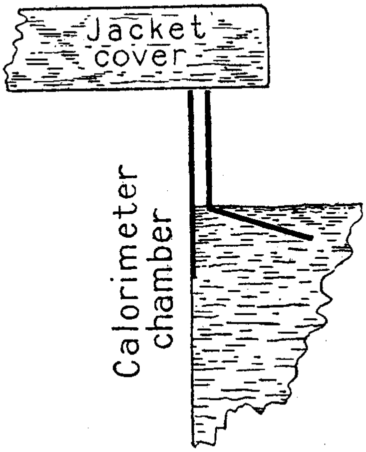

Fig. 4.—Arrangement of shielding rim preventing the influence of the room temperature upon the upper part of the wall of the calorimeter chamber.

If a cold calorimeter is used in the same jacket, the copper rim may surround it also.

If the thermoelement then passes directly from one chamber to the other, evaporation into the working calorimeter chamber can be prevented by packing the orifice through which the thermoelement passes with plasticine or other soft wax, or else by pouring heavy oil on the water surfaces inside and outside the cold calorimeter.

Prevention of evaporation is recognized as important in thermostats of precision, and it is of course desirable or necessary for the jacket water with the type of installation just described. A quick and easy way to secure it is by casting paraffin on the surface of the water. The paraffin will not continuously support much weight, and hence must be supported, either by the water or otherwise. It is a good plan to use fixed paraffin to fill in around corners and irregularities, leaving the large, clear spaces protected by bodies of simple outline, either floating or otherwise supported.

It is an advantage to paint the jacket vessel white inside, which makes objects in it far more easily visible. The paint may be protected by a thin layer of paraffin.

(*c*) *Lever Adjusters.*—Some adjustment of the amount of water in the calorimeters is desirable or necessary in nearly all calorimetric work. With the compensated calorimeters the quick method of Dickinson and George[1] gives more than sufficient precision and will often save a tedious adjustment of the weight on a balance. This method consists in sucking out excess water down to a desired level. The level reached is more constant, however, if the tube used is of different shape from that of Dickinson and George. Fig. 5 shows the adjuster used with our working calorimeter. It is made of a large cork, three nails and a little glassware. The nails, serving as a gage, rest on the calorimeter rim when the adjuster is in use.

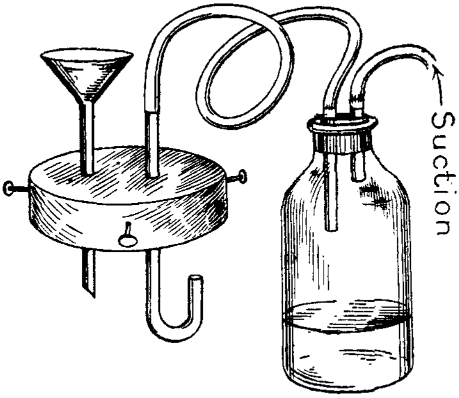

Fig. 5.—Apparatus for quickly adjusting the water level in calorimeter.

(*d*) *Temperature Adjustment.*—The required adjustment of the temperature of the cold calorimeter to approximate equality with that of the jacket is practically the only special manipulation called for by the compensated calorimeter system, once the installation is completed. With the submerged cold calorimeter, this adjustment, as already pointed out, is nearly automatic. With a cold calorimeter not submerged, the adjustment is readily made on a similar principle, by sucking out the water into a large bottle, and then refilling from the jacket. If the jacket is made into a thermostat, these manipulations become unnecessary.[2]

9. Essentials of a Differential Calorimeter Installation.

The essential apparatus of the calorimetric system described in the present series of papers are here listed together.

A. Calorimetric Arrangements.

I. The *calorimeter* proper, or "working calorimeter," has no restrictions placed upon it by the differential methods here presented.

II. The *cold*, or *comparison calorimeter*, which is merely a vacuum jacketed bottle, and

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[1] H. C. Dickinson, E. F. Mueller and E. B. George, "Specific Heats of Some Calcium Chloride Solutions between —35° C. and +20° C.," *Bull. Bur. Standards*, **6**, 388 (1910).

[2] As to the complication involved in this procedure it may be said that even in the most unfavorable case, where the cold calorimeter has a separate thermostat all to itself, the installation of the thermostat is simpler, and its maintenance less objectionable, than of the oil-filled thermostat around the Wheatstone bridge, which is generally considered the most desirable means of insuring high precision with the resistance thermometer.

III. A *completely inclosing jacket*, or jackets, equivalent to that of Figs. 1 and 3 above, are essential.

B. Thermometric Arrangements.

IV. The *Thermoelements* will be three in number, usually a main element of 24 couples, with two auxiliaries, one of 4 or 6 couples, and one of 1 or 2, this last shunted for the compensated calorimeter. These can, as experience shows, ordinarily be made in about two days by persons without special experience, barring accidents.

C. Auxiliary Electrical Apparatus.

There will also be needed:

V. An all-switch, constant-deflection, high precision *potentiometer*, with the usual auxiliaries, namely, storage cell, regulating rheostat (or two of each) and standard cell.

VI. A *galvanometer* of at least half microvolt sensitiveness, with regulating rheostat.

VII. A *copper knife switch*, or something equivalent, arranged as an *eliminating switch* for parasitic thermal electromotive forces.

VIII. Other similar *switches* for exchanging thermoelements.

IX. Neutral (antithermoelectric) *complementary coils*, to maintain the constant galvanometer circuit resistance necessary for rapid reading.

X. An equipotential leakage shield, or two such.

Of these, the galvanometer need not be especially expensive, the appropriate types of potentiometer are comparatively cheap, and the other apparatus is evidently far from costly. All are discussed in this and previous papers of this series.[1] Except where temperature differences and changes in the observing room are extreme or violent, they are sufficient, without further shielding or blanketing, to give readings precise to 0.1 microvolt, that is, to 0.0001°.

Often desirable, though not essential, are also a thermostat jacket, other thermoelements, a few switches enabling the potentiometer to carry simultaneously two independent readings, a governor for the calorimeter stirring, a water level adjuster, and sometimes a separate jacket for the cold calorimeter.

10. Details of an Ordinary Determination.

Following is a list of the various operations included in an ordinary determination with a compensated calorimeter system:

I. The working calorimeter is filled and placed in position, and stirring is started. All subsequent manipulations of this calorimeter will vary according to the kind of determination, and will not be any different on account of the 2-calorimeter method; hence their description is omitted.

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[1] *Loc. cit.*

II. The auxiliary current of the potentiometer is adjusted by means of the standard cell.

III. The cold calorimeter temperature is adjusted (if necessary), its difference from the jacket is observed, and also the jacket temperature—this latter so as to get the approximate temperature of the calorimeter.

IV. If the temperature adjustment does not involve adding water to the cold calorimeter, the amount of water in it will need adjustment once a week or so.

V. The galvanometer sensitiveness is adjusted (once a day).

VI. The equality of the 2 halves of the thermoelement is checked by reading them in opposition (once a day).

2,3 and the occasional 4, 5 and 6, are the only observations or operations demanded especially by the 2-calorimeter thermoelectric method.

VII. The main thermoelement is then connected so as to read differential temperatures, and regular observations begin. These are in number and purpose much like those usual in calorimetric determinations, except that they are shortened by omission of the "fore" or preliminary cooling period, which is not needed with the present method. More specifically, these readings are:

(*a*) Readings, 1 to 3 each, of the main thermoelement and of the combination auxiliary, made before the heat transfer to the calorimeter water, with the object of finding the readings of these two at the instant the transfer begins.

(*b*) Readings of the auxiliary during the period of heat transfer.

(*c*) Readings of both main thermoelement and auxiliary at the end of this period, and at the end of an equally long cooling period following it. Most of these readings include an adjustment of the galvanometer zero, made with the aid of the eliminating switch.

VIII. The cooling correction is calculated in microvolts, according to the formula:

$$C = \Delta E_3 \ \varphi_1/\varphi_3,$$

where ΔE_3 is the change of the main thermoelement reading during the cooling period, and φ_3 and φ_1, the averaged auxiliary readings for that and the transfer period, respectively.[1]

IX. The corrected final temperature, and the initial temperature, in microvolts, are each added to the cold calorimeter temperature, and the corresponding values in degrees are then taken from the thermoelement table.

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[1] This formula, and some short cuts in the calculations, are discussed in "Some Calorimetric Methods" (Walter P. White, *Phys. Rev.*, 31, 545 (1910)) and in "Some Calorimetric Apparatus" (*Loc. cit.*, p. 680). As given here, it applies when the temperature change due to stirring is compensated. Where that temperature change is merely kept constant, the formula becomes $C = (\Delta E_3 + W)\ \varphi_1/\varphi_3 - W$, where W is the change produced in each period.

11. Precautions and Safeguards.

This section gives, with an attempt at completeness, a list of features which must be provided in the apparatus, and of precautions which must not be forgotten in daily work, for observations of precision.

I. Features Required in the Apparatus.

(1) Generally necessary—that is, not peculiar to the differential thermoelectric, compensated calorimeter method.

A. Pertaining to the Calorimeter.

(*a*) Control of, or preferably prevention of, evaporation from the calorimeter.

(*b*) Sufficiently vigorous stirring in the calorimeter and especially in the jacket.

(*c*) Sufficiently constant speed of stirring in the calorimeter.

(*d*) Reduction of certain lag errors, which are usually negligible, but should not be assumed to be so.[1]

(*e*) (Occasionally) provision against excessive evaporation or other detriment to uniformity in jacket temperature.

B. Thermometric.

(*f*) To have sufficient depth of immersion of the thermometer.

C. Electric.

(*g*) To provide adequate insulation at all points.

(*h*) To provide equipotential leakage shields if necessary.

(*i*) To have it definitely known how much attention is needed by dial and other contacts.

(*k*) To have the coil corrections, if any, properly determined (usually there will be none).

I (2) Features Required in the Apparatus, Peculiar to the Compensated Calorimeter Method.

A. Pertaining to the Calorimeter.

I. Provision against friction of the cold calorimeter stirrer against the thermoelement.

II. Provision against appreciable heat of stirring in the cold calorimeter (or else against an appreciable difference between the two calorimeters).

B. Thermometric.

III. (In divided installations only) to have a copper temperature shield over the horizontal part of the thermoelement, to protect thermoelement and calorimeter from the effect of room temperature.[2]

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[1] *a* to *d* are discussed in: "Lag Effects and Other Errors in Calorimetry," *Loc. cit.* Irregular heat conduction to the calorimeter along the thermometer, which is troublesome with some electric thermometers, is, of course, impossible in the differential thermoelectric method with a single jacket, since the thermoelement is then completely included; and is prevented in divided installations by the sheet copper shield over the exposed portion of the thermoelement. A good thermal contact with the jacket where the thermoelement passes through may give additional security; it has proved sufficient by itself under severe tests.

[2] The observer should, of course, by all means, see to it that his thermoelement is sufficiently homogeneous at the place where the temperature gradient comes, but this amounts merely to saying that he must have a satisfactory thermometer, so I have not classed it as a precaution.

C. Electric.

IV. To have neutral (*i. e.*, practically, copper) wires and contacts outside of the eliminating switch.

V. To have an eliminating switch which has been thoroughly tested for neutrality.

VI. To have some provision against the effect of direct sunlight, or heat from lamps, upon neutral switches or contacts.

II. Precautions Needed in Operation.

(*1*) *Not Peculiar to the Thermoelectric Methods.*

A. Pertaining to the Calorimeter.

(*l*) To avoid moisture on the working calorimeter.

(*m*) To have the right amount of water in the same.

(*n*) To see that the jacket stirring does not accidentally become too slow; from slipping of the belt, for instance.

(*o*) To see that the proper speed of calorimeter stirring is maintained.[1]

(*p*) Not to overlook any change which may be produced in the heat equivalent of the calorimeter.

B. Thermometric.

There are no general thermometric precautions which remain necessary when the compensated calorimeter method is used.

C. Electric.

(*q*) and (*r*) To test insulation and shield whenever trying weather or other cause suggests the necessity.[2]

(*s*) *To Give the Contacts Needed Attention.*—(With the combination potentiometer this is almost nil if corrosive gases are absent. An overhauling twice a year will then prove more than sufficient.)

(*t*) To avoid laying wires, clothing, or other objects down so as to make a leakage path by the equipotential shield, and to avoid letting live wires, even if insulated, touch anything inside the shield in damp weather.

II (*2*) *Precautions Needed in Operation, Peculiar to the Compensated Calorimeter Method.*

A. Calorimetric.

VII. To let 10 minutes or so intervene between any considerable change in the cold calorimeter temperature (in adjusting it) and the beginning of observations.

B. Thermometric, nothing.

C. Electrical, nothing.

Of these precautions *n, o, q, r,* are the most troublesome, and their inconveniences are trifling. They are necessary for high precision by almost any method. The compensated calorimeter method itself evidently calls for practically no precautions.

12. Availability of the Differential Thermoelectric Methods.

The intrinsic advantages of the differential thermoelectric system in calorimetry have been stated at the close of a previous paper.[3] They give rise to methods superior in absolute precision, certainty, and freedom from precautions, in quickness, and in the power of combining numer-

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[1] Our speed is governed, and the governor operates by means of incandescent lights, whose winking shows when the governor is working properly.

[2] The tests given in "Leakage Protection by Shielding, Especially in Potentiometer Systems" (*Loc. cit.*), will usually be sufficient *in potentiometer systems.*

[3] "Potentiometers for Thermoelectric Work, Especially in Calorimetry," *Loc. cit.*

ous and varied observations. It will probably be clear from the present paper that the calorimetric arrangements necessary to secure these differential methods entail disadvantages which are slight, and are practically done with, once the original installation is accomplished. The same may be said of the electrical arrangements. The methods will therefore nearly always be satisfactory, even where they are not noticeably preferable. Wherever a variety of work is to be done the thermoelectric apparatus is likely to prove decidedly superior for some of it.

If apparatus is desired which can be made useful in work not calorimetric, the thermoelement installation will be useful not only for all thermoelectric work, including high temperature measurement, study of heat conduction, etc., but also for much potentiometer work where no temperature measurement is involved. For measurements which are naturally or necessarily differential (such as freezing point depressions, for instance) the thermoelement is especially advantageous. If, however, the electrical apparatus is likely to be needed for very accurate measurement of single temperatures (*i. e.*, not temperature intervals) as in determining fixed points with the highest precision, the resistance thermometer, which is more convenient for such measurements, is more likely to be preferable.

Summary.

In the calorimetric "Method of Mixtures," a precision approaching or reaching 0.1 per mille, though somewhat unusual, is often desirable, and is ordinarily not difficult to attain with appropriate apparatus. Its attainment is especially easy with a two-calorimeter installation, which secures the convenience and high precision of differential thermoelectric temperature measurement. This is the only advantage of the two-calorimeter arrangement; the diminution of heat-loss error, often counted an advantage, turns out upon examination to be largely illusory. By abandoning the twin calorimeters previously used to get this supposed advantage, and using for the comparison calorimeter a vacuum jacketed flask, there is a gain in convenience and precision. A special thermoelement combination renders the necessary temperature observations as simple as with the twin arrangement. A completely inclosing jacket of uniform temperature is necessary for this method, but this is no loss, for such a jacket proves to be necessary for highest precision with any other method. This method is quite as effective with two jackets, one around each calorimeter, and therefore with adiabatic methods.

Efficient complete jackets can be very easily realized according to several methods, which are described.

As compared with others, the present method is especially advantageous for observations of great absolute precision, and wherever it is desirable to secure the advantages which the thermoelectric system possesses in the way of rapidity and of facility in making varied observations.

Apparatus especially valuable for this method is described in a series of papers, of which this paper is the last.

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ALTERNATING CURRENT ELECTROLYSIS.

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PART I.

Manuevrier and Chappius[1] found that, when an alternating current is passed through electrodes of very fine platinum wires dipped into a sulfuric acid solution, there is an immediate and abundant evolution of gas. They also found that the higher the frequency the less the amount of decomposition.

Ayrton and Perry[2] used alternating currents having a frequency of 10,000 per minute, and made the interesting observation that a deposition of hydrogen gas on a platinum electrode hinders visible decomposition by alternating currents, while deposition of oxygen favors such decomposition. Hopkinson, Wilson and Lyddal[3] also investigated the nature of electrolysis by alternating currents, but they laid more stress on the physical side of the question. M. LeBlanc[4] passed an alternating current between copper electrodes in a cyanide solution and found that, with the rate of reversal of 1000 per minute, copper passed quantitatively into solution; while, with the rate of 38,000 reversals per minute, only 33% of the theoretical quantity dissolved. LeBlanc holds that the copper passes into solution if the copper dissolved at the anode has time to be converted into the complex cuprocyanide ion before the reversal of the current.

Brochet and Petit[5] do not share the view that the possibility of alternate current electrolysis depends on the formation of a complex ion. They conceive the general condition for the formation of a new compound to be, that the ion, on reaching the electrode, has had time to part with its charge before reversal produces the ion of the opposite charge. at the same electrode. Ostwald also holds the above view. It frequently happens that the immediate product of the chemical processes at the electrodes undergoes further changes which are difficult to reverse. He considers that reversibility is often merely a question of time and for short intervals of time is always present. This is shown by the fact that

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[1] *Compt. rend.*, 106, 1719–22; 107, 37–40.

[2] *Electrician*, 21, 299–300.

[3] *Proc. Roy. Soc.*, 54, 407–417.

[4] *Z. Electrochem.*, 11, 705 (1905).

[5] *Ibid.*, 10, 909 (1904); 11, 441 (1905).