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# CALORIMETRIC METHODS AND DEVICES.

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In the following pages the general rules for calorimetric precision, given in the preceding paper, are applied to certain structures, namely, jacket covers and stirrers; and to the following special devices: vacuum-jacketed vessels, the adiabatic method, aneroid or dry calorimeters, double or differential calorimeters, and measured-shield calorimeters.

1. **Covering the Jacket.**—In treating the jacket top we may leave it open, cover it with wood, cork, or similar non-conducting material, use a cover of conducting metal, or bring the water of the jacket entirely over the calorimeter chamber.

Two types of complete inclosure for calorimeters seem superior—the "submarine," of T. W. Richards, and the "water cap," which originated at the Geophysical Laboratory. In the submarine the calorimeter is simply inclosed in a case which is clamped together water-tight and immersed in a bath which is the jacket water. Tubes lead down to the case for transmitting the thermometer, stirrer, etc. This type of calorimeter is often easier to construct than the other, and easily gives a good chance for jacket stirring, but it is relatively inconvenient in use, and is, like certain other submarines, rather hard to see and get at.[1] The water cap is a box covering the calorimeter chamber and filled with water which is continuous with the rest of the jacket water below. By simply locating the stirrer at an appropriate place circulation through the cap is secured. The cap can be so made as to be moved aside at any time without interrupting the stirring. Hence the calorimeter may be always thoroughly accessible, and easier to manipulate in various ways, than when it is submarine. In our first apparatus, adopted with some improvements by the Bureau of Standards, the cap, when moved aside to expose the calorimeter chamber, rotated about the point where water entered and left it. With this form, in order to get a stirrer rod or a thermometer down through the top and yet leave that movable it is necessary to cut a deep notch in its edge, which is undesirable for several reasons. The Bureau of Standards, to avoid this, put thermometer and stirrer down through holes.[2]

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[1] This difficulty has been considerably diminished in our laboratory by the fol-owing device: A wide tube runs down to the calorimeter. In this slides a cylindrical eavy walled cup of copper, nearly fitting it. When in place the bottom of the cup forms a part of the top of the calorimeter chamber, being, of course, at the jacket temperature. When the cup is withdrawn access to the calorimeter is obtained through the wide tube.

[2] Hobert C. Dickinson, "Combustion Calorimetry," Bur. Standards, *Bull.* 11, 212 (1915).

The cap is now immovable as soon as the thermometer is in place, so that what is for many experimenters the special advantage of this type of complete inclosure is lost, though this is not a great drawback in the particular work for which the Bureau of Standards calorimeter is used. At the Geophysical Laboratory the rotating cap has been discarded, and much simpler caps used with entrance and exit for the water at opposite ends. When a pair of these is used, stirrer rods, etc., can pass between the two into the calorimeter chamber, and one can easily be moved aside, without interrupting the stirring, so as to give access to the calorimeter.[1]

Compared with these devices a thick copper cover in contact with the jacket water is not as much worse thermally as might be supposed, but neither has it as much advantage in ease of construction as might be supposed. The machining of a thick cover is apt to be more of a job than building up a box on a thin one. The cover which depends on conductivity is less satisfactory for adiabatic methods. The efficiency of a cover of given extent and thickness can be calculated to a rough approximation, and is easily measured after the cover is made. Definite data thereon do not seem to have been published.

Jacket covers of low thermal conductivity protect from the variations in room temperature, as they are intended to do, but only in part, and as this protection is increased by making the cover thicker the lag of the cover itself enters more and more. In such a case the exponential term characteristic of the cover would hardly ever die out during the experiment, but for determinations of the same time-period and same form of temperature curve the error would not usually be serious. It would be useful to be able to estimate this error for any given case, but no data seem available at present. The only reason for such covers, however, as compared to metal or water covers, is a possible saving in cost of construction.

### Stirring Arrangements.

The propeller stirrer is not only more efficient than the old up-and-down form, but lends itself far better to preventing evaporation. Several schemes have been used with it to do that while maintaining the constancy of the heat of stirring. The requirement of constancy demands that appreciable solid friction, on account of its almost inevitable irregularity, shall be kept away from the calorimeter itself; the main bearings are therefore on the jacket, and tight packings against evaporation are not admissible. One evaporation-restraining scheme (Bureau of Standards) is to lay over the hole in the calorimeter top a light washer wet with oil, perhaps 8 mm. in diameter, through which the stirrer shaft passes, just barely touching. Friction evidently is generally trifling, but apparently might become appreciable if the shaft is not truly centered. A second

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[1] Walter P. White, "Some Calorimetric Methods," *Phys. Rev.*, 31, 672 (1910); "Easy Calorimetric Methods of High Precision," THIS JOURNAL, 36, 2325 (1914).

scheme (Geophysical Laboratory) is to have a small umbrella, or inverted cup, on the shaft, dipping into an annular trough on the calorimeter top, so that the opening can be sealed by a few drops of oil. Appreciable heat from fluid friction seems possible here, but not likely if the surfaces are not too near together. The construction is a little more elaborate than the other. The use of oil can be avoided by simply running the shaft through a tube. In one test with 2 cm. length and 0.5 mm. clearance around a stationary shaft 5 mm. in diameter the evaporation was at the rate of 1 mg. per hour, corresponding, in 10 min., to 0.1 calorie of heat or (usually) less than 0.0001° temperature change. But there usually should not be as much as 2 cm. of space between the top of the calorimeter and the jacket. The scheme suggested in Fig. 1 enables the tube to be used in spite of this. The head H should be removable if the calorimeter top is not, since it may be necessary to remove water from the outer tube. Made shorter and with a little more clearance this makes an oil seal arrangement more compact than the one just described. If the tube, short or long, is of poorly heat-conducting material and runs up to the jacket (E. R. Edson, unpublished research) the protection must be practically perfect for adiabatic work, or for calorimeter temperatures below the jacket. If the stirrer shaft becomes bent the heat of stirring may change, though it will not from this cause during any one determination. A steel shaft 3 mm. in diameter only increases by about 3% the total leakage modulus of an ordinary calorimeter.

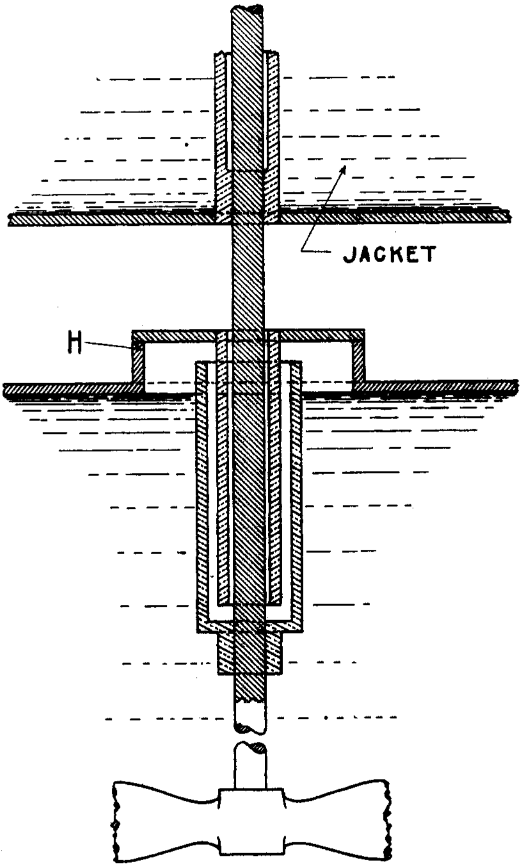

Fig. 1.—Arrangements for getting the shaft of a rotating stirrer through a calorimeter top without appreciable evaporation, without friction, without oil, and without any considerable structure projecting upward.

The jacket stirring and the calorimeter cover have been discussed in the course of the preceding papers.

## Vacuum-Jacketed Calorimeters.

The vacuum-jacketed glass vessel diminishes, usually some 3 or 4 times, the value of $K$, the thermal leakage modulus. It follows from the preceding paper that this has the following practical advantages: (1) Less care is required as to the thermal head $\varphi$ and less frequent readings of it; (2) many lag effects are smaller; (3) stirring can be less vigorous; (4) the adjustment of jacket temperature in adiabatic work is considerably easier. These advantages evidently do not mean any great increase in precision except for especially protracted or accurate determinations, but they are convenient.

From the point of view of construction or installation it may be said that the vacuum-jacketed calorimeter is simpler, and most successful where the other arrangements are simple also. One ready-made vessel constitutes not only most of the calorimeter, but an important part of the jacket, its inner wall. But it is difficult to fit satisfactorily to the glass vessel both a calorimeter cover and a chamber roof (belonging to the jacket) over it; a single cover at the top, belonging to the jacket and at jacket temperature, is easiest to fit, but with this there is free evaporation. If through the saturated air gap leads to an electric heater are to be carried down, thoroughly protected from dampness, yet with sufficient thermal insulation between calorimeter water and jacket, considerable difficulty appears. The support of a propeller stirrer is also relatively difficult, and the fragility of glass is always another drawback.

If a complete metal calorimeter is hung in a cylindrical glass vessel the most serious disadvantages disappear, though the reduction of $K$ is less than with a narrower neck. The construction is now rather less simple than with the metal calorimeter alone, and the avoidance of lag between metal and glass is a slightly uncomfortable problem, which is discussed elsewhere.[1]

The large temperature variation in the specific heat of glass adds to the disadvantages of this calorimeter. Its field seems to be, first, in crude work, where its use is almost clear gain, and second, in very exacting work where every advantage is badly needed. It may be well to say that the use of a vacuum-jacketed calorimeter, in spite of the reduction of $K$ it secures, usually makes it no easier to dispense with a cover for the jacket; for covering the jacket mainly concerns the top of the calorimeter, and the top of a vacuum-jacketed calorimeter is not vacuum-jacketed.

## The Adiabatic Method.

The adiabatic method is being introduced into commercial practice, and is otherwise attracting unusual attention. It has been discussed in

[1] Walter P. White, "Calorimetric Lag," This Journal, 40, 1870 (1918).

several connections in recent papers from this laboratory. Here it seems well to bring together the various conclusions stated, with some others.

(1) It does not diminish error by simply diminishing the amount of thermal leakage, as it seems to do on superficial consideration. For the decrease of leakage is secured by reducing, not $K$, the leakage modulus, but the thermal head $\varphi$; and the *errors* of the thermal head, which depend on circulation, room temperature, etc., are not thereby reduced; on the contrary, they are increased, since it is evidently harder to measure and control a changing jacket temperature than a stationary one. The success of the adiabatic method is entirely dependent on the fact that this error which it has been especially supposed to diminish is still negligible though increased.

(2) It does not diminish at all the rate measurement error (error in determining $V$) which, though never large, is in careful work usually the largest thermal leakage error there is.

(3) In common with some other methods, it eliminates the small $LK\eta$ lag effects.

(4) It eliminates error from variation in $K$, which includes, especially, cases of variation from Newton's Law.

These last two results, and especially (4), give the method especial value in protracted determinations.

(5) On account of the indifference it confers to variations from Newton's Law of Cooling the adiabatic method is specially advantageous with large temperature intervals.

(6) It greatly diminishes the liability to evaporation error.

(7) It makes the situation a little worse respecting thermometer lag, substituting for the perfect compensation between lag in the X-period and lag in the rating periods, usually present in ordinary methods, the compensation during the X-period between two different thermometers, one in the calorimeter and one in the jacket.

(8) Moreover, since thermometer lag partly depends on stirring, the calibration factor of the calorimeter may change if the *jacket* stirring changes, and this effect may be increased by other lags connected with the circulating liquid. The liability to all these effects decreases as the stirring becomes more vigorous.

(9) The effective lag of external bodies may become twice as great with the adiabatic method, though the error from a given shift of a convection shield is no greater. This lag and those of (7) and (8) tend to make the calibration factor of a calorimeter different in adiabatic work.

(10) A constant end temperature is often necessary in aneroid work. This generally demands a change in jacket temperature, which is con-

veniently secured by following the adiabatic method in toto, though this method, as such, is not necessary.

(11) The adiabatic method usually saves the time of one observation period.

(12) It also substitutes for the labor of computing the thermal leakage an experimental manipulation; a substitution which will appeal to most live experimenters, though ordinarily it may not mean more precision. In commercial work the same advantage can often be obtained more easily by other methods.[1]

(13) The adiabatic method is more easily operated with a small thermal leakage modulus, that is, with large, or vacuum-jacketed calorimeters, or with those having very wide air gaps. Its practical elimination of convection currents permits wide air gaps to be used without convection shields, though this must be done with caution.[2]

(14) Experimenter's Lag. The expression $LK\Delta\theta$ for the effect of a lag may be applied to determine the error when the experimenter is too late or too early with his temperature adjustment in adiabatic work, or with his reading in any case. Of course the experimenter's lag is never constant, so it must be made negligible. And since it varies during an experiment we have to consider, as we never need to do with true lags, how its effect varies at different periods. The answer to this question is easily obtained from Fig. 2. The effect is represented by the shaded area, and lag, being a time, is measured horizontally. Hence the error from a single reading is proportional to the product of the lag and the rate of temperature change (*i. e.*, the slope of the line) at the time the lag occurs. If we are thinking of the whole time of the experiment with $K = 0.002$, $L$ must be under 0.05 min. or 3 seconds, for a precision of 0.1 per mille, less than that, say 1 second, for safety. But if 0.9 of the temperature rise occurs in two minutes the lag for all the rest of the time may be 10 times the minimum value, or 30 seconds, with no more error than from a 3-second lag for that two minutes. And there may evidently be periods

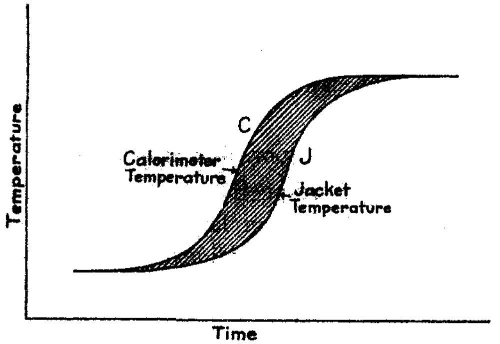

Fig. 2.—Representing the effect of a given lag at different times during the X-period.

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[1] Walter P. White, "Some Points Regarding Calorimeter Efficiency," *J. Franklin Inst.*, 186, 279 (1918); "The Conditions of Calorimetric Precision," THIS JOURNAL, 40, 1878 (1918).

[2] Walter P. White, "Thermal Leakage and Calorimeter Design," THIS JOURNAL, 40, 389 (1918).

when a lag of a minute will be quite permissible.[1] The observer in the adiabatic adjustment, therefore, may usually concentrate his attention on a small part of his observing, but the requirements at that time are really rather severe. It is clearly very desirable to diminish this requirement by decreasing $K$. If this is done, either by a vacuum-jacketed vessel or by thermal shielding, the error and inconvenience thus avoided would sometimes be far greater than those introduced by the lag of either of these devices.

(15) In protracted determinations there is correspondingly more danger from irregularity in stirring. It therefore seems desirable to stir at two different speeds; first to stir vigorously during the rapid temperature rise, in which, as we have seen, the danger of error from internal lag is mainly concentrated, and then more slowly during the remaining and usually larger portion of the time.[2] This is especially advantageous with the adiabatic method, since the temperature differences to be equalized are almost nil after the first temperature change.

It may not be out of place to call attention to one feature of such a treatment of stirring. If a temperature rise is continuous and slow it will not do to reduce the stirring on that account. The temperature differences are small, it is true, but they last a long time, and that makes up for their smallness. The danger from internal lag is as great as with a rapid rise. When it is possible to neglect a period of slow rise the reason is because only a small part of the total comes in it, not just because it is slow. For this reason we may stir slowly during any one small part of a long slow rise, but not during all of it.

## Aneroid Calorimeters.

By using the excellent thermal conductivity of copper or silver to equalize temperature we avoid all the mechanical and thermal complications connected with stirring and evaporation. The inevitably greater irregularity of surface temperature can be taken care of during the X-period by differential thermoelements, and done away with at the final readings by bringing the jacket to the calorimeter temperature. The method has especial advantages at extreme temperatures but has proved to be nearly as accurate as any at ordinary temperatures also.[3] It has already been suggested[4] that the only errors *peculiar* to this method come, first, from inconstant final jacket temperatures and second, from incorrect distri-

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[1] Of course the permissible error *in degrees* will be the same at one time as at another. Indeed this amounts to saying that the permissible error in time will *not* be the same if the rate varies.

[2] As far as I know this method has not yet been employed, but I have planned to use it.

[3] H. C. Dickinson and N. S. Osborne, "An Aneroid Calorimeter," Bur. Standards, *Bull.* **12,** 47 (1915).

[4] "Calorimetric Lag," *Op. cit.*

bution of the junctions of the differential thermoelements, combined with an insufficient amount of conducting metal, and with temperature distributions varying from one experiment to another, and the chance of avoiding this triple combination is excellent. Lags and other errors resulting from imperfect thermal contact between thermojunction and calorimeter have been shown to be negligible. Hence there is no ground of objection to the striking procedure of the Bureau of Standards, who run the (insulated) thermoelements through tubes soldered to the surfaces, an admirable way of protecting them and keeping them out of the way.

A very important peculiarity of aneroid calorimeters concerns the choice of dimensions. From the fundamental differential equation of heat flow it follows that in two similar bodies the time required for a given amount of equalization of temperature varies inversely as the square of the diameter. Hence a body of $1/n$ diameter will usually require only $1/n^2$ of the time for a determination to be made with it, which opens up the possibility of decreasing very greatly the labor and tedium of the observing. Moreover since the shortened time tends to diminish the amount of heat lost by thermal leakage, the decrease in labor will usually be accompanied by an actual gain in precision. The amount of this gain will vary in different cases, since the errors are not affected alike by the change in dimensions. The diminution increases the ratio of surface to mass, and with that the value of the thermal leakage modulus $K$, at a rate usually nearly proportional to the first power of the ratio of change, that is to $n$, and this increase in $K$ works against the gain in speed. (1) Lag effects, being independent of time and proportional to $K$,[1] will always be increased, but lags are especially likely to be harmless in aneroid work, except the experimenter's lag in adiabatic work, mentioned above. Appreciable error from this lag, however, can usually be avoided by abandoning the adjustment of jacket temperature, and, instead, observing the thermal head with a steadily heated jacket, and computing a small correction. The great saving in time seems sufficient compensation for any disadvantage that may be thought to lie in this procedure. (2) Errors which are themselves unaffected by the change in dimensions or time, such as errors from defect in uniformity of surrounding temperature or in precision of thermoelement or reading, will have their final effect diminished, since their multiplier $KT$ is multiplied by $n \times 1/n^2$, and so decreased. At high temperatures, where these errors predominate, precision alone almost demands very small dimensions. A pair of twin calorimeters, briefly described in 1911,[2] used up to 1500° in a platinum-wound furnace, could both be hidden behind an ordinary postage stamp.

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[1] Preceding paper; also "Calorimetric Lag," *Op. cit.*

[2] Walter P. White, "The Detection of Small Heat Effects at High Temperatures," *Phys. Rev.*, **32**, 606 (1911).

(3) The final error from incorrect distribution of junctions is affected in a way intermediate between the last two. If the heating of the calorimeter takes the same time as with a larger one the heat loss and error during it will be proportionately larger, owing to the larger value of $K$, though this will be partly offset by the fact that the total temperature irregularity produced by heating will be less. During the subsequent temperature equalization the shortened time, as in the preceding case, will more than make up for the greater value of $K$. On the whole, error from incorrect distribution seems likely to be less and at any rate unlikely to be much greater in a smaller calorimeter.

This last statement will not be true if $K$ increases much faster than the diameter decreases. Heat loss by radiation is simply proportional to surface, so, as far as it is concerned, $K$ for similar bodies will be strictly proportional to $1/n$. But a small body in air loses heat by conduction at a rate greater in proportion to surface than a larger one. For a reduction in diameter, however, of a long cylinder from 2 cm. to 1 cm., with an air gap around the cylinder of 1.5 cm., the ratio of conduction loss to mass increases only about 2.44 times, or $^1/_5$ more than for the radiation loss. Even for a reduction from 1 to 0.5 cm. the figure is only 2.64, while for 8 to 4 it is 2.16. 1.5 cm., moreover, is about the largest air gap that would ordinarily be chosen,[1] and for narrower gaps the results are more favorable to the smaller calorimeter. For very short calorimeters they are less favorable than those just given, but even for a sphere a reduction from 2 to 1 cm. with 1.5 cm. air gap only increases the ratio of conduction loss to mass $^2/_5$ more than for the radiation loss. It thus appears that the probability of increasing precision by reducing diameter holds down to 1 cm. at least, which means that the experimenter may confidently reduce dimensions until either the delicacy of construction required begins to be excessive, or the temperature changes become too rapid to follow satisfactorily.

## Double, or Twin, Calorimeters.

Between 1869 and 1891 Pfaundler developed a method characterized by the use of two calorimeters, as much alike as possible, similarly heated by the same electric current, with the slight differences in their temperatures measured by a sensitive thermoelement. The thermoelectric twin calorimeter work done in 1900 and later in Nernst's laboratory is only the logical application of Pfaundler's calorimeters to the measurement of chemically derived heat. This method, like the ice calorimeter, not only tended to neutralize the effect of the surrounding temperature, but diminished the errors in the thermometer, and in determining the heat capacity of the calorimeter itself. Pfaundler's original introduction of it was felici-

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[1] "Thermal Leakage and Calorimeter Design," *Op. cit.*, p. 384.

tous, for at that time absolute electrical measurement of heat or temperature was far less advanced than today, but the production of two equal heats, or the very precise measurement of a small temperature difference, could be accomplished very effectively. The diminution of thermal leakage error by means of the compensating effect on the second calorimeter appears to be the least important feature of the method, and was not stressed by Pfaundler, though some of Nernst's pupils emphasize it. The method evidently eliminates only the effect of general changes in the environment; it tends to render more effective the *irregularities* which cause the real thermal leakage errors. Moreover, it has errors of its own if the calorimeters differ[1] in leakage modulus. In itself, it is certainly less valuable against thermal leakage error than is complete jacketing.

Not only can modern methods of jacketing deal with thermal leakage better than the twin method, and so well that the twin method probably adds little precision when both are used, but the great development that has taken place since 1891 in the measurement of electric quantities, and of temperature by electric means, leaves to the earlier null methods little of their original superiority in precision. Nevertheless, the greater simplicity of the null methods is still important, and was, I think, not sufficiently emphasized when I wrote of them in 1914. Even today it is worth while to dispense with large storage batteries for constant current, thermoelements calibrated with high accuracy, and potentiometers of maximum precision to use with both, when one can get actually better results without these. But the method does not approach its maximum value unless the two calorimeters can be given great likeness to each other. Recently L. T. Fairhall and A. B. Lamb,[2] developing this method, have shown that T. W. Richards' method of chemical heating can well be substituted here for electric heating. For though an absolute amount of heat can very likely be given with more precision electrically, the production of two chemical heats in a given ratio is merely a matter of accurate weighing, while batteries, conducting leads, and trouble with resistance changes, with insulation, and with vagrant currents, are all avoided.

An examination of the possible thermal leakages of a twin system shows[3] that the errors from lack of similarity are least when the temperature of one calorimeter remains equal to that of the jacket. A method characterized by such equality has been used in this laboratory, but it is really a new method, lacking the advantages as well as the disadvantages of the original twin method and not requiring the two calorimeters to be alike. It is, in fact, essentially a device for using the thermoelement under the best possible conditions.

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[1] Treated in "Easy Calorimetric Methods, Etc.," *Op. cit.*, p. 2316.

[2] *Thesis*, Harvard University, 1917.

[3] "Easy Calorimetric Methods, Etc.," *Op. cit.* p. 2316.

## A New Method for Thermal Head; The Measured Shield.

It has already been shown that measuring the thermal head of a calorimeter by means of thermo-junctions distributed over its outer surface may easily be made a more accurate method than the usual determination by means of a single thermometer. Its usefulness is restricted by the inconvenience and danger in having the delicate thermoelement wires attached to the calorimeter, hence it has only been used where it seemed almost indispensable. There appears to be a more convenient arrangement, which increases the applicability and usefulness of the device.

This arrangement is to use a convection or "radiation" shield[1] of very thin metal, and run thermoelements from this to the jacket wall. These thermoelements are used to measure the thermal head. They do not have to be touched except in case of accident, and the calorimeter is freely removable.

The shield, though stationary, is now treated thermally as a part of the calorimeter. A novel combination of properties results. The cooling rate and leakage effect are diminished in comparison to the temperature change in the calorimeter, as by any convection shield, but are not diminished in comparison with the thermal head as measured. It follows that: (1) The effect of experimenter's lag in adiabatic work, and the required frequency of observing in all work, are less. (2) The precision needed in the measurement of thermal head is as great as if no shield were used. (3) But the effect of irregular jacket temperature is greatly reduced by the distributed junctions, and the thermal leakage error which is probably the most intractable in precision work, that connected with stirring and temperature distribution within the calorimeter, is doubly diminished; for the distributed thermo-junctions make uniformity less necessary, and the air gap between calorimeter and shield smooths out the original differences. A shield destitute of conducting power should reduce them to less than half; experiment indicated that a silver shield only 0.1 mm. thick will usually reduce them to less than $^1/_4$, even for points 14 cm. apart; such a shield, therefore, supplied with thermo-junctions, is more effective than vacuum-jacketing in diminishing stirring difficulties or errors from uneven temperature distribution.

The effect of a measured shield on the apparent heat capacity of the calorimeter comes only through its final change of temperature, from which it follows that the danger of error from change in the capacity effect of such a shield is nothing in adiabatic methods, and twice as great as for an ordinary shield in other cases.

In the two places where I have previously discussed convection shields the necessity of keeping their capacity effect constant has been pointed out. The chance of error from displacement has been shown to be so

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[1] "Thermal leakage, Etc.," *Op. cit.*, p. 391; "Calorimetric Lag," *Op. cit.*, p. 1863.

small that only gross carelessness seems likely to cause trouble in this way. In order to find how great the chance of error is from change in the radiating power of the surfaces the cooling rate of a silver cylinder 2 × 5 cm. in a glass inclosure 4.6 cm. wide was measured for various conditions of surface, with a crude and simple temperature control, giving results apparently reliable to 1%. What seemed like a complete coat of tarnish, produced by dil. ammonium sulfide, increased the total heat loss from conduction and radiation by about 3%. A tarnishing to intense browns and blues gave an increase of 12%; a film of olive oil, 36%. Since the other surface was glass, which at 100° and below absorbs nearly as well as a black body, these changes in emissivity are far greater than would occur opposite a bright metal surface, and greater than would occur from the similar change in a pair of surfaces. Since for an ordinary calorimeter the actual capacity of a convection shield will be from 2 to 4 per mille, its effective capacity from 0.5 to 1 per mille, it follows that with one pair of surfaces incredibly tarnished the error will not reach 0.1 per mille, while as to the effect of grease or handling, the maximum possible error is only 0.4 per mille where one pair of surfaces is perfectly dirty. It is also necessary for these results that while two opposite surfaces are changed, the other pair remain clean and bright, since a change in emissivity which affects both air gaps alike leaves the ratio of the leakage moduli unaltered and hence causes no error. For the measured shield, used non-adiabatically, the above errors must be doubled.

## Summary.

1. Various forms of jacket covers and of stirrer mountings are described and compared.
2. Vacuum-jacketed vessels are mainly useful either in relatively crude or in very exacting work. They are convenient and simple in crude work, but cause difficulty and complication if the work to be done demands more elaborate arrangements.
3. The adiabatic method does not diminish either of the two main sources of thermal leakage error, but has advantages in a dozen other ways.
4. The Pfaundler twin calorimeter method still enables high precision to be attained with relatively simple apparatus, but is most successful when applied to liquids, and to the comparing of two things which are nearly alike.
5. Aneroid calorimeters work quicker, and within limits also more accurately, the smaller they are.
6. The *measured shield method*, where a convection shield supplied with thermocouples is used, diminishes very greatly the difficulties of thermal head measurement and stirring, which are among the greatest in work of high precision, and is more convenient than glass vessels.

WASHINGTON, D. C.