Of two errors peculiar to the aneroid calorimeter one comes from improper distribution of the thermojunctions (or equivalent devices) which measure the surface temperatures. This error becomes zero if the surface temperature distribution does not change from one experiment to another. The other special source of error is inconstancy of final temperatures due to inconstancy of final jacket temperature.

On account of the lag effect the effective heat capacity of a shield midway between calorimeter and jacket is only one-fourth the actual capacity, and *with due regard to the possibility of change* such shields may often, with great profit, be used to reduce the thermal leakage. Used as a cover such a shield has a specially small error, and offers a particularly easy method of dealing with evaporation. Ordinary non-metallic covers, on account both of their lag and their heat capacity, are very undesirable

Although a normal lag effect characterizes even thick and heterogeneous packings around a calorimeter, the loss of time due to the lag is a sufficient objection to the practical use of anything which is not either very small or in very close thermal connection with calorimeter or jacket.

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[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY OF THE CARNEGIE INSTITUTION OF WASHINGTON.]

THE CONDITIONS OF CALORIMETRIC PRECISION.

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Within the past two decades calorimetry has made great advances, but there remains considerable uncertainty or difference of opinion as to the value of individual devices, and as to the most reliable or efficient methods in different cases. Apparently much of the uncertainty can be removed and efficiency promoted by a further examination of the various methods and devices. The present paper is an attempt in this direction.[1] It deals with the general rules or principles, and is followed by a paper on special methods.

The heat measured by a calorimeter is usually given as the product of its heat capacity by the temperature change. If the heat capacity is determined, as it usually is now, by a direct calibration, that is, by making regular determinations of a standard quantity of heat, the only errors affecting it are, practically, those of the regular determinations apart from the capacity, which are the errors in determining temperature change, so that these errors are the only ones to consider. The significant change is given as the sum of two quantities, first the actual change directly observed, and second, the allowance made for the heat which may leak to

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[1] A similar and briefer discussion, dealing with commercial work, has been published, *J. Franklin Inst.*, **186**, 279 (1918).

or from the calorimeter. The error in measuring the actual change is almost entirely a matter of thermometry. The *thermal leakage* effect gives calorimetry most of its interest and peculiar character; it gives rise, directly or indirectly, to 7 possible sources of error; which are distinct in being often affected differently by the same causes. These 7 sources, now to be considered, are: (1) measurement of thermal head; (2) measurement of rate of temperature change; (3) change in the leakage modulus, that is, the thermal leakiness of the calorimeter; (4) lags; (5) heat of stirring; (6) evaporation; (7) leakage along metal connections to the calorimeter.

The effect of these sources of error is dependent upon the procedure used for determining the thermal leakage effect, hence it seems well to formulate or define what will here be considered as essential in this well-known calculation.

The Determination of the Thermal Leakage Effect.

If *thermal head*, φ, means the temperature difference which causes the flow of heat, that is, the mean difference of calorimeter and environment, then the rate of temperature change, V, in the calorimeter will be $K\varphi$, where K is the *thermal leakiness* or *leakage modulus* of the calorimeter, often called the cooling constant. The determination of the leakage effect normally consists in measuring the head φ during the experimental period (or X-period),[1] the period when the unknown heat quantity is communicated to the calorimeter, and then multiplying this head by K. K is usually determined by taking the ratio of rate, V, to head, φ, for one or two *rating* periods, during which thermal leakage is the only cause of temperature change. The effect therefore equals

$$V_r \; T_x\varphi_x/\varphi_r \qquad (1)$$

where the subscripts indicate the periods (experimental or rating) to which the observed quantities belong, and T is time, *not* temperature. This illustrates the principle, but in practice there is usually present also a constant rate, due to the heat of stirring or from other causes; moreover φ usually can not be known exactly, since the effective environing temperature is usually uncertain. Hence, instead of φ the calorimeter temperature is generally used, and two rating periods are observed, and in such a way that the effect of the room temperature cancels out, and with it the heat of stirring. The method of doing this seems to be too well known to need description. It seems worth while to say, however, that the essential condition of the method is that the rate of change in calorimeter temperature shall be divisible into two parts, of which one is constant, the other, proportional to thermal head or to calorimeter temperature; that is, that the rate may be expressed as $a + b\varphi$, where a

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[1] This period usually gets the rather unmeaning name of Main Period. A better name seems to be "Experimental Period" or "X-Period." A. Dumas, *Arch. sci. phys. nat.*, **27**, 454 (1909).

and b are constants. This assumption usually holds well enough for most of the disturbing actions upon the calorimeter temperature, as heat conduction and heat of stirring. It does not hold if calorimeter temperatures only are used and if at the same time the surrounding temperature changes,[1] since then the change of cooling rate will evidently not be proportional to change in the measured temperature alone. That is, the environing temperature must either be constant or be measured.

1. The Thermal Head Measurement.—The most striking and important difference, perhaps, between different calorimeter installations, next to the character of the thermometer, is in the completeness of the measures taken to make definite and exact the determination of the thermal head, or mean temperature difference between calorimeter and jacket, or other environment. It is probably generally understood that in measuring thermal head there is seldom any danger of error due to the thermometer. In (1), the expression for the leakage effect, the thermal head, φ, is multiplied by T_xK. K seldom exceeds 0.003, and T_x seldom exceeds 10 minutes. Hence φ and all its thermometric errors are multiplied by 0.03 or less, although these errors can be made as small as those occurring in the main temperature measurement. In keeping uniform, though, the jacket temperature on which the value of the measurement depends, there is more chance of error. Nevertheless, since the temperature irregularity may evidently be at least 20 times the smallest permissible error, or 0.02° in working to 0.001°, this chance seldom need be a serious matter. The final error from the thermal head is, in fact, usually quite negligible, where the jacket completely encloses the calorimeter. The only cases where it may constitute much of a problem appear to be, first in commercial, and other relatively crude work, where the experimenter may find it hard to decide how far he may safely go in economizing by simplifying his jacket construction; and in work of very high precision, where a jacket temperature uniformity exceeding 0.002° may be necessary, especially in long-continued experiments. Errors in φ are especially likely to cancel out, partly for the reason given near the end of Section 5, and particularly in the uniform determinations of commercial work. Hence the final error from thermal head error is usually less than would be indicated by the method just presented, of calculating the possible thermal head error by itself. The tendency of errors to cancel out, however, is an uncertain thing. The extra cost involved in making them safely negligible is usually almost trifling in comparison to the total involved in the work done. This applies to other errors beside those from thermal head.

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[1] This seems to be well known, but has been denied by a high authority (Pfaundler, in Müller and Pouillet's *Handbook*, 1907, German edition, Vol. III, p. 177, middle) hence it seems worth repeating.

As to methods of diminishing errors in φ: In the matter of design, it is clear that 5 things are desirable: bringing the jacket completely over the calorimeter; prevention of evaporation from the jacket water; adequate stirring power; simple, wide, and suitably disposed channels for the circulating water; and thermal insulation of the jacket. It is almost impossible at present to give exact specifications regarding these matters; in this laboratory, where propeller stirrers in tubes have been used, we have come to make these from 8 to 13 cm. in diameter, with a preference for the larger size. This gives at least a little advantage in economy of power, and affords a large reserve capacity which is always likely to prove important.

It also seems as if more might well be done, in high class work at any rate, to assure by actual measurement the uniformity of the jacket temperature. Since a thorough measurement is rather difficult, a factor of safety should still be allowed; and the test should of course be made under what seem to be the worst conditions, such as maximum difference from the room temperature, and slowest stirring. Where the jacket temperature is not observed, and must therefore be assumed constant, an attempt to deal definitely with the sources of error calls for an estimate of the effect of a failure of constancy. It is easy to show that if the mean environment varies regularly q degrees a minute and T is the length of each period, the expression $(\theta'x - \theta'a)/(\theta'r - \theta'a)$ in Formula 3, below, becomes: $(\theta'x - \theta'a + qT)/(\theta'r - \theta'a + 2qT)$ from which the error is at once determinable for any estimated or otherwise given value of q, and any given values of the other quantities.[1] For calorimeters water-jacketed at bottom and sides but open to the air, the air may safely be taken as effectively one-fourth of the whole environment, since it will probably be nearer one-sixth. That is, the rate of change of the environment may be put as 0.25 of the air rate plus 0.75 of the jacket rate. Covers of poorly conducting material tend to change about half as fast as the air, but depend on the *previous* air temperature, and are affected also by changes in the calorimeter in a way that renders only determinations of equal period strictly comparable.

With the thermal head, as generally in calorimetry, the resultant error may be affected by the method of conducting the determination, as well as by the design of the apparatus. It sometimes appears to be assumed that any procedure or device which causes a diminution in the total amount of thermal leakage will diminish the thermal leakage error. It seems important to distinguish the cases where this notion applies from those where it is fallacious. With regard to the final error from error in the thermal head, we may readily reach these two conclusions:

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[1] For example, if the calorimeter at the start is at the same temperature as the jacket, if K is 0.003, T, 5 min., θ_x/θ_r 0.8, all customary values, and if q is 0.02 $\Delta\theta$ per minute, or 0.04° per minute for a temperature change, $\Delta\theta$, of 2° in the calorimeter, then the error on account of q is 1.5 per mille.

(A) The final error is seldom diminished by a diminution of thermal leakage which is due to a diminution of the thermal head, for the simple reason that the thermal head *error*, depending mainly on jacket irregularity, etc., will not be much affected, and will be multiplied by KT_x as before. Moreover, the diminution of φ is evidently equally valueless (*as far as this particular error is concerned*) however it is secured, whether by the adiabatic or the improved Rumford method, that is, the method where the calorimeter passes from below to above the jacket temperature in such a way as to make the integrated φ_x nearly zero.

(B) The final error due to thermal head error *is* diminished by diminishing KT_x, since this diminishes the multiplier of the thermal head error. But this is of less importance since usually the thermal head error can easily be made negligible for ordinary values of KT_x. If T_x is very large, say an hour, a reduction of K, as by using a vacuum-jacketed calorimeter vessel, may be very desirable.

2. **The Rate of Temperature Change.**—Although closely associated with the thermal head, the rate V presents the strongest contrast to it as far as amount and character of error are concerned. In careful work the error from the measurement of rate is usually, though not large, yet the largest connected with thermal leakage. The rate is determined by measuring temperature change and time, and also depends on the constancy of the leakage modulus K during the experiment. Inconstancy of K should usually be quite negligible, and is treated in another section of this paper; hence we have to consider here only the measurement of change during the rating periods, which is purely a temperature measurement. The relation of error in this measurement to final error depends on the way the leakage effect is computed, and may be found by aid of Formulas 2 and 3. These formulas are specially arranged for this purpose, but are exactly equivalent to the more convenient formulas used in actual work.[1] The notation is as follows: θ denotes single readings of the temperature, made with maximum precision and used to determine the rate V; φ, mean readings of thermal head for a period of time, made with less precision, θ', readings of calorimeter temperature of corresponding use and precision, T, the number of minutes in any observation period. The period is the time between two readings. If 3 periods are run, there are 4 of the θ readings. The first, anterior, or auxiliary rating period (subscript a) extends from θ_1 to θ_2, the X-period from θ_2 to θ_3, the regular rating period from θ_3 to θ_4. In Formula 2 the a-period is omitted so that θ_2 is the first precision reading. w is the total constant rate independent

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[1] If an exact knowledge of the derivation of these formulas is desired and proves not readily deducible from the usual forms, the presentation given in "Some Calorimetric Methods," Walter P. White, *Phys. Rev.*, **31**, 546–9 (1910), may prove helpful. The subscripts have here been changed.

of φ, as a rule largely or wholly due to the heat of stirring. The thermal leakage effect is η. Formula 3 is identical with the Regnault-Pfaundler formula, the one most used.

$$\eta = T_x\{(w(1 - (\varphi_x/\varphi_r)) + ((\theta_3 - \theta_4)/T_r) \times (\varphi_x/\varphi_r))\} \qquad (2)$$

$$\eta = T_x\{((\theta_1 - \theta_2)/T_a)\ (1 - (\theta'_x - \theta'_a)/(\theta'_r - \theta'_a)) + \\ ((\theta_3 - \theta_4)/T_r) \times ((\theta'_x - \theta'_a)/(\theta'_r - \theta'_a))\} \qquad (3)$$

The effect η is here given in terms of the original temperature observations. For (2), w must be known, as well as the environing temperature. (2) is evidently only (1) with an added term for w; (3) is (2) with a substitute for w and a substitute for φ in terms of θ'.

Since the accurate temperatures θ enter in pairs their systematic errors tend to cancel; the only errors remaining in them may be taken as accidental, with the possible error about the same for each observation. Consider, first, that all periods are, as usual, equal in length, in which case the T's cancel out. Then in (3) if θ'_x is nearly equal to θ'_r, the multiplier of $\theta_1 - \theta_2$ is near zero, and we have only the errors of the two readings θ_3 and θ_4, each multiplied by approximately unity. If θ'_x becomes less than θ'_r the multiplier of $\theta_3 - \theta_4$ diminishes, and with it the effect of the errors in θ_3 and θ_4, but the multiplier, and effect, of the errors in $\theta_1 - \theta_2$ evidently increases at exactly the same rate. Hence:

(A) For equal periods with the Pfaundler method, regardless of the value given to θ'_x (or φ_x), the possible final accidental error from error in the rating measurements remains that of two final temperature observations. That is, the determination of the leakage effect about doubles the possible thermometric error of the whole determination. It follows that with the customary formula (3) the improved Rumford method, by which the calorimeter is started at so low a temperature as to make θ_x', or φ_x, nearly equal to zero, and which is often supposed[1] to also diminish the error connected with η, is quite without effect in diminishing the final effect of the important errors in measuring the rate V, as we have already seen it to be with the final effect of the errors in the thermal head. Moreover,

(B) The final error from measuring V, contrary to the thermal head error, is, in general, not in the least affected by changing K or T, since the separate errors of θ_3 and θ_4 are not affected by the value of the difference $\theta_3 - \theta_4$.

There are, however, several ways of diminishing the final effect of the error in measuring V.

(C) If Formula 2 is used, diminishing φ_x does diminish that final error, though it increases the possibility of an error from using an incorrect value of w, corresponding in the formula to the $\theta_1 - \theta_2$ error of (3). With

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[1] This device appears to have been rather widely used. It has been recommended by very high authority.

φ_x nearly equal to φ_r the result by this formula is really almost independent of the knowledge of w. (Of course w must be constant during the experiment in all cases, with (3) as well as (2).)

(D) If the times T_a and T_r of the rating periods are made greater than T_x the errors in the θ's are multiplied by a proper fraction and thus their effect is diminished. The main objection to this procedure is its tediousness.

(E) If K is constant from day to day it can be measured once for all and very carefully. No rating periods will then be needed with each individual determination, and instead of their errors there will be merely the error of the very careful determination of K. Of course this method, like C, just above, demands also an accurate knowledge of the constant rate w, and of the jacket temperature.

The maximum possible gain from any of these schemes is only to cut in two the total accidental thermometric error.

Method E is of interest in commercial work, where it is valued rather as a time saver than with any great concern as to its possibilities in the way of accuracy. It has been used with accurate[1] results at the Bureau of Mines laboratory in Washington, with the jacket made a thermostat and the calorimeter initially at the same temperature as the jacket. This procedure brings the advantage that, used with the very uniform combustion determinations which form the bulk of this (and of most commercial) work, it makes the curve of temperature rise during the X-period have always the same shape, so that φ_x, and therefore the leakage effect itself, bear always the same ratio to the main temperature change $\Delta\theta$, whence the leakage effect is merely a constant correction to $\Delta\theta$, and requires no special attention whatever.[2] This last scheme is rather a labor saver than a time saver. It appears to necessitate a practical suppression of evaporation. It is congenial to the usual type of resistance thermometer installation, which is relatively poorly adapted to the measurement of rapidly changing temperatures such as come in the first part of the X-period. If instead of starting with calorimeter and jacket together the improved Rumford method is used (still omitting the rating periods), K does not need to be very constant, so that accuracy may be greater, but observing must now be done during the X-period. The necessity for the thermostat is also avoided, but if the demands of economy are not too

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[1] The very high precision quoted in *J. Franklin Inst. Op. cit.*, p. 282 proves to have been exaggerated. The maximum disagreement was 1 per mille in the best work, but this is satisfactory in view of commercial demands, and of the quickness with which the observations can be made. ("A Convenient Multiple-Unit Calorimeter Installation," J. D. Davis and E. L. Wallace, Bureau of Mines, *Tech. Paper* 91, p. 45).

[2] Of course this condition should never be assumed without experimental tests. If the calorimeter is too far from following Newton's Law of Cooling a slight correction will be needed for different values of $\Delta\theta$.

rigorous the use of a thermostat is one of the easiest ways of caring for the jacket temperature, and also simplifies temperature adjustments generally.

It is easy to show that:

(F) The adiabatic method usually saves the labor of one rating period, but does not materially affect the precision as far as the rating error is concerned. For if w is not known there must be a rating period with the errors of two θ's, as with other methods. If w is known there is no rating period error at all, but neither is there when Formula 2 is applied to the improved Rumford method. The number of rating periods is one or none, against two or one for similar conditions without the adiabatic method, except that with constant K (method of (E) above), there is also no rating period. The method of (E) with K constant, with a thermostat, is less expensive and easier in operation than the adiabatic, and, while probably not capable of as great precision, has proved itself more than precise enough for commercial work.

3. **Error from Variation in the Thermal Leakage Modulus** K.—If K varies during an experiment, it is obviously best to diminish as far as possible its multipliers, φ and T. This is a case where diminishing the thermal head φ may diminish error. There is, however, seldom any reason to fear that this variation of K will come from change in the calorimeter or jacket. A failure of the calorimeter to follow Newton's Law of Cooling is practically a variation in K. This has been fully discussed elsewhere,[1] and the conclusion drawn that to avoid such variation the adiabatic method is to be recommended for protracted determinations.

The question whether K varies from day to day is important, if it is desired to omit rating periods, gaining speed, and often precision also. Some of the very best work has been done with K varying 1 or 2% from day to day, and I do not know that anything better has been reported for an ordinary fluid calorimeter. A variation of 1%, though, is not incompatible with a concordance of 0.2 per mille between *short-period* determinations. The highest precision has been obtained by measuring K each time, or by the adiabatic method.

4. **Lags.**—Lags have been already treated in another paper. As general rules for them, comparable to the rules already given for φ, V and K, we have:

A. The error depends on the variability of the lag.

B. It varies with K if the lag is not external.

C. It is independent of time, T, and thermal head.

D. The lag effect in degrees or calories is proportional to the temperature change $\Delta\theta$, hence the proportional error is independent of $\Delta\theta$.

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[1] Walter P. White, "Thermal Leakage and Calorimeter Design," THIS JOURNAL, **40**, 379 (1918).

5. The Constant Rate and the Heat of Stirring.—The rate w of Formula 2 which is eliminated in (3) without appearing explicitly, may consist of two different parts. One, the heat of stirring, will always be present, except in aneroid (fluidless) calorimeters. The error in it comes from its variations, which may be due to (1) a variation in the amount or viscosity of the calorimeter fluid or to (2) a variation in speed of stirring. (1) Variations in the fluid are, in general, special matters, though change of temperature always causes a change of about 2% per degree at ordinary temperatures in the viscosity of water; what effect this has on the heat of stirring at constant *propeller* speed appears to be unknown. The very small effects from these changes tend to be eliminated in finding the leakage effect, whether by (2) or (3).[1] Changes in fluid character occurring from day to day evidently conflict with methods of securing rapidity or precision which depend on accurate knowledge of w.

(2) The heat produced by stirring varies as the cube of the speed; the rate of temperature equalization, the object of the stirring, varies about as the first power of the speed. It follows that a variation of 1% in speed makes an error of almost 3% in the heat; a halving of the speed reduces the heat and the error from a given proportional change in speed to $^1/_8$ of their first values. This rapid variation of error with speed renders it easy to state a practical rule for speed of stirring. Make the stirring so slow that the error of its variation is safely negligible. Nothing is gained, and effectiveness of temperature equalization is lost by decreasing speed after this. An increase of speed brings danger of heating error more rapidly than it brings better equalization. Of course effectiveness of equalization can not be exactly defined, nor is it altogether easy to measure. Hence it is probably well to take as a working rule the consensus of such experience as is available, which indicates that stirring is sufficient if the rise is 0.001° a minute in a well-designed calorimeter holding 1 or 2 liters. But this evidently demands a speed constant to $^1/_3$% for a precision of 0.0001° if the period is 10 minutes, hence for this performance, and still more for higher precision or longer time, closer figuring will be necessary. Indeed, for high precision the stirring seems to present the hardest problem there is. Either of two procedures will usually be adequate. (*a*) Suitably governed motors are readily obtainable which are good to 10 times the precision of $^1/_3$%, and better than this is known to be possible. With due precautions against error from the slipping of belts such a motor should be more than sufficient in most cases. (*b*) If the leakage modulus K is made a little less than half of its usual value

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[1] It is easy to show that the temperature effect is eliminated always with (3); with (2) if φ_x nearly equals φ_r; and with (2) also if w is determined at the jacket temperature; that changes occurring near the beginning of the X-period are eliminated with both (2) and (3) if φ_x nearly equals φ_r, and with (2) anyway, if w is determined as the later value.

the error from an irregular surface temperature decreases similarly, and with it the necessary speed of stirring. Thus the heat can be made ten times smaller, which decreases the error without requiring greater constancy in speed. In this way it might be possible to get with a synchronous motor, constant to 2%, a precision which would otherwise require a governor. To be sure the experimenter will seldom know definitely how much equalization he is getting or how much he needs, but the gain will be there, whether he can identify it or not. We have the same right to say that a heat of stirring of 0.0002° per minute means satisfactory speed for a calorimeter whose leakage modulus has been reduced nearly to half value by a convection or "radiation" shield[1] as to say that 0.001° was satisfactory in the first place.

A decrease in the modulus has this advantage over an increase in constancy of rate, that it diminishes the effect of all changes, such as changes in viscosity, which affect the heat for a given speed. This is evidently especially important where it is desired to be sure of the constancy of w from day to day.

Of course the design of the calorimeter should not be neglected. According to E. F. Mueller[2] a propeller stirrer in a tube gives the least heat, in proportion to the equalization accomplished, of any stirrer now in common use. The exact design of the propeller is probably of secondary consequence, but throttling of the stream is important. For the same flow of water the heat is, ideally, 9 times as great in a tube of $^1/_3$ the diameter. It is therefore easily possible that by the somewhat heedless use of too small a stirrer tube the heat of stirring might be increased 8-fold or more, enough to offset what is in many cases the main advantage gained by a convection or "radiation" shield or even by use of a vacuum jacket.

Speed and effectiveness of circulation are so difficult to measure exactly that, presenting as they do no special problem in ordinary work, they have received less attention than their importance in precision work demands.[3]

We have, as general conclusions:

For a given effectiveness of temperature equalization the stirring error:

(A) Varies as K^3T.

(B) Depends on the design of the calorimeter.[4]

(C) Is independent of the thermal head.

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[1] "Thermal Leakage and Calorimeter Design," *Op. cit.*, p. 391.

[2] Quoted by Dickinson, p. 194; "Combustion Calorimetry, Etc.," Bur. Standards, *Bull.* **11**, 189 (1915).

[3] Cf. T. W. Richards and L. L. Burgess, "The Adiabatic Determination of the Heats of Solution of Metals in Acids," THIS JOURNAL, **32**, 446 (1910); also Walter P. White, "Lag Effects and other Errors in Calorimetry," *Phys. Rev.*, **31**, 575 (1910).

[4] For a discussion of the relation of size to stirring error, see "Thermal Leakage, Etc.," *Op. cit.*, p. 386.

(D) Like φ and V errors, and unlike the lag errors, is not much affected by the amount of temperature rise, and thus becomes more serious as the heat quantity measured is smaller.

The constant rate w may be defined as that rate which persists when the thermal head is zero. That part of it not due to heat of stirring may be due to evaporation in calorimeters open to the air; otherwise to error, as from faulty measurement of φ, the thermal head, or from leakage through the jacket along copper lead wires, etc. Since these effects, *if constant*, are eliminated by the use of the Pfaundler method (Formula 3) or by the method of (2) if $\varphi_x = \varphi_r$ nearly, it may be said to be one of the advantages of these methods that they eliminate certain errors. If other methods, such as that of 2 (E), above, are desired, more care must be taken with φ.

6. Evaporation.—Evaporation offers an admirable opportunity to anyone wishing to show how unnecessary precautions in calorimetry can be avoided with safety. There are in the literature very few statements as to the separate effect of evaporation, and apparently none as to its possible variation under different conditions or as to the probable error chargeable to it.

Evaporation fails, in two ways,[1] to follow the law, leakage $= a + b\varphi$, which is usually assumed in thermal leakage calculations, and is also especially liable to irregularity and uncertainty if conditions are not carefully controlled,[2] while its thermal effect is usually a very large fraction of the total leakage. Hence in work of very high precision evaporation has usually been suppressed, though such suppression is so inconvenient that there has been a strong tendency to let evaporation occur and treat it as sufficiently regular for the particular case in hand. Two things can contribute considerably toward making easier the prevention of evaporation; one is the use of stirrers (such as propellers) with rotating shafts, the other, the use of metallic covers, as elsewhere described.[3] Some other points regarding evaporation have recently been briefly stated in THIS JOURNAL.[4]

7. Leakage through the Jacket.—The leads of electric thermometers or heaters, and half the wires of a thermoelement, are usually of good conducting copper, and usually run from the outside air through the jacket

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[1] It may cause the total leakage to vary by 30% if φ changes sign (see, *e. g.*, Richards and Burgess, *Op. cit.*, p. 449; "Thermal Leakage, Etc.," *Op. cit.*, p. 381); and even if φ is kept positive throughout, evaporation can readily be shown, for jacket at 20°, to follow approximately the formula P $(1.13\ \varphi + 0.03\ \varphi^2)$ where P depends on the geometrical dimensions and will often be 0.3 K.

[2] Walter P. White, "Specific Heat Determination at Higher Temperatures," *Am. J. Sci.*, Jan., 1919.

[3] "Calorimetric Lag," *Op. cit.*, p. 1863.

[4] "Thermal Leakage, Etc.," pp. 381 and 390.

wall to the calorimeter, so that they may produce an effect which is due to the room temperature, and not taken account of in the thermal head measurement. Metal stirrer rods may also act in this way, but need not; in general the effect is one characterizing electric arrangements, and important only on account of the high precision which these make possible. It tends to behave as part of the constant rate *w*, just treated, but may cause error if the room temperature changes; it is an obstacle to operating with invariable leakage modulus, *K*, which involves a rate, *V*, proportional only to thermal head, φ; and it interferes more or less with the testing of *K* which is almost certain to be sometimes needed in careful calorimetric work. It therefore seems worth while to indicate how the order of magnitude of this effect can be determined.

The flow of heat along a wire is defined by the parameter $\mu = \sqrt{KA/\epsilon P}$, where *KA* is the conductance, equal to conductivity, *K*, times area of cross section, *A*, and ϵP the emittance per cm., or emissivity, ϵ, times perimeter, *P*. For a wire running X cm. from an infinite body at temperature θ_0 to another at θ_2 through a medium whose temperature may be taken as the zero, if the zero of coördinates is at the junction with the body at θ_0, the temperature at any point is, from a well-known equation:

$$\theta = (1/(e^{\mu X} - e^{-\mu X}))\{\theta_0(e^{\mu(X-x)} - e^{\mu(x-X)}) + \theta_2(e^{\mu x} - E^{-\mu x})\} \quad (5)$$

and the flow of heat at any point is *KA* times the derivative of this or

$$KA\,(d\theta/dx) = (KA\mu/(e^{\mu X} - e^{-\mu X}))\,\{-\theta_0(e^{\mu(X-x)} + e^{\mu(x-X)}) + \theta_2(e^{\mu x} + e^{-\mu x})\} \quad (6)$$

If 2 wires with different μ are in series between θ_0 and θ_2, if we introduce the condition that at their junction point the flow is the same in each wire and solve for the temperature of that point, we find it to be:

$$\theta_i = \frac{2\mu\, KA\theta_0(e^{\nu Y} - e^{-\nu Y}) + 2\nu K'A'\theta_2(e^{\mu X} - e^{-\mu X})}{\mu KA(e^{\mu X} + e^{-\mu X})(e^{\nu Y} - e^{-\nu Y}) + \nu K'A'(e^{\nu Y} + e^{-\nu Y})(e^{\mu X} - e^{-\mu X})} \quad (7)$$

with the aid of which all temperatures along the compound conductor can be determined. ν, *Y*, *K'* and *A'* are used for μ, *X*, etc., of the second wire.

It will be sufficient to treat the case where θ_2 is at the same temperature as the air, that is, at zero, and where the wire is the same, but μ differs on account of the medium. The *KA*'s then cancel out. The simplified Equation 7 then can conveniently be written:

$$\theta_i = 2\theta_0 \cdot \frac{(e^{\nu Y} - e^{-\nu Y})/\nu}{(e^{\mu X} + e^{-\mu X})(e^{\nu Y} - e^{-\nu Y})/\nu + (e^{\nu Y} + e^{-\nu Y})(e^{\mu X} - e^{-\mu X}/\mu)} \quad (8)$$

and by substituting this in (6) for θ_2 or for θ_0 with $\theta_2 = 0$ the heat flow at any point can be found.

We may consider first a copper wire of 1 mm. (No. 18), for which $KA = 0.0075$, nearly. The radiation from a wire of this size, even with a black surface, is a small part of the conduction-convection loss in air, so that the character of the surface does not much matter. In the open air we may apply Langmuir's empirical rule, that the heat loss is equivalent to that passing to a perfect conductor through a 4 mm. layer of still air. This makes ϵP roughly 0.0002 c. g. s., and μ therefore 0.16. Where the wire goes through the jacket we may (1) suppose it to run between two copper plates, tangent at opposite ends of a diameter, separated by well-shellacked silk insulation 0.1 mm. thick, whose thermal insulation can be neglected in comparison with the air. A rather rough approximation based on the geometry of the air space then gives 0.0018 for ϵP, or 0.48 for ν. (2) If we suppose a flat strip of the same sectional area 0.1 mm. thick and therefore 8 mm. wide, insulated by mica of here negligible thermal resistance, but with equivalent air gap 0.2 mm. thick, due to imperfect fitting, P is 0.004 and ν 0.73.

In determining the heat conducted to the calorimeter we may first find the temperature of the wire where it leaves the jacket for the outside air. It is easy to show by trial for the values of μ and ν just given that if the distance X in the air is not less than 20 cm., and in the jacket wall not less than 6 cm., either wire behaves regarding its initial temperature nearly enough as if it were infinitely long. For an infinite wire the equation is: $\theta = \theta_0 \, e^{-\mu x}$ so that $d\theta/dX$ at the beginning of the wire ($x = 0$) is $-\mu\theta_0$. Hence, by putting the initial flow equal in both wires we find that the difference of temperature between wire and jacket is $\mu/(\mu + \nu)$ times the jacket-air difference, or about $0.16/(0.16 + 0.48)$, or $^1/_4$ of it, in the worst case here supposed, and nearly $^1/_5$ in the other, where a strip continues the wire. In calculating the effect of this initial temperature we may preferably take the calorimeter at the temperature of the jacket, since the effect of any difference between them will count as part of the ordinary thermal leakage of the calorimeter; it is only the effect of the room outside that we are now seeking. Equation 6 therefore applies, modified by use of (8), and yields the following results in different cases:

Heat flowing to the calorimeter in 10 minutes per degree difference of air and jacket:

Through	6 cm. No. 18 wire between plates	+ 2 cm. air inside........	0.03 cal.
	6 cm. No. 18 wire between plates	+ 6 cm. air inside........	0.012
	12 cm. No. 18 wire between plates	+ 2 cm. air inside........	0.0017
	6 cm.	air only.............	0.33
	6 cm. flat strip	+ 2 cm. air inside........	0.0061

In the last two cases the initial temperature on the wire was not taken at $^1/_4$ the room-jacket difference, but $^1/_2$ or $^1/_5$ of it, respectively. The strip is supposed to be continued by a wire in the outer air. Some of the heat lost through the inner air gap goes to the calorimeter, but this is a minor effect.

It is clear that under proper conditions a pair of No. 18 copper wires will not conduct enough heat through a jacket to cause appreciable error, but the thermal contact with the jacket may easily be worse than that here supposed. A flat strip rolled around a copper rod or tube, with shellacked silk between, gives a better thermal contact than that assumed here, and gives it very easily.

The 6 cm. of air alone comes rather near to being the condition prevalent in the stem of the Dickinson-Mueller calorimetric resistance thermometers, which have at least three No. 20 wires, about equivalent to two No. 18. Hence it is clear that very appreciable amounts of heat will often be conducted along these thermometers unless precautions are taken against it. This does not necessarily imply that the temperature reading of the thermometer will be directly affected appreciably. The 50 wires of a 24-junction thermoelement usually have, all told, less than half the thermal conductance of a single No. 18 wire, and of course their heat emitting power per cm. of length is very much greater. Hence it appears that a thermoelement can safely be used under any but the most exceptional conditions, if the precaution be taken of running it 6 cm. or more in approximate contact with the jacket. This conclusion has been directly supported by experiments in this laboratory.[1] A 24-couple element inclosed in a glass tube 5 mm. in diameter, which made a barely easy fit in a brass tube 6 cm. long, ran from a submarine, vacuum-jacketed calorimeter to an ice bath. The thermal head was zero, the stirring too slow to produce appreciable change of temperature. In one case, with the room 6° colder, the temperature read constant to 0.00005° for 4 hours, changing 0.0002° in the next two hours. Another trial showed a fluctuation of 0.00015° in an hour, though without final change. A more certain indication, perhaps, is offered by the result when a 96-junction thermoelement was also inserted in the same calorimeter, for the value of $K\mu$ with this was 6 or more times that with the smaller one, and effects from other causes were consequently less likely to falsify the results. The change was now 0.0001° (0.1 calorie) in 10 minutes per degree of air to bath temperature difference, which corresponds to less than 0.02 calorie with the smaller thermoelement. (When this larger thermoelement was itself used for reading to 0.000012° in a calorimeter holding only 200 cc. it was covered with a carefully fitted "straddler," or sheet copper cover dipping in the jacket water, thus virtually bringing the whole thermoelement inside the jacket.)

Summary and Reclassification of Conclusions.

In a calibrated calorimeter practically all the errors come in temperature measurement, and the most, though often not the greatest of these come

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[1] Due to Mr. E. R. Edson of the Mellon Institute of Industrial Research.

in the "cooling correction," that is, the determination of the effect of the thermal leakage between calorimeter and environment.

This leakage effect is equal to $K\varphi_x T$, where T is time, φ_x is the thermal head (difference of calorimeter and environment temperature) for the experimental period, and K the thermal leakiness, or leakage modulus, of the calorimeter. If any of these three quantities is diminished its own errors are usually little changed, but the errors of the others now have a smaller multiplier. Thus:

1. By diminishing K (as by means of a vacuum) we diminish the effect of errors in φ_x, which lie (*a*) in getting the environing (jacket) temperature sufficiently uniform, (*b*) in getting the calorimeter temperature uniform without too great an error from heat of stirring. This latter difficulty grows in importance as measurements become more delicate. Usually, errors in φ may easily be made negligible, and great diminution of K is then of secondary importance.

2. A diminution in φ, as by the adiabatic method, or by methods similar to that of Rumford, diminishes the effect of errors in K, such as variation from Newton's law. But owing to the peculiarities of the computation, it does not much affect the main error connected with K, that in determining K by means of the cooling rate, unless methods can be used which presuppose an accurate knowledge of the heat of stirring. For this and other reasons, the diminution of φ, though the commonest of operative devices, is in practice largely illusory as far as concerns the end chiefly sought. The determination of K generally results in about doubling the accidental *thermometric* error, but this is usually the largest thermal leakage error there is in well-planned work. This error can be diminished by devices, some of which are adapted to commercial work and which save time as well as error.

3. Lags have a law of their own; they usually vary with K, are independent of T and φ, and can usually be made to cause little or no error.

4. The stirring introduces a possible error from irregular heat production, due to irregular speed. Since the heat varies as the cube of the speed, the error tends to vary as the cube of the efficiency of stirring, and thus may become very important in delicate measurements. A remedy can usually be found by controlling the speed, or, more effectively, by diminishing K, as already noted. The type of stirrer, and the design of the calorimeter with reference to stirring, may be very important.

Evaporation is also touched, and a discussion is given of the error from heat flow along wires or rods.

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