formulas make the gyroscopic properties exactly those of a magnetically equivalent orbital electron of the classical type, and therefore exactly those required by the Barnett and Einstein-de Haas effects. This makes it highly probable that the elementary magnets of ferromagnetism, and probably of paramagnetism and chemical bonds also, are really magnetons.

Thus it appears that we can class the magneton hypothesis not as an assumption made a priori, but rather on the surer basis of a most probable deduction from the experimental facts. As such it cannot be lightly tossed aside even if the assumptions that go with it are somewhat complex. Consequently it seems probable that the alpha ray phenomena should not be taken as valid evidence against the magneton theory, but simply as evidence for the existence of the nucleus along with its non-electrical repulsion for magnetons.

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THERMAL LEAKAGE AND CALORIMETER DESIGN.

BY WALTER P. WHITE.

Received November 15, 1917.

In measuring a quantity of heat in a calorimeter most of the care and time expended is usually demanded, directly or indirectly, on account of the thermal leakage, or interchange of heat between the calorimeter and its environment. Most of the ingenious devices which lend interest to calorimetry have been introduced, wholly or in part, in order to deal with this leakage. And yet until very recently there have been almost no quantitative data upon the effect of the air gap around the calorimeter, although the thickness of this gap, more than anything else, determines the rate of the leakage, and hence the efficiency of any method of dealing with it. As a result it has happened, almost inevitably, that some of the most skilful and carefully planned researches have been conducted with air gaps whose needlessly small dimensions caused an excessive thermal leakage, and so multiplied several times the leakage difficulty or error. One of these researches, for instance, although it incidentally included investigations which led to important improvements in calorimetric method, was yet made with a gap so small (3 mm.) that a change to better dimensions would have brought all the reduction of the leakage and its errors that is obtained by substituting the frail Dewar bulb for a well-designed simple calorimeter. And two very recent articles specially describing improvements in method make mention of air gaps so small (5 and 6 mm.) that they probably neutralized in the apparatus described the advantages gained. On the other hand, in this laboratory a special method dealing with inconstant leakage rates was developed and used, at the cost of considerable labor and inconvenience, for three years, which would have been needless if the air gap around our calorimeters had not been too large.

Within a few months investigations, begun independently at the Bureau of Standards[1] and at the Geophysical Laboratory,[2] have been published bearing on thermal flow in air spaces such as usually surround a calorimeter, which seem to make it now possible to handle thermal leakage with a reasonable approach to maximum effectiveness. The present paper deals with the problem of doing this.

The most important means of reducing the uncertainties due to thermal leakage is undoubtedly a definite control of conditions, such as is secured by proper jacketing, or by preventing evaporation. The last word has not been said regarding such measures, but as far as they are concerned there has been little doubt in which direction efficiency lay, and they are not in view in the present paper, which deals with the effect of the air space around the calorimeter.

It has already been pointed out that a gap of too small dimensions means an insufficient amount of insulating air around the calorimeter. The increase of insulation from an increase in the gap, however, though considerable at first, soon falls off, and before long a minimum point appears beyond which the leakage rate actually increases. But even before this point is reached another difficulty is encountered; the leakage ceases to be sufficiently nearly proportional to the *thermal head*, or temperature difference between the emitting and the receiving surface. That is, Newton's Law of Cooling, on which nearly all methods of treating the leakage are based, fails to hold. The advantage of the law is merely its simplicity; a different law can be made to give satisfactory accuracy even over 20° intervals.[3] But there is little doubt that most experimenters would very greatly prefer to retain the simpler methods; moreover, the point of minimum leakage ordinarily is not so very far beyond the point where the variation from Newton's Law becomes troublesome, so that the experimenter will gain but little who disregards the variation from the law in endeavoring to get the absolute minimum of leakage. It therefore seems best in this paper to take a following of Newton's Law as one of the requirements which is to be met in deciding upon the size of air gap.

Transfer of heat through the air may occur by radiation, conduction, convection, and evaporation, and in connection with these it seems best

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[1] "The Testing of Thermal Insulators," H. C. Dickinson and M. S. Van Dusen, *A. S. R. E. Journal*, **3**, 5 (1916).

[2] "Heat Convection in Air, and Newton's Law of Cooling," Walter P. White, *Phys. Rev.*, 10, 743 (1917).

[3] See, *e. g.*, "Some Calorimetric Methods," Walter P. White, *Phys. Rev.*, **31**, 553–557 (1910).

to consider the heat capacity of the air. Of these various things we may say at once, with sufficient accuracy for all practical purposes:

1. The heat capacity depends on the amount of air alone.
2. Radiation depends on the area of the calorimeter surface, and on the character of that and the surrounding surfaces.
3. Conduction depends in a known way on the dimensions of the air layer.
4. Evaporation presents two aspects: there may be, first, a change in the saturation of the air space, which is avoided only by preventing evaporation altogether, and second, distillation, which is avoided in the strictly adiabatic method, and also (T. W. Richards) by keeping the calorimeter always colder than the environment.

Of all these factors, evaporation is the most uncertain. It may vary with the actual temperature, with the temperature difference of calorimeter and environment, and with the geometry of the air space, and is very sensitive to the presence of films on the surface of the liquid. Its effects are liable to considerable lag. It causes the cooling to follow an altogether different law if the thermal head (temperature difference) changes sign.[1] The safest and also the simplest way to proceed is of course to prevent evaporation, unless doing so brings greater disadvantages.

The other factors show practically no lag, and no uncertainties not chargeable to imperfect knowledge of the temperatures concerned.[2] They do show, however, a variation from Newton's Law, that is, a lack of strict proportionality between leakage and thermal head, which next demands examination.

It follows readily from familiar laws, and with far greater accuracy of approximation than is needed in practical calorimetry, that for a given mean temperature radiation and conduction are simply proportional to the thermal head, but that with increasing mean temperature of the two surfaces concerned radiation increases about 1% per degree at room temperatures, and conduction 0.0017 per degree. It therefore follows that: (1) if the mean temperature changes from day to day or from season to season the thermal leakage will bear a different ratio to the thermal head, that is, to the interval; but this will ordinarily not interfere with the cus-

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[1] "The Adiabatic Determination of the Heats of Solution of Metals in Acids," T. W. Richards and L. L. Burgess (THIS JOURNAL, **32**, 449 (1910)).

Measurements made in our laboratory by Mr. E. R. Edson, of the Mellon Institute, show that for a free water surface 1 cm. below the top of the calorimeter chamber the excess heat transfer with jacket colder will be about 0.01 calorie per minute per square cm. for 1° of thermal head, corresponding to a variation of about three-tenths in the thermal leakage of an ordinary calorimeter holding about a liter, with 1 cm. gap. It involves 1 mg. per *hour* per sq. cm. per degree.

[2] Radiation will, of course, vary with the cleanness or chemical condition of the surfaces. But it is not likely to change from these causes *during a determination*.

tomary calculation of the "cooling correction" by assuming Newton's Law;[1] (2) for constant environment (*i. e.*, constant jacket temperature) during an experiment, where any given change in the calorimeter evidently produces half as much change in the mean temperature of both, the heat leakage from conduction and radiation will not be proportional to the interval and the variation from proportionality will be for a given change in the interval half as great as that stated above for a variation in the mean temperature.

This variation from Newton's Law is clearly inevitable, but it is fortunately very small. For both these reasons it may here be dismissed without further consideration.

With regard to convection the situation is very different. In convection we have the motion of bodies of air whose temperature differences are proportional to the differences between the solid surfaces. But the velocities of these air currents will evidently also increase with this temperature difference. Hence the heat transferred will increase more than in proportion to the temperature difference. During every calorimetric determination where the temperature difference of calorimeter and environment varies appreciably (as it usually does) the convection transfer will vary by a large part of itself, and Newton's Law will hold for the whole transfer only if the convection is relatively small. The problem of securing a constant ratio of thermal leakage to temperature difference in calorimetry

TABLE I.

Heat transfer, in the usual cgs unit, *i. e.*, calories per second per degree of thermal head per sq. cm. of flat surface, at 22.8° *mean* temperature.

Where two values are given they show the range among determinations with different methods of getting the temperature of the outer plate. It will be seen that the value of the convection is practically unaffected by this difference of method.

Thermal head.	8 mm. gap.		12 mm. gap.		24 mm. gap.	
	Total.	Convection.	Total.	Convection.	Total.	Convection.
0.99°	....	....	0.0000839	.....	0.000065	....
			0.0000848	.....	....	....
1.98°	0.000109	....	0.0000840	0.0000001	....	....
	110	....	0.0000852	0004	....	....
4.95°	0.000111	0.000001	0.0000866	0.0000028	0.000090	over
	....	....	881	0037	....	0.000025
9.89°	0.000112	0.000003	0.0000937	0.000010	0.000106	over
	113	003	952	0.000011	....	0.000040
19.76°	0.000116	0.000007	0.0001077	0.000024	0.000126	over
	....	....	1094	026	....	0.000060

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[1] This variation, however, should have been taken account of in a previous paper of mine, where I discussed the possibility of computing the cooling correction from a known value of the heat leakage ratio. ("Lag Effects and Other Errors in Calorimetry," *Phys. Rev.*, **31**, 577 (1910).)

is then, practically, the problem of diminishing convection. The difficulty of this problem lies in this: convection increases with the thickness of the air layer between calorimeter and jacket, and is thus made larger by the very same procedure which diminishes the conduction and therefore tends to diminish the total thermal leakage. The designer of a calorimeter must therefore strike a balance between opposing advantages, and will want to know how thin to make the air layer in order to just avoid undesirable convection without unnecessarily increasing conduction.

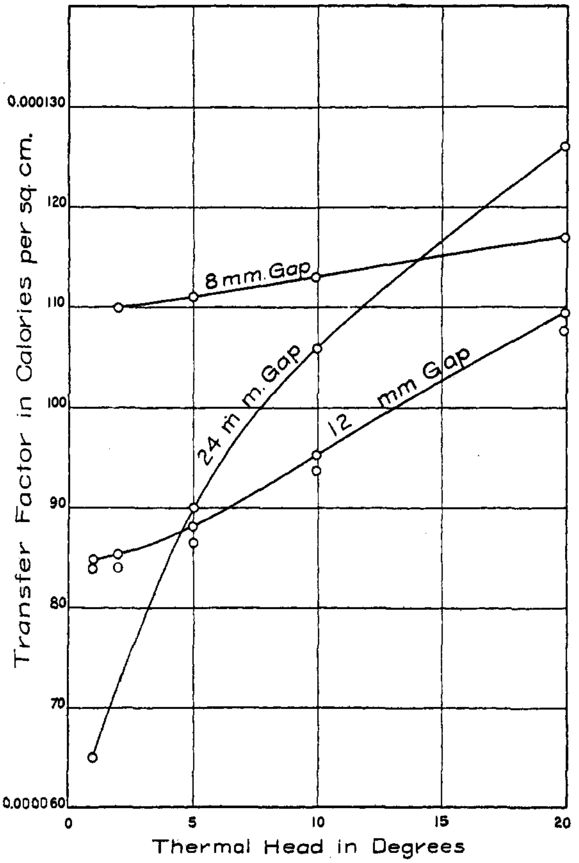

Fig. 1.—Rate of heat transfer through the air for different widths of air gap between plates 8 cm. high.

Table I and Fig. 1, taken from the paper on convection in air already referred to, show the actual values of convection for the calorimetric range and for spaces 8 cm. high. These values are probably a little high, perhaps 10%, but this uncertainty is less than others present in convection phenomena, and does not impair the practical value of the results. These results, for narrow gaps, follow fairly well the laws, obtained theoretically: (1) The total convection heat transfer is independent of height, that is, the transfer per sq. cm. is inversely proportional to height. Convection heat transfer is proportional (2) to the square of the temperature difference, and (3) to the cube of the gap width. As the temperature difference increases there is a tendency for the transfer to increase more rapidly than according to (2), which appears clearly in the 12 mm. gap results; with still more vigorous convection the increase with temperature grows less, as appears with the 12 mm. gap for 20° thermal head, and very markedly with 24 mm. These variations from the simple laws are probably due to the development of turbulence. The quantity actually shown in Fig. 1 and Table I is not the the total heat transfer, but is the heat transfer factor, or transfer per unit of thermal head (temperature difference) which is constant when Newton's Law holds.

1. Width of the Air Gap around the Calorimeter.

For the present purpose, the most significant thing about convection is that it varies about as the cube of the gap width. From this fact it follows that large changes in convection can be made at the cost of slight ones in conduction. Hence comes the practical rule; make the width small enough to render convection negligible and stop there; to go any further will only increase conduction; to go in the opposite direction will increase convection rapidly while giving only a slight gain in decreasing conduction. What is necessary to make convection practically negligible depends on the required precision, the time, and the temperature range, and can be estimated for given conditions. Such an estimate can be made as follows: In the first place it has been shown[1] that in the most unfavorable case an unregarded deviation from Newton's Law produces an error in the thermal leakage allowance (cooling correction) about equal to one-sixth of an allowance calculated by taking the deviation alone as the cooling rate—that is, about equal to $^1/_6 Tk' \ \Delta\theta$, where T is the time, $\Delta\theta$ the change in calorimeter temperature, and k' the change in the leakage factor due to the change $\Delta\theta$. In nearly all cases likely to occur in practice the error is much less than half that given by this rule, so that by taking $^1/_6$ as the numerical coefficient we are allowing a large factor of safety. If, now, we suppose that the high precision of 0.1 per mille is sought, that is, a precision of 0.0001 $\Delta\theta$, the maximum allowable variation from Newton's Law will be such as to make $^1/_6 Tk' \ \Delta\theta$ equal to 0.0001 $\Delta\theta$ and this, for a 10-minute interval, gives k' as 0.000001 per second. If we suppose, further, that the calorimeter holds a liter, its surface will be around 600 sq. cm. or 0.6 sq. cm. for each gram of water, so that the allowable variation of 0.000001 per second will be 0.000001 per 0.6 sq. cm., or 0.0000017 per sq. cm. per second. This means that the change in the thermal head may be allowed to change the convection rate by 0.0000017 cal. per degree per sq. cm. per second. (This would ordinarily be from 2.5 to 3% of the total thermal leakage, but has the same absolute value whatever the total leakage may be.) A glance at Table I shows that the convection factor 0.0000017 would be reached in a 12 mm. gap at a temperature interval of about 3°, for a 1 cm. gap at about 5°, while an 8 mm. gap would make a 7° interval permissible. If the calorimeter should hold nearer 2 liters it would probably be 16 cm. high; in that case the convection effect would be half of that recorded in Table I for 8 cm. plates, and the safe temperature limits would be around 5° for 12 mm. gap thickness,

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[1] "Some Calorimetric Methods," *Loc. cit.*, p. 554.

7° for 1 cm. and 10° for 8 mm. If the precision desired should be 0.3 per mille, a precision which has proved sufficient for researches of great value, the convection factor may be 0.000005 per sq. cm. per second, and the safe gap for a 5° interval (and 16 cm. height) is 17 mm. This is not so very different from 12 mm., the value for three times as great precision, but it seems well worth while to know that it, rather than 8 mm., or even 1 cm., is the permissible limit, since a doubling of the narrow gap cuts in two (approximately) not only the total thermal leakage, but most lag effects,[1] and errors from uncertain temperature distributions.

It is impossible to say much as to the permissible gap width for differences of 1° or less, since it is evident that the precision of the measurements, high as it was, was not sufficient for the exceedingly small quantities involved. The course of the 24 mm. curve in Fig. 1 shows that convection was appreciable at 1° for that gap width. But for differences of a few tenths of a degree it seems safe to apply the general laws stated above; these lead to the conclusion that gaps as great as 3 cm. may sometimes be advantageous in such cases.

If the time of the experiment is longer, the thermal leakage allowance will be greater (other things equal, of course), and less convection can be tolerated. Herein lies an additional reason for favoring the adiabatic method in protracted determinations.

2. Large vs. Small Calorimeters.

The choice of the best dimensions is of course presented to nearly every designer of calorimeters, and has received much more attention than the more important question of the air gap. All previous discussions of size (including my own) treat the rate of thermal leakage as proportional only to surface and thermal head, which evidently involves the assumption that the thickness of the air gap must or should be the same regardless of the size of the calorimeter. Of course the conclusions reached will be modified as soon as we take account of the fact that the gap can advantageously be larger for a larger calorimeter. The modification, to be sure, is not at all striking, but it involves a quantity about as large as the original result, and so seems worth noticing. Another reason for taking up the matter is that all conclusions so far stated are unsatisfactory, even on the basis of an unvaried air gap thickness. The almost universal conclusion hitherto has been that since in the larger calorimeter the ratio of surface to mass is less, and the calorimeter consequently leaks less of the heat imparted to it, it is bound to give less thermal leakage error.[2] Making a

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[1] This follows directly from the lag equation given further on.

[2] The argument, here and elsewhere, applies to calorimeters measuring the same quantity of heat; if the heat can be made proportional to the size of the calorimeter, as often in thermochemical work, there is no question that the larger vessel and larger heat quantity give a more accurate measurement in a stirred calorimeter. *In aneroid*

logical application of this reasoning, A. Magnus even[1] used vessels holding 60 liters. This conclusion I have ventured to condemn,[2] taking the ground that the principal source of error lies usually not in the temperature change within the calorimeter but in the uncertainty of the environing (jacket) temperature. There is of course no question that in the larger calorimeter with larger surface a given external temperature difference will cause a greater total flow of heat, and an external discrepancy will therefore cause a greater error. My underlying assumption, however, has been challenged by a high authority, who holds that the main source of error is not without, but within, the calorimeter. It therefore seems worth while to show further that error from internal causes tends to be less in a small calorimeter, provided we treat the gap thickness as fixed. It does not seem legitimate to assume that the leakage error is necessarily larger where the leakage itself is larger. The causes of error need to be examined. (1) It is clear in the first place that the mere measurement of the calorimeter temperature need never cause appreciable error in determining the thermal leakage, since this leakage is a small fraction of the total heat measured, and we can, if necessary, use the same thermometric precision for one as for the other. There remain, as sources of error, (2) the lack of uniformity of the calorimeter temperature and (3) lag effects.[3] Most lag effects are greater with a small calorimeter (see Equation 1, below) but most of them (including the thermometer lag) are constant, and therefore introduce no error in a calibrated calorimeter. The only exception is the lag of the internal temperature, but this lag depends entirely upon the lack of uniformity of temperature, already given as one source of error. And since this uniformity depends upon stirring, the question at issue resolves itself into this: "Is it easier to stir effectively a large or a small calorimeter?" If n is the ratio of the linear dimensions of the two calorimeters then the ratio of their surfaces will be n^2, of their volumes, n^3. If we make the very probable assumption that temperature equalization is proportional to the quickness with which the water makes a circuit, that is, to the speed with which it moves divided by the length of its path, then since in the larger calorimeter the temperature differences will originally tend to average $1/n^3$ times as great, on account of the greater mass to be heated, the differences left by the stirring will be $1/n^3 \div V/n$ times as great, and hence the

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calorimeters, however, this is far from true; an important point which may be considered further at another time.

[1] "Ueber die Bestimmung spezifischen Wärmen," A. Magnus, *Ann. Physik.*, 31, 598 (1910).

[2] "Easy Calorimetric Methods of High Precision," Walter P. White, THIS JOURNAL, 36, 2317 (1914).

[3] In adiabatic work a timing error on the observer's part may enter. Hence the conclusions of this section do not apply strictly to adiabatic methods, which are considered in the next section.

resulting chance of error from insufficient stirring, equal to these differences multiplied by the n^2 times as great chance of loss of heat from the greater surface, will be $1/V$ times as great, that is, independent of the size, but inversely proportional to the speed. But the heat of stirring is probably approximately proportional to ldV^3, where l and d are length and diameter of the path of stirring,[1] that is, to n^2V^3. Hence for constant heat of stirring, n^2V^3 constant, the error due to imperfect equalization, being proportional to $1/V$, is proportional to $\sqrt[3]{n^2}$, a result which reinforces slightly that obtained by considering the external uncertainties, and is opposite to and about as large as the result generally reached; that is, it makes the smaller calorimeter nominally less liable to error.

The experimenter who tries to suit his air gap to the other conditions of his work will find this conclusion modified as follows: As far as the *conduction* through the air is concerned, or the heat capacity of the surrounding air, it is fairly evident that any principles which may govern the gap width for any calorimeter will call for a gap thickness approximately proportional to the linear dimension, that is, to n. As to convection, we have the temperature interval only $1/n^3$ for the larger calorimeter; the circumference, n times as great, will tend to increase convection n times; the change in height produces no effect; the convection from the ends increases as n^2. The change in *calorimeter* dimensions thus decreases the convection a little less than n^2 times, which may be offset by increasing the gap nearly $\sqrt[3]{n^2}$ times, since convection varies as the cube of the gap thickness. The final result is to make the effect of a change in dimensions even less important than it is for unvaried gap thickness, as far as internal sources of error are concerned. The effect of external irregularity remains considerable, though diminished.

The practical conclusion seems to be that the size of the calorimeter is, within limits, of very little importance as far as thermal leakage is concerned provided it is not forgotten that the jacket temperature needs to be kept uniform with more and more care as the calorimeter becomes larger. There will rarely be a question of changing the capacity by more than a factor of 10, so that n will seldom much exceed 2, in any case.

3. Adiabatic Calorimetry.

One exception should probably be made to the statement that the size of the calorimeter is ordinarily unimportant as regards thermal leakage, and that is in adiabatic work. It has been sometimes recognized, though apparently not yet definitely stated in the literature, that usually in adiabatic work no convection and therefore no deviation from Newton's Law is to be feared, and hence that that method has a peculiar advantage where

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[1] This rule is derived by multiplying the ordinary engineer's formula for the friction head by Vd. This gives $VPd^2 \propto ldV^3$ (P = pressure), and the first member is evidently the rate of doing work on the circulating stream, and therefore equivalent to the heat.

large temperature differences are necessary or desirable, that is, with small calorimeters. The method, however, is easier to operate with large calorimeters, for the following reason: The conduct of an adiabatic determination calls for more or less rapid adjusting of the jacket temperature to the varying temperature in the calorimeter, and the effect of a delay in this adjustment is similar to a lag. The general formula for a lag[1] effect or error is

$$LK\Delta\theta, \tag{1}$$

where L is the lag in minutes or other unit of time, K is the thermal leakage factor of the calorimeter in the same unit, and $\Delta\theta$ is the temperature rise. It follows from this formula that the time error in the adiabatic adjustment diminishes as the thermal leakage factor. The large calorimeter thus has an advantage in any case, but the advantage may be augmented by increasing the air gap, as recommended above. If such an increase makes it possible to get the same quasi-lag effect by following the calorimeter temperature within 10 seconds instead of 5, the advantage may be almost a doubling of the precision of the thermal leakage elimination.

This kind of gain may be carried still further in adiabatic work. If there is nothing to fear from convection, the gap, in calorimeters both small and large, may be made considerably larger than in ordinary, non-adiabatic (merodiabatic?) methods, diminishing the thermal leakage factor, and with it, all lag errors as well as the heat produced in stirring. This possibility adds new value to the adiabatic method in general.

There is perhaps less real difference of opinion now existing as to the adiabatic method than might appear from the literature, some of which is not so very recent, but this is, if anything, rather a reason why attempts at restatement regarding the method might be worth while. When it was first employed and advocated by T. W. Richards, in 1905, the sources of calorimetric error had received very little systematic study, and, more particularly, the various lags had not even been listed, and were mainly known as indefinite possibilities of error. This entanglement of uncertainties was outflanked by the adiabatic method, which seemed to reduce the whole problem to simpler terms. Since that time, direct attacks on the problem have changed the situation materially. The lags have proved to be decidedly different from what was at first surmised,[2] and it has been shown[3] that the redoubtable error in the thermal leakage determination becomes absolutely negligible (ordinarily) if there is applied to it the same means which are necessary with the adiabatic method, namely, a complete

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[1] W. Jaeger and H. von Steinwehr, *Verh. der Deutsch. Physik. Ges.*, **5**, 50, 353 (1903); *Z. Physik. Chem.*, **54**, 428 (1906); W. P. White, *Phys. Rev.*, **31**, 569 (1910).

[2] "Lag Effects and Other Errors in Calorimetry," Walter P. White, *Phys. Rev.*, 31, 562 (1910).

[3] "A Test of Calorimetric Accuracy," Walter P. White, *Phys. Rev.*, **31**, 696 (1910).

inclosing jacket, whose temperature is measured. Dickinson,[1] also, emphasized still further the fact that the adiabatic is liable to much the same errors as the ordinary method. In fact, the conclusion was reached that for ordinary calorimetric experiments, lasting ten minutes or less, the adiabatic method does not so much avoid or destroy the thermal leakage errors .as furnish a valuable alternative method of dealing with them, although for protracted determinations or aneroid calorimeters it is usually superior. The consequences of this conclusion are exemplified in the practice of the Bureau of Standards. The adiabatic method is used exclusively in aneroid calorimetry, where it is indispensable, but for ordinary calorimeters it is used alongside the older method as a means of diminishing *systematic* errors, and with results neither better no worse than those given by the older method.

But while it is clear, as a result of increased knowledge and of the improvement of ordinary methods, that the adiabatic can no longer claim, in ordinary work, the unique superiority which it originally had, it has, nevertheless, several recognizable advantages which do not appear to have been stated.

Two of these are those already mentioned, which arise out of the disappearance of convection in the adiabatic method: First, the greater *ease* with which large temperature rises can be handled, and second, the greater *precision* which should result when the thermal leakage factor is diminished by increasing the air gap.

The use of wide gaps in this way, however, is subject to three restrictions.

1. Of course it will not do unless the calorimeter is to be confined to adiabatic work.

2. The large air space increases evaporation trouble, and its use will generally make it desirable or necessary to seal the calorimeter altogether against evaporation. That is to say, the experimenter by virtue of the adiabatic method may have *either* freedom from distillation *or* a specially small thermal leakage factor, but can not, in general, have both.

3. The wide gap must be applied with caution to rapid temperature changes. For instance, if an experimenter, thinking that convection was banished, should reduce the thermal leakage factor of a small calorimeter to 0.001 by using a gap of 4 cm. and should therefore suppose that he might permit a lag of 20 seconds in his jacket temperature, and act on that supposition in a determination where a rise of 3° occurred in the first minute he would have a thermal head of 1°, and convection enough to make his calculations false by perhaps 100%.

Another unstated advantage of the adiabatic method is its effect in

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[1] "Combustion Calorimetry and the Heats of Combustion of Cane Sugar, Benzoic Acid, and Naphthalene," H. C. Dickinson, *Bull. Bur. Standards*, 11, 206 (1914).

diminishing evaporation errors by (practically) avoiding distillation,[1] leaving only the slight increase in the saturation of the air gap which comes with changes of temperature. Dickinson and I, in our earlier discussions of the adiabatic method, both had in mind, and I expressly specified,[2] calorimeters such as we were using, in which evaporation was prevented altogether. There is little doubt that this is in general the most accurate practice. Nevertheless, where circumstances still counsel the use of open calorimeters the adiabatic method evidently has a distinct advantage. T. W. Richards and his school have often availed themselves of it.[3]

Professor Richards has called my attention to a possible calorimetric error which indirectly has some bearing on the adiabatic method, though it is itself a question of lag. In a discussion of thermometric lag[4] which was repeated in neater mathematical form, by Harper,[5] I stated that in calorimetry the lag was negligible *if the same thermometer was used* in the calorimeter *for both final and transfer period readings.* The reason for this, as shown in the discussion, is that the lag of the thermometer during the main temperature rise of the calorimeter will then exactly offset the lag effect which occurs while the calorimeter is cooling. Professor Richards points out, however, that in determinations of heat of mixing there has frequently been no attempt to follow the almost instantaneous temperature rise with the thermometer; the rise has been dated from the time of mixing; the final temperature reading therefore has its lag error uncompensated, by the usual earlier reading; and yet the rule has been complied with of using but one thermometer. The difficulty, of course, is merely a matter of statement or interpretation of the rule; to date the temperature rise from the actual mixing is *equivalent* to measuring it with a lagless thermometer, that is, a different one from that used to read the final temperature. Properly understood, the rule covers the case perfectly; its spirit is violated by the procedure pointed out by Professor Richards; a restatement, more explicitly covering this case, removes all difficulty, and is of course desirable. If we say: "There is no error from thermometer lag *if the thermal behavior of the calorimeter is determined throughout by the*

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[1] Dr. Dickinson suggests that the adiabatic method is still subject to this limitation; it cannot avoid distillation from an open calorimeter if used in the valuable form (H. C. Dickinson, *Loc. cit.*, p. 207) where the *mean* thermal head, and not the instantaneous head, is kept equal to zero.

[2] "Lag Effects and Other Errors in Calorimetry," *Loc. cit.*, p. 576.

[3] The discussion immediately preceding has dealt mainly with the question of *precision*. Of course the adiabatic method may under various circumstances have advantages in *convenience* where both it and the ordinary method are more than sufficient in precision, as they usually are.

[4] "Lag Effects," *Loc. cit.*, p. 565.

[5] "Thermometric Lag," R. N. Harper, 2nd, *Bull. Bur. Stand.*, 8, 706 (1912).

same thermometer,"[1] all chance of mistake seems removed. This matter affords a good illustration of the logical simplification introduced by the adiabatic method, for with that method in universal use the problem would never have arisen. Of course it is also possible to get correct results by thermal observations on the temperature rise, or by making a correction for the lag.

4. "Radiation" Shields.

Shields of thin metal between calorimeter and jacket are still described and used. If we suppose that the total air gap is not altered on their account, it is fairly evident that conduction through the air is scarcely affected, though radiation, usually a subordinate cause of thermal leakage, is diminished to one-half for a single shield. Convection is greatly diminished, but this is not important if Newton's Law is holding in the first place, as it usually is. If, however, we suppose that in the shielded calorimeter each gap is as great as the single gap without a shield, it is clear that heat transfer both by conduction and by convection is also reduced nearly to half value in the shielded arrangement, whose main advantage is that it enables conduction to be diminished without increasing convection. It is doubtful if this has been generally recognized. The shield is preferably called a *convection shield.*

Another thing not always recognized regarding such a shield is that it adds something to the *effective* heat capacity of the calorimeter. There are cases where an experimenter has determined the heat capacity of his calorimeter by calculation, without taking any account of the shield. The capacity effect (on the calorimeter) of the shield is very different from the capacity of the shield, and is, in general, hard to determine exactly. But a demonstration which I hope soon to publish shows that, whatever may be the form of the curve expressing the temperature change in the calorimeter, the net final effect of the heat capacity of the shield is always the same (for constant jacket temperature), and proportional to the temperature interval, so that it is a typical lag (Equation 1), in being equivalent to a small *constant* term added to the calorimeter heat capacity.[2] This term depends on the rate of transfer of heat to and from the shield, and therefore varies (on account of the change in radiation) if the condition of any of the surfaces concerned changes, and also, of course, if the shield is displaced. It is of course important that this fact should not be forgotten, but with constancy of conditions preserved the shield would introduce no error in a *calibrated* calorimeter. If the shield is midway between calorimeter and jacket surface, its effective heat capacity is about $^1/_4$ its true capacity. The change in this constant capacity from a shift in the

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[1] That is, if a complete temperature curve for every part of the experiment is obtained.

[2] It is not proportional to K, however, and in this it differs from other lags.

position, or a one-sided change in the radiating power, of any portion of the shield is proportional to the change in distance from the calorimeter, or, to the total change in emissivity. It follows that the shield should be as thin as is mechanically possible; it should never be thicker than 0.1 mm. At 0.1 mm. its effective capacity will seldom exceed, though it may approach, 1 per mille of the total calorimeter capacity.[1]

With two shields the leakage factor of a very well designed calorimeter can be reduced to about 0.4 of its original value. This gain is almost as great as can be secured by using a vacuum-jacketed vessel, and is obtained in a way which is vastly preferable in many cases.

It is also possible, by using a thin shield and running thermoelements from it to the jacket wall, to determine or eliminate the thermal leakage more accurately than by the customary arrangements, and even more accurately and more conveniently than by putting thermoelements directly on the calorimeter. The full discussion of this improvement, however, seems to belong in another connection.

5. Heat Capacity of the Air.

The demonstration just mentioned shows that the net final effect of the heat capacity of the air around the calorimeter is also equivalent to a nearly constant addition to the heat capacity of the calorimeter. This result is important to the purposes of the present paper, since it shows that there is no heat capacity error introduced in a calibrated calorimeter by using the wide air gaps here recommended for certain cases.

The effective capacity of the air will rarely reach 0.001 that of the full calorimeter, and even then a temperature change of 20° or a barometer change of 5 cm. will be required in order to change this extreme value by 0.00007 of the total heat capacity.

Summary.

The interchange of heat between a calorimeter and its environment (thermal leakage) is practically proportional to their temperature difference except for the effect of evaporation, and for that of convection, which is, for ordinary calorimetric conditions, more nearly proportional to the square of that difference.

1. If evaporation is suppressed the advantages of a constant thermal leakage factor are obtained by preventing convection. Recent investigations upon convection show how this may most advantageously be done. Diminishing the width of the air gap around the calorimeter diminishes convection very rapidly, and this can be carried far enough to be effectual without too great an increase of the total thermal leakage, which is then

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[1] Dickinson ("Combustion Calorimetry," etc., *Loc. cit.*, p. 201) has also discussed the "radiation" shield though with results very different indeed from those indicated here. Further discussion of the differences will come more properly with the proof of my own statements.

mainly due to *conduction*, and therefore increases about in inverse proportion to the gap width. Gaps of from 1 cm. to 1.7 cm. according to circumstances, are best with ordinary calorimeters.

2. With large calorimeters, where the temperature change is less, freedom from detrimental convection is compatible with gap widths greater than those most desirable for small calorimeters.
3. In adiabatic work there is little fear of convection, hence either very large temperature intervals or very large air gaps can be profitably employed.
4. Very thin reflecting shields around the calorimeter may be used so as to diminish conduction, and thus decrease the total thermal leakage, without increasing convection.
5. Incidentally, it is pointed out that the ordinary rule, that thermometer lag causes no error where only one thermometer is used, deserves careful interpretation, or else re-statement, in the case of some thermochemical determinations.

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THE FREE ENERGY OF DILUTION OF SULFURIC ACID.

BY MERLE RANDALL AND O. E. CUSHMAN.

Received November 16, 1917.

The number of accurate measurements from which the free energy of dilution of electrolytes involving bivalent ions may be calculated is limited. We have, at present, insufficient data, except in very dilute solutions, from which to calculate the degree of ionization or the activity of the ions of substances such as sulfuric acid. The occurrence of intermediate ions, such as HSO_4^-, which are probably present in considerable amount, and our inability to estimate their concentration, makes the problem of the interpretation of the result even less certain.

Lewis and Lacey[1] have studied the e. m. f. of the cell

$$H_2, H_2SO_4(aq), Hg_2SO_4, Hg,$$

at the two concentrations of sulfuric acid, 0.005 and 0.05 M. They found

$$H_2, H_2SO_4\ 0.05\ M, Hg_2SO_4, Hg;\ \mathbf{E}_{298} = 0.7545.$$

$$H_2, H_2SO_4\ 0.005\ M, Hg_2SO_4, Hg;\ \mathbf{E}_{298} = 0.8160.$$

Cells of this type have no liquid potential and the electromotive force determines the free energy of the reaction.[2]

Brönsted[3] has studied the above cell at various temperatures and over

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[1] Lewis and Lacey, THIS JOURNAL, **36,** 804 (1914).

[2] $\Delta F = -n\mathbf{EF}$. Lewis, *Ibid.*, **35,** 1 (1913).

[3] Brönsted, *Z. physik. Chem.*, **68,** 693 (1910).