The sugars of this group may be readily distinguished by their optical properties, for which purpose the following determinative table may be used:

TABLE VII.—DETERMINATIVE TABLE FOR THE ALDOPENTOSES.

Immerse a few grains in an oily liquid with refractive index n = 1.53 and examine with polarizing nicol in and diaphragm partly closed.

One refractive index decidedly lower than that of the liquid; between crossed nicols shows 2nd or 3rd order colors; in convergent light frequently yields interference figures. . . . . α-XYLOSE.

One index about equal to that of liquid; between crossed nicols shows first or second order colors; in convergent light rarely yields figures. . . . . α-LYXOSE.

All indices decidedly higher than that of liquid; between crossed nicols shows mostly 2nd order colors; in convergent light rarely yields figures. . ARABINOSE.

(Lowest index of α-form less, of β-form greater, than 1.553).

Identification should be confirmed in each case by the measurement of one other refractive index, according to data previously given.

Summary.

The crystallography and optical properties of three aldopentose sugars are described in detail, and the close resemblances existing among them pointed out. The usefulness of optical properties for distinguishing these substances is indicated, a determinative table being given.

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CALORIMETRIC LAG.

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This paper makes an addition to the mathematical treatment of lag effects in calorimetry, and also derives therefrom several suggestions for advantageous experimental arrangements.

Calorimetry is a subject in which a very simple measurement, that of a temperature change, is considerably complicated by the tendency of heat to leak to or from the apparatus. The complication is three-fold: there is first the necessity of calculating the loss or gain of heat; then in order to make any definite temperature measurements possible the irregularity produced by the leakage must be overcome, usually by employing a liquid that can be stirred, which brings in errors from fluid friction and evaporation; finally, in spite of this procedure there still are some uncorrected irregularities, or lags. These lags, with one partial exception, the lag from insufficient stirring, depend on the spontaneous flow of heat, that is, on conduction and radiation. Exact data regarding these processes are nearly always hard to get, hence experimenters, whenever they have recognized a lag, have usually felt safer at first in eliminating or abolishing it as far as possible. On the other hand, the fundamental laws of conduction and radiation are simple, hence it may be possible to find ways of eliminating a lag error which are more advantageous than to abolish the often very useful structures which exhibit the lags. The present paper makes some attempt in this direction.[1]

The problem presented by a calorimetric lag is a problem in heat flow, but it is heat flow as affecting a special procedure, namely, that of calculating the thermal leakage. It therefore seems best to define what will here be regarded as the essentials of the well-known determination of the thermal leakage effect, or "cooling correction." If thermal head, φ, is the temperature difference which causes heat flow, that is, the difference between calorimeter and environment, if V stands for the rate of temperature change of the calorimeter, then for satisfactory work $V/\varphi =$ constant $= K$, where K is the *thermal leakage modulus*, or thermal leakiness, of the calorimeter. It has recently been shown how K may in fact be made sufficiently constant.[2] The thermal leakage effect is therefore $\varphi_x T_x K$, where T is time, and the subscript x refers to the "experimental period," or period during which the unknown heat quantity is communicated to the calorimeter. K may be determined as V/φ for another, or *rating period*, during which the calorimeter changes through thermal leakage alone. The leakage effect, then, is

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

In practice the formula is more complex than this, but the additional complications do not affect the principle, and do not seem to be important in a discussion of lag.

Lags may pertain to the thermometer, to various portions of the calorimeter, and to outlying bodies, including the air.

Strictly speaking, the lag, L, is a time, the interval by which the temperature of one body is behind that of another when both are changing at the same constant rate. It is easy to show that the leakage modulus, K, of a body is the reciprocal of its lag. Often associated with lags are temperature differences which can not be expressed as time effects only, and which are therefore not lags, properly speaking. For example, a thermometer is always behind the calorimeter in temperature, and shows no difference when the calorimeter temperature is stationary; this is an example of uncomplicated lag. With a projecting portion of a calorimeter,

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[1] The principal literature regarding lags seems to be covered by the following: W. Jaeger and H. von Steinwehr, *Verh. deut. physik. Ges.*, **5**, 50 and 353 (1903); *Z. phys. Chem.*, **54**, 428 (1906); T. W. Richards, L. J. Henderson and G. S. Forbes, *Proc. Am. Acad.*, **41**, 4 (1905); *Z. phys. Chem.*, **52**, 551 (1905); W. P. White, *Phys. Rev.*, **31**, 562 (1910); THIS JOURNAL, **40**, 390 (1918); D. R. Harper, 3rd, Bur. Standards, *Bull.* **8**, 659 (1912) (reprint No. 185); H. C. Dickinson, *Ibid.*, **11**, 189 (1915).

[2] Walter P. White, "Thermal Leakage and Calorimeter Design." THIS JOURNAL, **40**, 383 (1918).

on the other hand, the difference in temperature, though it tends to change with the temperature rate, may also show a tendency to vary with the thermal head, and to remain even though the calorimeter is held constant, as long as the thermal head does not become zero. Such differences, though not pure lags, are still heat flow effects, and have been and properly may be considered along with lags, but some chance of confusion seems removed by calling attention to the distinction.

The lag may affect the final calorimeter temperature, the thermal head, φ, or the determination of the modulus V_r/φ_r. (1) The effect of a true *final temperature lag* is $KL\Delta\theta$, where L is the lag considered as a time and $\Delta\theta$ is the whole observed change in calorimeter temperature. This formula comes from the fact that the difference in temperature between the two bodies in question is LV, where V is the common temperature rate. But $V = K\varphi$, (modulus times thermal head), hence the change in V is $K\Delta$, which is $K\Delta\theta$ for a change $\Delta\theta$ in calorimeter temperature, and so the temperature change of the lagging body differs from that of the calorimeter by

$$KL\Delta\theta. \tag{2}$$

Of course putting $\Delta\varphi$ equal to $\Delta\theta$ assumes that the environing or jacket temperature is constant, and this assumption has been made in all treatments of calorimeter lag. It is sufficiently near the truth in nearly all cases, and should be made so for accurate work, since practical dealing with lags becomes much more difficult if it is not. (2) *A lag affecting* φ_x may have the same effect, $KL\Delta\theta$, though for a slightly different reason. The resulting temperature difference is LV, but we wish the integral of this for the X-period, which is $L\Delta\theta$. This is the change in φ_x, and by (1) must be multiplied by K to get the effect on the calorimeter temperature. (3) *A lag affecting* φ_r, which is, of course, a lag peculiar to the rating period, evidently bears the same relation to the thermal leakage effect, as most other lags do to the main temperature rise, and is therefore ordinarily negligible.[1] Where the leakage effect is large this kind of lag also must be considered. The preceding discussion is illustrative rather than extremely rigorous. More rigorous treatments of some lags have been given,[2] with no essential change in the result.

The point of immediate concern about the first two effects just treated is that, being equal to $LK\Delta\theta$, they will ordinarily vary only with $\Delta\theta$, the observed temperature change, and will be independent of the way in which this change takes place. But the heat as finally measured by the

[1] $LV = LK\varphi_r$, and this error is added to φ_r, and therefore instead of $T_x\varphi_xK$ or $T_x\varphi_x\ V_r/\varphi_r$, which equals $T\ \varphi_x\ K\varphi_r/\varphi_r$, the correct leakage effect, we have, as the leakage effect actually observed, $T_x\varphi_x\ K\varphi_r(1+LK)/\varphi_r$, with an error $T_x\varphi_xKLK$, or the leakage effect times LK as against $\Delta\theta$ times LK for the other lags.

[2] W. P. White, *Phys. Rev.*, 31, 566 (1910); *Op. cit.*; D. R. Harper, 3rd, *Op. cit.*

calorimeter is $H(\Delta\theta + \eta)$, where H is the heat capacity and η the thermal leakage effect. If we put $\Delta'\theta$ for $\Delta\theta + \eta$, that is, for the final temperature change as "corrected" for thermal leakage, then the lag effect is $LK(\Delta'\theta - \eta)$. If η is small it can be neglected, and by combining the lag effect with the main measurement we get:

$$H(\Delta'\theta + LK\Delta'\theta) = (H + HLK)\Delta'\theta = \mathrm{H}\,(1 + \mathrm{LK})\Delta'\theta \qquad (3)$$

That is, the final effect of the lag, if the jacket temperature does not change too much, is merely to modify the heat capacity of the calorimeter. When the calorimeter is calibrated, it is calibrated, lag effects and all. These effects will change only if L or K changes, that is, if some change in the calorimeter is made which is likely to change its heat capacity for other reasons also. If, however, the leakage effect η, is large the lag effect will have to be treated as consisting of two parts, which follow different laws. The second part, $LK\eta$, has the same law as was obtained for the third or rating-period lag treated above. Since it varies with η, that is, according to the character of the temperature change, it will produce an error unless (1) LK can be known, or (2) η always bears the same relation to $\Delta\theta$, or (3) η can be made small, as by diminishing K, by shortening the time T_x, or by making φ_x small, as in the adiabatic method. Therein lies one of several reasons for using the adiabatic method in protracted determinations, though any method of diminishing φ_x will answer as well in this particular respect. The neglect of $LK\eta$ in most cases is easily justified. K seldom much exceeds 0.003, a lag of 20 seconds is only $^1/_3$ when expressed in minutes, so that a relatively large lag only changes the result by one per mille; η is ordinarily less than $0.03\,\Delta\theta$, whence $LK\eta$ is not likely to be more than 0.03 per mille.

The error from the principal lags just discussed, $LK\Delta\theta$, evidently depends on (1) the variability of the lag and (2) the magnitude of K, and on nothing else. Not only is the whole lag effect almost always small, one per mille or less; the variability will usually be small, and the error will then be vanishingly small, provided due regard is had to changes tending to alter K or L.

Absence of variability, however, may not be too readily assumed where lag is a matter of stirring. A discussion of this case and of methods for testing the stirring lags was published in 1910.[1] It was there suggested that the testing can be done by means of a number of thermoelements running from the surfaces concerned. But if the thermoelement is good

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[1] *Phys. Rev.*, 31, 568; *Op. cit.* Another case where variation in lag is a matter of stirring occurs in adiabatic work. There it is usually necessary to have a constant difference in the lags of two different thermometers, one of which is in the jacket. Hence a difference in stirring, even if only in the jacket, may alter some lag and so cause lag error. Of course this effect decreases as the stirring becomes vigorous.

enough to test methods of measuring thermal head, it should be a superior means of making the measurements themselves. The lag error and most of the difficulties connected with stirring would thus be greatly diminished. Indeed, the only reason for not so using the thermoelement generally is that still simpler procedures are usually quite sufficient. In aneroid, or fluidless calorimetry, where temperature equalization is relatively slow, the thermoelement has been of the greatest value. The high precision recently attained, as at the Bureau of Standards, would have been impossible without it, or its equivalent. The question of importance in the present connection, however, is the lag of the thermoelement in this kind of work. A good deal of attention has been given to attaching each thermojunction to the surface in such a way that the difference of temperature between them shall be as small as possible, and this both with regard to lag and to the effect of a steady temperature difference between the surface and the air surrounding it. It can be shown that no great care in this respect is needed. (1) Lag produces no error in any case, unless it is so very large that there is a chance that its variation may be appreciable. For the effect of the lag of any single junction is always to change the integrated thermal head by $L\Delta\theta$, that is, always to change it by the same portion of the total rise. (The jacket is supposed to be initially and finally at the same temperature as the calorimeter.) (2) A junction temperature systematically affected by the environment is of no account as long as all junctions are exactly alike; it is then merely equivalent to a slight change in the sensitiveness. But if one junction differs from the rest, that is equivalent to a change in the sensitiveness of that one, and that, in turn, is equivalent to using that one to measure a specially large or small extent of the surface. Hence it is sufficient if the difference, from one junction to another, in the very small effect produced upon the reading by the temperature of the air, does not correspond to anything greater than the inevitable uncertainty in distributing the junctions equally over the surface.

Such incorrect distribution of the junctions, which may include an insufficient number of them, is a real source of error, and seems to be one of the only two errors peculiar to the aneroid, of which the other is irregularity of initial or final temperature due to inconstancy of initial or final jacket temperature. The point is that the distribution must be proportional, not to the number of square centimeters of surface, but to the heat emitting power, which is greater at ends and corners by an amount usually unknown. If the distribution of thermal-head-measuring junctions does not correspond to emissivity, and if, in addition, the temperature distribution over the surface varies from one time to another, the same total distribution of temperature as measured may not accompany the same total heat loss in a determination as in the calibration. If, for instance, 20% of the surface has a 20% excess of thermoelement assigned to it, and if the thermal head of this portion is 20% of the temperature rise higher, compared to the mean for the whole calorimeter, at one time than at another, the resulting discrepancy will be 0.20 × 0.20 × 0.20, or 0.008, of the whole thermal leakage effect, and therefore possibly 0.0003 of the whole heat quantity. Even this appears to be a large estimate, but it is clearly desirable, since a true distribution of the junctions is hardly to be hoped for, to diminish surface temperature differences by using thick metal or by sufficient stirring, as the case may be, to verify this diminution, and to take measures so that the differences shall not vary too much from one experiment to another.

The thermometer lag has been treated very completely, and the lags due to imperfect stirring appear to have been sufficiently treated; the rest of the present paper deals with the lags and other heat-flow effects in bodies more or less external to the calorimeter. It treats, first, external "radiation" or convection shields, used to diminish heat loss, where a knowledge of the magnitude of the lag effect is desirable, and second, larger or less definite masses, where it is enough to know the general laws of the effects.

Let us first suppose, between a calorimeter and its complete jacket, a thin metal shield, between whose different portions there are no temperature differences great enough to prevent the average temperature of the shield from being treated as a single uniform temperature.

Let u be the temperature of the shield, θ, of the calorimeter, C, of the calorimeter chamber, *i. e.*, the jacket.

K_1 be the leakage modulus of the shield with respect to the calorimeter, that is, the value the modulus would have if the leakage took place only to the calorimeter.

K_2 that of the shield with respect to the chamber.

K_3 that of the calorimeter with respect to the shield.

K_4 that of the calorimeter with respect to the chamber directly.

(This evidently supposes that the shield does not inclose the calorimeter completely.)

The meaning of these *partial leakage moduli* is defined by the following equations:

$$du/dt = K_1\,(\theta - u) + K_2\,(C - u) \tag{4}$$

$$d\theta/dt = K_3\,(u - \theta) + K_4\,(C - \theta) \tag{5}$$

Evidently K_1 and K_3 have to do with the same transfer of heat, and their ratio is that of the heat capacities of shield and calorimeter, respectively. That is, if H is heat capacity of the calorimeter, h of the shield,

$$h/H = K_3/K_1$$

From (4) follows readily, by integration:

$$\int_x [K_1\theta + K_2C - (K_1 + K_2)u]dt = \Delta u \qquad (6)$$

where $\int_x$ means the integral over the X-period. The essential facts regarding external lag will perhaps be more readily seen if the demonstration is first outlined in an approximate form sufficient for most practical purposes, after which the results of closer approximation may be indicated. The final temperature rate of the calorimeter, that is, the change during the rating periods, which is very slow compared to that in the X-period, may therefore be first taken as zero. We then have for that final condition:

$K_2(u - C) = K_1(\theta - u)$, that is, the same amount of heat leaves the shield as enters it. Solving for u we get:

$$u_r = \frac{K_1\theta + K_2C}{K_1 + K_2}, \text{ whence } \Delta u = \frac{K_1\Delta\theta + K_2\Delta C}{K_1 + K_2} \qquad (7)$$

or

$$(\theta - u)_r = \frac{K_2}{K_1 + K_2}(\theta - C)_r \qquad (8)$$

But Δu in (6), referring to the ends of the X-period, refers to the rating period conditions which hold for (7) and (8), hence substituting the value of Δu from (7) in (6) we get:

$$\int_x [K_1\theta + K_2C - (K_1 + K_2)u]dt = \frac{K_1\Delta\theta + K_2\Delta C}{K_1 + K_2} \qquad (9)$$

Now the thermal leakage from the calorimeter during the X-period is, really:

$$K_3\int_x (\theta - u)_x\,dt + K_4\int(\theta - C)_x\,dt \qquad (10)$$

But in getting it we ordinarily measure, not $\theta - u$ but $\theta - C$ during the X-period, and instead of getting K_3 and K_4 we measure the leakage during the rating periods, dividing it also by the thermal head $(\theta - C)$. That is, we actually find:

$$\int(\theta - C)_x\,dt\,\frac{K_3(\theta - u)r + K_4(\theta - C)_r}{(\theta - C)_r} \qquad (11)$$

The difference between (10) and (11) is the error due to the shield and its lag. (8) and (9) enable us to find it. First, however, it is evident that the coefficient of K_4 is the same in both equations, that is, the lag of the shield does not interfere with a correct determination of that part of the leakage which flows by the shield. If (10) is subtracted from (11) to find the lag effect the terms in K_4 cancel, and therefore contribute nothing to that effect. Hence we may omit them.

Formula 11, the observed leakage effect, thus abbreviated, becomes, by (8),

$$\int (\theta - C)_x \, dt \, \frac{K_3 K_2}{K_1 + K_2}. \tag{12}$$

If we now modify the integral in (9) by adding and subtracting $K_2\theta$ and uniting the θ-terms with those in C and u, and finally multiply the whole by $K_3/(K_1 + K_2)$, we get:

$$K_3 \int (\theta - u)_x \, dt - K_3 \int \frac{K_2(\theta - C)_x \, dt}{K_1 + K_2} = K_3 \left[\frac{K_1 \Delta\theta + K_2 \Delta C}{(K_1 + K_2)^2} \right]_r \tag{13}$$

Here the first term is the true leakage of (10), the second is the leakage as found, or (12), and their difference is the second member, which is the desired lag effect.

It will be convenient to eliminate K_3 by means of the relation $h/H = K_3/K_1$. We thus have the lag effect as:

$$\frac{h}{H} \, \frac{K_1^2 \Delta\theta + K_1 K_2 \Delta C}{(K_1 + K_2)^2} \tag{14}$$

in terms of the relative heat capacity of shield and calorimeter and of leakage moduli pertaining to the shield. We have seen that lag effects have generally been simplified in discussion by taking ΔC as strictly zero. Unless this is done in practice it is impossible to treat the lag as a constant modification of the heat capacity. The adiabatic method, however, also deserves consideration, in which $\Delta C = \Delta\theta$. For these two cases, (14) evidently becomes:

$$\text{Constant jacket, } \frac{h}{H}\left(\frac{K_1}{K_1 + K_2}\right)^2 \Delta\theta \tag{15}$$

$$\text{Adiabatic method, } \frac{h}{H}\left(\frac{K_1}{K_1 + K_2}\right) \Delta\theta \tag{16}$$

A word may be in order as to the physical meaning of these expressions. The expression (16) is, strictly not a lag effect at all, but the heat lost to the shield. If K_1 is very large that means that the shield is very near the calorimeter. The expression then reduces practically to $h\Delta\theta/H$; that is, the capacity of the shield is directly added. If the shield is about half-way out, so that $K_1 = K_2$, (16) becomes $^1/_2 h\Delta\theta/2H$, in accordance with the evident fact that half of the heat gained by the shield now comes from the calorimeter. Expression (15) is the resultant of the heat given to the shield (in this case $hK_1 \Delta\theta/H(K_1 + K_2)$, all of it from the calorimeter) and a true lag effect in the leakage from the shield. The calorimeter gives less heat to the jacket through the shield while it is heating up the shield. The lag effect alone, equal to $-hK_1K_2\Delta\theta/H(K_1K_2)^2$, can easily be obtained directly by a calculation similar to that already employed. Although it does not look so at first sight, this is equivalent to the $LK\Delta\theta$ X-period lag listed above, for $1/(K_1 + K_2) = L$, the lag of the shield, $K_1\Delta\theta/(K_1 + K_2)$ is the temperature change of the shield, K_2 is the leakage modulus by which its integrated temperature must be multiplied to get the leakage to the jacket, and hK_2/H is this modulus in terms of the effect on the calorimeter. Dickinson[1] has also treated the convection shield mathematically, with results which at first sight appear quite different from those given here. The difference, however, is easily explained, and comes from the fact that, wishing merely to illustrate possible errors in existing procedure, he found approximate methods sufficient. Thus his much larger value for the effective heat capacity of the shield is precisely the one obtained here when the effect of lag on that capacity is disregarded.

To obtain a more rigorous treatment of the external lag effect we need to solve (4) and (5) to get the relations of u, θ, and C for the rating period. The solution, carried out by standard methods, shows that for constant C u-C and θ-c are each equal to the sum of two exponentials, one of which has essentially the time-rate of decay of the shield temperature, and is to be omitted, since we have not reached a "final" value till this has become negligible. The other exponential is essentially the cooling rate of the calorimeter. The expression for u-C and that for θ-c have the same exponential. Taking the ratio of the coefficients of this exponential we have

$$\frac{u - C}{\theta - C} = \frac{K_1}{K_1 + K_2 - K_3 - K_4 + K_3K_n} \tag{17}$$

where K_n is a series of terms containing increasing powers of $K_3/(K_1 + K_2)$, or something similar, which may be neglected if K_3 is small compared to K_1 or K_2.

Equation 7 now changes from

$$u_r = \frac{K_1\theta + K_2C}{K_1 + K_2} \text{ to } u_r = \frac{K_1\theta + (K_2 - K_3 - K_4)C}{K_1 + K_2 - K_3 - K_4},$$

that is, with the calorimeter cooling, the shield, on account of its own lag, does not take quite the same intermediate temperature as it would with the calorimeter constant. Carrying the calculation through for the changed value of (7) we get for the lag effect, instead of (14):

$$\frac{h}{H}\left\{\frac{K_1^2\Delta\theta + K_1(K_2 - K_3 - K_4)\,\Delta C + K_1^2(K_3 + K_4)\int_x(\theta - C)dt}{(K_1 + K_2 - K_3 - K_4)\;(K_1 + K_2)}\right\} \tag{18}$$

Here the difference between the first two terms and(14) is not important, since as far as they are concerned we still have a constant multiplier of $\Delta\theta$ if ΔC is zero, or else get the same value as (16) for the adiabatic method. But the value of the integral term is dependent on the way in which the temperature rises, and corresponds closely to the small $LK\eta$ or $LK^2\varphi_xT_x$ term in the other lag effects which have been considered.

With the preceding demonstration in mind it is easy to solve the problem of a very large number of shields, and this is of practical importance,

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[1] *Loc. cit.*, p. 204.

since it enables us to treat the case of a thick insulating *layer*, by considering that as made up of a large number of shields packed together.

Suppose, then, a number of shields, S_2, S_4, S_6, ... $S_p - 2$, whose heat capacities are h_2, h_4, etc. Let their temperatures be u_2, u_4, etc., with $u_0 = \theta$, the temperature of the calorimeter, and $u_p = C$, that of the chamber. Let K'_1, K'_3, etc., be the thermal leakage moduli between each two adjacent pairs of shields, expressed as *calories* transferred per degree of temperature difference. The ordinary leakage modulus for the nth shield is then $K'_{n \pm 1}/h_n$.

The only assumptions are that the h's and K's are constant. This evidently includes the assumption that Fourier's equation for heat conductivity holds.

Let us first treat the terminal or rating period values of the u's and C as constant, and let us take ΔC, the change in the jacket, as either $= 0$ or $= \Delta\theta$, since we have seen that only in these two cases do we get a definite result practically.

Now for any shield, say the 4th, we have, as in (6):

$$\Delta u_4 = \frac{K'_3}{h_4}\int_x (u_2 - u_4)dt - \frac{K'_5}{h_4}\int_x (u_4 - u_6)dt \qquad (19)$$

Whence:

$$K'_3\int_x (u_2 - u_4)dt - K'_5\int_x (u_4 - u_6)dt = h_4 \Delta u_4 \qquad (20)$$

By combining these equations one after the other we can get expressions connecting $\int(\theta - u_2)$ and $\int(u_4 - u_6)$, $\int(\theta - u_2)$ and $\int(u_6 - u_8)$, etc., from which we can, by addition, get a relation between $\int(\theta - u_2)$ and $\int(\theta - C)$. The only multipliers needed are the K's, which are constants. The various Δu's will appear in this final equation multiplied by terms composed of these constant K's. But each Δu is, as in (6), the difference of initial and final values, here provisionally assumed constant. Moreover, in these terminal states the temperature distribution, depending only on the distribution of insulating and conducting matter, is always the same, that is, each final Δu is always the same fraction of $\Delta\theta$, and the final term containing all the Δu's may therefore be written $f(K, h)\,\Delta\theta$, where $f(K, h)$ is constant as long as the apparatus undergoes no change. Our relation between $\theta - u_2$ and $\theta - C$ may therefore be written:

$$K''\int_x (\theta - u_2)dt - f^1(K, h)\,\Delta\theta = K'''\int_x (\theta - C)dt, \qquad (21)$$

where K'' and K''' are more or less complex combinations of the constant K's.

For the final temperature distribution we may evidently write:

$$K'_3(u_2 - u_4)_r = K'_5(u_4 - u_6)_r, \text{ etc.,} \qquad (22)$$

since the heat flowing into each shield is now equal to that flowing out. But this series corresponds exactly to the series of integrals (19) with the heat capacity terms left out. Hence if we find a value for the relation of $(\theta - u_2)_r$ to $(\theta - C)_r$ it will have the same coefficients made up of K's as the corresponding result for the integrals. Hence we may write, referring to (21):

$$\frac{K'''\int_x(\theta - u_2)dt - f_1(K, h)\Delta\theta}{K''\int_x(\theta - C)dt} = 1 = \frac{K'''(\theta - u_2)_r}{K''(\theta - C)_r} \qquad (23)$$

Whence, multiplying by $K_1K''\int_x(\theta - C)dt/K'''$, where K_1 is the modulus of the calorimeter with respect to the shield next to it:

$$K_1\int_x(\theta - u_2)dt = K_1\int_x(\theta - C)dt\left(\frac{\theta - u_2}{\theta - C}\right)_r + f_2(K, h)\,\Delta\theta \qquad (24)$$

Here the first term is the true thermal leakage; the second is the computed leakage, derived from observations of $(\theta - C)_x$, of $(\theta - C)_r$, and of the actual leakage $K_1(\theta - u_2)_r$; and $f_2(K, h)\,\Delta\theta$ is the lag effect, corresponding to (15), but unknown as to its exact value.

The problem can be still further generalized. Instead of a series of shields we may take any constant distribution of matter whatever, with the heat liable to flow in any direction. Equations 19 and 20 will then be replaced by something far more complex, but what is essential for the present demonstration will remain, namely, that the only difference there is between the law of heat flow or temperature distribution in the X-period and in the rating period will be due to the heat capacity of the material, and will have an effect which is a constant multiple of $\Delta\theta$. Equation 24, therefore, will still hold, though with $\theta - u_2$ now as a mean. A layer of heat insulating material, therefore, or any other layer, has a constant lag effect, like a single shield, a fact which many experimenters have probably suspected, though it does not appear to have been proved before, and is only true with certain restrictions.

Equation 24 is a generalization of (13), and like it, neglects the effect of any change in the calorimeter during the rating period. Analogy indicates that a more rigorous solution would correspond to (18), and contain a small term in $\int(\theta - C)dt$, like the $LK\eta$ term of other lags.

Practical Cases of External Lag.

It should of course be borne in mind that the above demonstrations regarding external lag hold only where the X-period is made so long that the exponential which is characteristic of the lagging material sinks to a negligible value. For a bright silver shield 0.1 mm. thick one cm. from calorimeter and jacket the temperature has gone about

99% of the way to equilibrium in 3 minutes (25)

while if 0.5 mm. thick the shield would still be about

10% away after 8 minutes. (26)

The long time required for equilibrium will generally constitute a decisive objection to the use of thick layers of external material or thick covers, except where these are of good conducting metal, in close thermal contact with either jacket or calorimeter.

There appear to be only 4 cases of external lag calling for discussion.

1. **External Lag of an Intermediate Shield.** — The old-fashioned scheme of a shield between calorimeter and jacket affords the simplest case of external lag. The benefit of such a shield[1] is a cutting in half of the effective leakage modulus, often an appreciable advantage, and one obtained at a trifling cost. A failure of constancy may come from a change in the radiating power of any one of the 4 surfaces concerned, or from a bending of the shield. By making the shield thinner we evidently gain indefinitely as far as error from change in radiating power goes; and we may also gain in the matter of error from bending until we reach the point where the shield is very unsteady. If we assume that $K \propto 1/s$ where s is space, or gap width, and let S be the total space, and L the lag effect, it is easy to show from (15) that:

$$\frac{dL}{ds_1} = \frac{h}{H}\frac{2s_2}{S^2} \qquad (27)$$

and a displacement of one mm. from the middle of a two cm. gap amounts to $^1/_{20}$ the heat capacity of the shield, or $^1/_5$ of its effective capacity with the jacket temperature constant. A bending or displacement of the shield would always bring some parts nearer the calorimeter as others receded, so that the resultant effect would be relatively small; hence with due support metal as thin as 0.1 mm. would doubtless prove satisfactory.[2] Silver of this thickness would have, for a liter calorimeter, an effective heat capacity of about one per mille, with a change of 0.2 per mille for a *net total* shift of one mm. Another reason appears in (26) why metal much thicker would not be profitable.

In adiabatic work such shields are less needed.

2. **Outlying Calorimeter Covers.**—In 1906, with a view to avoiding at once evaporation and external lag, we used a thin floating cover for the calorimeter, and this practice was soon followed at the Bureau of Standards, where, to control evaporation more completely, a few drops of oil were used on the very narrow annular water surface. In our case, for the same purpose, a cover set in an oil seal was substituted, which bent down to make contact with the water surface. This arrangement, in most ways very satisfactory, delays the closing of the calorimeter in specific heat work. It therefore seems worth while to inquire whether our present greater knowledge of lag effects will enable a different cover to be used without loss of precision. If the opening to be covered is 10 cm. in diameter, a cover 0.1 mm. thick would have a volume of 0.8 cc.,

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[1] "Thermal Leakage, Etc.," *Op. cit.*, p. 391.

[2] In a later paper it will be shown that changes in radiative power also may easily be made negligible in changing the effective heat capacity of a convection shield.

a heat capacity perhaps equivalent to 0.48 g. of water, and an *effective* heat capacity 0.12 per mille of that of a calorimeter holding a liter, which heat capacity (it is easy to show by a formula similar to (27)) would change $^1/_{12}$, or 0.01 per mille of the calorimeter capacity, for a change of one mm. in the water level,[1] and only 0.03 per mille as a result of preventing or restoring free evaporation[2] from the water to the under side of the cover. Moreover, the outer part of the cover will be heated by metallic conduction from the calorimeter wall, so that only the center will be much affected by the changes of the water surface. Indeed, a silver or copper cover 10 cm. in diameter, even if only 0.1 mm. thick, will have its final temperature governed much more by conduction along the metal than by that through the air. For this reason it *may* be as well, or better, to use a heavy cover (provided this is metal of high conductivity!), along which so much heat would flow that the heat coming from the water, and all effects resulting from it. would be negligible in comparison. Of course the supply to the cover of heat passing up the calorimeter wall must be sufficient, and the thermal contact between cover and wall should not vary much. Tubes for stirrers, etc., passing through the cover can be made to help here, and if the assistance is carried further by means of copper rods dipping into the water we have an arrangement which can undoubtedly be made adequate, and whose difference from a cover bent down to touch the water is really only a matter of detail. On account of the varied possibilities the probably good performance of the heavy cover seems to need verification before being trusted in any particular case, while the adequacy of the thin cover is fairly certain, since the error is at worst only a fraction of the heat capacity of the cover. The dropping back, however, from a thin cover of the colder evaporated and condensed water may often prove fatal in work of precision; in such work, of course, no cover should be used so as to permit this. The rate of evaporation for a one cm. gap is about one mg. per *hour* per sq. cm. per degree of temperature difference. Covers of poorly conducting material, such as wood or hard rubber, unless excessively thin, seem to be always relatively undesirable and likely to be seriously detrimental.

3. **Outlying Layers of the Calorimeter.**—Where copper blocks have been used as calorimeters they have usually been set in vacuum-jacketed glass vessels, and the same arrangement has seemed advantageous for metal water-filled calorimeters in several cases, some of which are not yet published. In Nernst's laboratory, where the lag of the glass parts was appreciated, these were brought into good thermal contact with the

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[1] The level can easily be kept constant to better than this by Dickinson and George's device of an internal overflow.

[2] "Thermal Leakage, Etc.," *Op. cit.*, p. 381.

calorimeter proper by casting Wood's metal in the narrow intervening space. This is apt to be very hard on the expensive glass vessel, and was, after some experience, abandoned by A. Magnus for that reason. Mercury should prove an effective substitute in small vessels, but its continued great hydrostatic pressure might endanger large glass vessels.[1] Water, however, as is clear from the demonstration leading to Equation 24, will make a satisfactory thermal connection,[2] or even heavy oil, in spite of its more than 3-fold greater thermal resistance, compared with water. The calculated lag of a 1.5 mm. glass wall outside of a two mm. layer of water is only about 25 seconds, so that it is within 1% of equilibrium in two minutes, and oil would require only 7 minutes. And from (24) we are sure that the error from the lag may be made negligible.[3]

4. **Miscellaneous Projections.**—The thermometer, the stirrer rod, various supports, and sometimes other structures necessarily pass between calorimeter and jacket. The formulas just given do not treat these completely, but indicate that their lag effects are at least very near to constant. It appears to be sufficient, as a rule, to make these projecting structures as small and as *definite* in temperature as possible. The error can never correspond to more than the heat capacity of the body

Summary.

The lag effects of bodies external to calorimeters, although more complicated in expression, are found to follow the same general laws as the simpler lag effects already described. More carefully stated than previously, these effects prove to be three: one, equivalent to a change in the heat capacity of the calorimeter; this can be eliminated if a calorimeter is directly calibrated; another, much smaller, depending on the amount of thermal leakage; this can be avoided, if necessary, by using the adiabatic method; and a third, dependent on the jacket temperature, which disappears for constant jacket temperature. This one causes the calorimeter to have a different effective heat capacity when used adiabatically.

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[1] Possibly a solid copper amalgam might be found less liable to fracture the glass than Wood's metal. This has not been tried, however.

[2] The water can be practically protected from evaporation by a little oil on top. It might then be still better to use instead of the water a salt solution of vapor tension a little below the lowest ordinarily prevailing in the room.

[3] Magnus ("Die Spezifische Wärme des Platins und des Diamanten bei hohen Temperaturen," A. Magnus, *Ann. Physik*, **48**, 983 (1915)) when he discarded his metal layer, instead of substituting the next best conductor available, put in a layer of flannel! He gives no explanation of this surprising procedure, which compelled him to wait about an hour for equilibrium, and so probably more than neutralized all the advantage of the vacuum. In view of the real importance of his new and ingenious methods, and their publication in one of the world's leading journals of physics, it has seemed desirable to point out that this particular feature of them is not necessarily to be imitated.

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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THE CONDITIONS OF CALORIMETRIC PRECISION.

BY WALTER P. WHITE.

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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).