ART. XXX.—*On the Conditions required for attaining Maximum Accuracy in the Determination of Specific Heat by the Method of Mixtures*; by F. L. O. WADSWORTH.

Introductory Note.—In the last volume of the Proceedings of the American Academy, which has just been received at the Observatory, I find a paper by Professor Holman* discussing methods of making the "cooling corrections" in determining specific heat by the method of mixtures. In this paper the author has suggested that this correction may be simplified by a modification of the usual method which "is supposed to be new." This suggestion is of the same nature as one which I made some years ago and embodied in a paper which formed part of my report in laboratory work at the Ohio State University for 1888–89, but which was never published. The investigation was undertaken as preliminary to an accurate determination of the specific heat of the metal of one of Professor Rogers' standard bars, a sample of which had been sent to Professor Thomas for that purpose. No opportunity was given at that time to put the suggested method to actual test, as it was subsequently decided to use the ice calorimeter instead.

The method differs from that suggested by Professor Holman in that it goes further and eliminates the necessity for the cooling correction entirely. Except for that part of the paper (pp. 274–277) which deals with the conditions for securing this result, there is nothing novel or particularly original in the treatment. But as the whole discussion is more or less linked together and as it will serve to supplement to some extent Professor Holman's paper, which deals only with the cooling correction (the most important but not the only source of error in calorimetric determinations), it has been decided to let the paper stand as it was first written (except for a slight rearrangement of the order of the paragraphs), supplementing the original text with footnotes where it seemed necessary. At the end will be found a few general notes relative to the arrangement and use of apparatus in the determination of specific heat by both the method of mixtures and the method of the ice calorimeter. These notes did not form part of the original paper, but have been added from time to time as suggested in my laboratory experience. The method of discharging the hot body from the heating vessel and receiving it in the calorimeter, and of maintaining the jacket of the latter at a con-

* "Calorimetry: Methods of Cooling Correction," Proc. Amer. Acad., vol. xxiii, p. 245, 1896.

Second, W. This may be determined in two ways.

(a) By calculation from the formula

$$W = \frac{M'c' + M''c''}{c}$$

where M' and M'' are determined by weighing, and c' and c'' either determined by experiment (best) or taken from tables.

(b) By experiment in the usual manner (introducing known quantity of hot water).

Its effect on s and the limiting error will be discussed under effect of M .

Third, M. To find the error in s , due to error in observing the weight, M , we have, by differentiation,

$$\frac{ds}{d(M+W)} = \frac{c(\theta-t)}{w(T-\theta)} = \frac{s}{M+W}$$

Suppose $M+W = 300$ grms. Then in order that the error of s should be within 0.1 per cent, the weight must be taken to 0.3 grms.; with 200 grms. to 0.2 grm. But with the degree of accuracy ordinarily obtainable in reading temperatures to $\frac{1}{10}^\circ$ (see below), the weight need not be taken closer than 0.5 grm. for a weight of 200 grms.; so that unless the error in observing temperatures can be reduced there is no necessity for correcting for evaporation, for loss of weight in air, etc., etc. For the same reason it is not necessary to obtain the weight of w closer than 0.5 grm. for a weight of 50 grms.

Fourth, c. Likewise to find $\frac{ds}{dc}$, we have $\frac{ds}{dc} = s/c$; or since $c \approx 1$, it must for an accuracy of 0.1 per cent be correct for the interval employed to 0.001. But the extreme variation of c , for 10° (from 4° to 14° C.), is 0.00033, which makes it apparent that all correction for c is entirely unnecessary, although Kohlrausch makes note of the fact that such a correction should be applied.

Fifth. Effect of errors in observing temperatures.

(A) Error in t .

From equation (2) we have

$$\frac{ds}{dt} = \Delta_t s = - \frac{(M+W)c}{w(T-\theta)} = - \frac{s}{\theta-t}. \quad (3)$$

From the first of these values we see that in order to diminish the effect of the error in t upon s , we must make $M+W$ as small and $T-\theta$ as large as possible, conditions which conflict with each other; for the larger w , and the smaller $M+W$, is, the smaller will be $T-\theta$. But the condition of things for which $\frac{M+W}{w(T-\theta)}$ will be a minimum, will evidently be $M+W = 0$, a condition which cannot be realized, but which shows

that the minimum quantity of water should always be used, so far as effects of errors in t are concerned. From (3) we get directly the percentage variation of s for a given error in t , when $\theta - t$ is known.

E. g. Suppose $\theta - t = 10^\circ$, then $\Delta_t s = 0.1 \Delta t \cdot s$. Now if we assume the maximum allowable error to be 1 in 1,000, or .1 per cent,

$$\Delta_t s = 0.001 s \dots \text{and } \Delta t = 0.01$$

or the temperature t must be read to .01 of a degree. If $\theta - t = 5^\circ$, the temperature t must be read to 1.200 of a degree. On the other hand, if $\Delta t = \frac{1}{50}^\circ$ (and we cannot read much closer than this with a thermometer)

$$\Delta_t s = 0.002 \cdot s \text{ for } (\theta - t) = 10^\circ, \text{ an error of } \frac{1}{5} \text{ per cent.}$$

$$\Delta_t s = 0.004 \cdot s \quad \text{“} \quad \text{“} \quad = 5^\circ \quad \text{“} \quad \text{“} \quad \text{“} \quad \text{nearly } \frac{1}{2} \text{ per cent.}$$

(B) Error in T.

Errors in T may arise in three ways:

1st. By error in reading T (the *only* error which affects t).

2d. By the fact that the actual temperature of the body may not be that of the atmosphere which surrounds and is heating it, as indicated by the thermometer placed therein. This is avoided by keeping it surrounded for a long time with an atmosphere maintained at a constant temperature (one and one-half to four hours or more, according to the thermal conductivity of the body in question). Theoretically it would require an infinite time for complete equalization of its temperature with that of the surrounding air. The time required for equalization will be very considerably diminished by making the surface of the body as large as possible compared with its volume, or by using thin sheets of the metal or a ball of wire in place of a solid mass. This will be of advantage also in diminishing the time required for the hot body to impart its heat to the water.

3d. By the loss of heat during the time while the body is being transferred from the heating chamber to the calorimeter, which is of course diminished by making the time as short as possible, and by protecting it as well as possible during transfer.

The error of s due to error in T, or $\frac{ds}{dT} = \Delta_T s$, will be

$$\left. \begin{aligned} \frac{ds}{dT} = \Delta_T s &= - \frac{(M+W)c(\theta-t)w}{\{w(T-\theta)\}^2} \\ &= - \frac{c}{w} \cdot \frac{(M+W)(\theta-t)}{(T-\theta)^2} \end{aligned} \right\} \quad (4a)$$

$$= \frac{s}{(T-\theta)} \quad (4b)$$

From (4a) we see that to diminish the effect of an error in T we must, as for t , decrease $M+W$, and increase $T-\theta$, as much as possible; but that contrary to the previous case of t , an increase in $\theta-t$ will act injuriously. Likewise by reference to (4b), we see that an increase of $T-\theta$ would really be beneficial, although from (4b) it would seem to be in conflict with the condition that $\theta-t$ should be a minimum.

Since, however, an increase of $T-\theta$ involves an increase in $M+W$, and this, as we have seen in case of t , to be highly undesirable, it is best to decrease the value of $T-\theta$, even at the expense of an increase in the involved error of s , which is much less in this case than in the preceding.

If, as before, we let the maximum error of s be 1 in 1,000, or 0.1 per cent, we have

$$\begin{aligned}\text{When } T-\theta &= 50^\circ, \Delta t = 0.05^\circ \\ \text{" } T-\theta &= 80^\circ, \Delta t = 0.08^\circ\end{aligned}$$

Or if we read T to $\frac{1}{2}^\circ = 0.04^\circ$ the resulting error in s will be less than that involved in reading t to $\frac{1}{100}^\circ$ or $\frac{1}{200}^\circ$.

(C) We have last to consider the effect of an error in determining θ . This is the most important of the errors in the temperature readings, both because of its effect upon s , and the numerous causes which go to produce it, combined with the difficulty of guarding against them.

1st. The error produced in s will be found as before, by differentiating (2).

$$\left. \begin{aligned}\frac{ds}{d\theta} = \Delta_\theta s &= \frac{(M+W)c(T-\theta) + (M+W)c(\theta-t)}{w(T-\theta)^2} \\ &= \frac{c}{w} \cdot \frac{(M+W)}{(T-\theta)} + \frac{c}{w} \cdot \frac{(M+W)(\theta-t)}{(T-\theta)^2}\end{aligned} \right\} (5a).$$

$$= \frac{s}{\theta-t} + \frac{s}{T-\theta} \quad (5b)$$

thus involving both corrections already found. Here, since the first correction is generally larger than the second, the most desirable thing to do will be to increase $\theta-t$ (by decreasing $M+W$), rather than to increase $T-\theta$, except by increasing T , which in most forms of heating apparatus has its limit at 100°C .

If as before, we take the maximum allowable error as 0.1 per cent, we have

$$\begin{aligned}\text{For } \theta-t &= 10^\circ \text{ and } T-\theta = 50^\circ, \Delta\theta = 0.0083^\circ \cong \frac{1}{120}^\circ \\ \text{" } \theta-t &= 5^\circ \text{ " } T-\theta = 80^\circ, \Delta\theta = 0.0047^\circ \cong \frac{1}{212}^\circ\end{aligned}$$

Conversely, if we read θ to only $\frac{1}{2}^\circ$ we get

$$\Delta_\theta s = 0.0024 = \frac{1}{4} \text{ of one per cent for the 1st case.}$$

$$\Delta_\theta s = 0.00425 = \frac{2}{3} + \text{ " " " " " 2d case.}$$

2d. There is another class of errors in θ , not due to errors of reading, but which are even more important than these, viz: errors due to θ never reaching its maximum value required by theory because of the heat received or lost by radiation. Hence θ_n , as observed, will not be the true value suitable for use in (2), but some value lower than this; unless indeed, we start with a temperature so low that the final temperature θ is less than that of the air; in which case θ_n will be too high. To eliminate this error, due to radiation, several methods have been proposed.

(a) Those methods which take account of the temperature of the external air.

The simplest of these is that of Rumford (compensation method). This is to determine by preliminary calculations the rise of temperature in the calorimeter while the body is cooling and make the initial temperature of the water as much lower than that of the surrounding air as the final temperature is higher. The fallacy of this method lies in the fact that the time required for the last part of the operation is much longer than that required for the first. If we make the initial temperature of the water $\frac{2}{3}(\theta - t)$ lower than the external air, we will come nearer to "compensating" for radiation.

(b) Methods of Jamin and Regnault.

Both of these methods depend on a series of observations begun four or five minutes before and continued as long after the introduction of the heated body into the calorimeter. Radiation is proportional to three factors,—time, excess of temperature, and surface. For any given calorimeter, then, the loss per unit of time is a constant $\times (\theta - \beta)$, where β is the temperature of external air or calorimeter jacket. The lowering of temperature due to this loss is, therefore, $\Delta(\theta - \beta)$, during each unit of time for which $\theta - \beta$ is the mean excess of temperature.

Let a series of readings be taken at intervals x_1, x_2, x_3, x_4, x_5 , etc., from the instant of immersion to the time when the reading of the thermometer becomes steady, giving a series of temperatures $\theta_1, \theta_2, \theta_3, \theta_4$, etc. Then during the intervals $x_2 - x_1, x_3 - x_2$, etc., the mean excess of temperature is

$$\frac{\theta_2 + \theta_1}{2} - \beta, \quad \frac{\theta_3 + \theta_2}{2} - \beta, \text{ etc.}$$

And the loss of temperature then is

$$\Delta_1\theta = \left(\frac{\theta_2 + \theta_1}{2} - \beta \right) (x_2 - x_1)\Delta$$

for the interval $(x_2 - x_1)$

$$\Delta_2\theta = \left(\frac{\theta_3 + \theta_2}{2} - \beta \right) (x_3 - x_2)\Delta$$

for the interval $(x_3 - x_2)$, etc., etc.

Then if we take the algebraic sum of these variations we obtain $\Sigma\Delta\theta$ as the total correction for the observed temperature θ_n at the end of the experiment, which added to this observed temperature gives the correct value of θ to use in formula (2). This method requires us to know both the temperature of the external air and the quantity A . The first is known from observation; the second can be determined from the formula for loss of heat by radiation, which is given on p. 91, vol. i (Jamin's Physique), as

$$Q = \text{loss of heat per sec} = \frac{1}{4000} kS(\theta - \beta)$$

$$\text{hence } \Delta\theta = \text{ " temp. " } = \frac{1}{4000} \frac{kS(\theta - \beta)}{(M + W)c}$$

where

S is the surface of the calorimeter.
 k " value of a (small) calorie.

Hence

$$A = .00025 \frac{S}{M + W}^* \quad (6)$$

c being taken as unity.

Method of Regnault.†—To render the observation of the external temperature (a temperature always hard to determine with accuracy) unnecessary, the readings are taken at intervals as before, but commenced before and extended after the time during which equalization is taking place. The whole operation comprises three periods, the first a short period just before the introduction of the body; the second beginning with the introduction of the body into the calorimeter and ending with the maximum temperature; the third, during which a few additional observations are made on the rate of cooling. Let x be the interval between successive readings, a , n , and b the number of readings in the three periods respectively, and $\theta_0, \theta_1, \theta_2, \dots$ to θ_n , the readings of the thermometer during the second period, the body being introduced at the beginning of the $a+1$ th interval, ($\theta = \theta_0$). Also let t_1, t_3 equal the mean temperatures during the first and third periods, and Δ_1, Δ_3 the mean loss of temperature for these periods for the time, x , and let $\theta_{m'} = \frac{\theta_0 + \theta_1}{2}$, $\theta_{m''} = \frac{\theta_1 + \theta_2}{2}$, etc., and $\Delta_2', \Delta_2'',$ etc., be the mean temperatures and corresponding losses of temperature due to radiation during the successive intervals of the middle period.

* The value of the constant term in this formula will of course depend on the nature of the radiating surface of the calorimeter.

† This method of correction is essentially that described in Professor Holman's paper, in which a somewhat different method of reduction is adopted.

Then the maximum observed temperature θ_n at the end of the second period will be less than the true maximum by an amount $\Delta\theta = \sum_1^n \Delta_2$. To determine this quantity we make use of the same principle as before, viz: that the loss of temperature is proportional to the difference of temperature between the calorimeter and external air, or

$$\left. \begin{aligned} \Delta &= \kappa(t - \beta) \\ &= \kappa t - C \end{aligned} \right\} \quad (7)$$

the equation of straight line cutting the Δ axis at a point, $-C$, from the origin.

1.

The observations just given furnish data for drawing the line of which (7) is the equation. Thus in fig. 1 lay off $OA = t_1$, the mean temperature for the first interval, and AC , proportional to Δ_1 , the mean loss per interval, x , for same period; likewise lay off $OB = t_3$, the mean temperature for the third interval, and BD , proportional to Δ_3 , the corresponding mean loss. Draw through D, C , the straight line DCm ; this will be the line required. Then it is evident that for any other temperature, as some temperature θ_m during the second interval, the loss, Δ_2 , will be the ordinate to this line at a point whose abscissa is θ_m . The total loss during the whole of the interval $= \sum \Delta_2$. This summation may be effected by a formula derived from inspection of fig. 1. For

$$\begin{aligned} \sum_1^n \Delta_2 &= \Delta_2' + \Delta_2'' + \dots + \Delta_2^n \\ &= ab + cd + fe + \dots + \text{ordinate at } \theta_m^n \end{aligned}$$

Draw CE parallel to axis of t . Then

$ab=ao+ob$; $cd=co+od$, etc., etc.

$$\begin{aligned}\therefore \sum_1^n \Delta_2 &= n(ao) + bo + do + \dots + no \\ &= n\Delta_1 + \text{tang } \delta \{ \theta_m - t_1 + \theta_{mn} - t_4 + \dots + \theta_n - t_1 \} \\ &= n\Delta_1 + \text{tang } \delta \left\{ \frac{\theta_0 + \theta_1}{2} - t_1 + \frac{\theta_1 + \theta_2}{2} - t_1 + \dots + \frac{\theta_{n-1} + \theta_n}{2} - t_1 \right\} \\ &= n\Delta_1 + \text{tang } \delta \left\{ \sum_1^{n-1} \theta + \frac{\theta_0 + \theta_n}{2} - nt_1 \right\}\end{aligned}$$

Then to find $\text{tang } \delta$ we have

$$\text{tang } \delta = \frac{\Delta_3 - \Delta_1}{t_3 - t_1} \quad (\text{from fig. 1})$$

or as a final result

$$\sum_1^n \Delta_2 = n\Delta_1 + \frac{\Delta_3 - \Delta_1}{t_3 - t_1} \left\{ \sum_1^{n-1} \theta + \frac{\theta_0 + \theta_n}{2} - nt_1 \right\} \quad (8)$$

and true temperature after equalization will be

$$\theta = \theta_n + \sum_1^n \Delta_2$$

Other precautions which are of advantage will be readily noted by observing that loss by radiation depends upon three factors: 1st, excess of temperature of calorimeter above the temperature of the surrounding air. This excess will be diminished by making the mass of water M large, so that the rise in temperature, $\theta - t$, will be small. This cannot be carried too far, however, because when the interval becomes small the difficulty of reading temperature to the required degree of accuracy is greatly increased (see 5A and 5C). 2d, surface exposed. Theoretically the best form of calorimeter vessel would be a sphere; but as that is difficult of construction the next best form is that of a cylinder of maximum capacity per superficial area, viz: one in which the altitude equals the diameter of the base. 3d, time. The time element will be reduced by keeping the water well agitated and by using the body in the form of flat strips or wires rolled up into a ball instead of a solid mass.

Finally, there is an error in the observed temperature due to the thermometer itself, which, when its stem is exposed to a temperature below that of the bulb, indicates a lower reading than it should. This error can only be determined in any given case by careful experimental observations of the "time lag" and "stem lag" of the thermometer. To make it as small as possible, the thermometer should be of the smallest possible size, and immersed so deeply in the calorimeter that only enough of the stem projects to make the readings possible.

A better arrangement for observing both the temperature T and the temperature θ would be thermo-elements placed respectively in the heating chamber and in the calorimeter.*

(c) *New Method.*—Returning now to the method of Rumford, it is evident that we might indeed find such a value for the external temperature that the maximum reading θ_n would be the same as though there were no radiation. Thus in the figure below (fig. 1a), if we let the ordinates represent temperature and the abscissas time, we have, when no radiation takes place, the curve BC, whose equation is of the general form $x=f(\log \theta)$. Hence the maximum θ is *never* reached. When we consider radiation, however, we find that the curve BA will, when β has a certain value between t and θ (β being as before the temperature of the air), reach a true maximum at A, which is equal to the theoretical maximum θ . At this point the heat imparted to the water from the body just equals the heat lost by radiation.

1a.

$$\text{The heat lost by radiation, } dq_r = AS(\theta - \beta)dx \quad (9)$$

$$\text{The heat gained from the body, } dq_g = \frac{1}{\sigma} S_1(T_0 - \theta)dx \quad (10)$$

where σ is the coefficient of external thermal resistance; S

* A still more promising method of observing temperatures is the use of the platinum thermometer recently brought to such a degree of perfection by the work of Callendar. Either this, or the thermo-element (now immensely improved by the work of Barus and others), ought on account of its small mass, rapid response to change of temperature, and sensitiveness, to be far better adapted to accurate calorimetric work than the mercurial thermometer now so commonly employed. About the only advantage of the latter is its simplicity and cheapness,—qualifications which determine its use in ordinary laboratory work, but have far less importance in accurate research work.

and S_1 the surfaces of the calorimeter and the body respectively, and T_0 , the temperature of the cooling body. In general σ is itself a function of $T - \theta$ (see Rankine's Treatise on the Steam Engine, p. 260). Thus for a plate of thickness y and thermal resistance ρ immersed in a liquid the flow of heat through the plate is $\frac{1}{2\rho} \cdot \frac{T_x - T_x'}{y} \cdot S_1 dx$; T_x and T_x' being the temperatures of the two sides of the plate. The flow of heat from the liquid of temperature θ_x into the plate on one side is $\frac{1}{2\sigma}(T_x - \theta_x)S_1 dx$, and from the plate into the liquid on the other is $\frac{1}{2\sigma}(T_x' - \theta_x)S_1 dx$. If the temperature is uniform throughout the plate, i. e. if $T_x - T_x'$ is zero, as will be practically true if the thermal resistance ρ is very small compared to the external resistance σ , we get for the total flow of heat from the plate into the liquid at the time, x ,

$$dq_x = \frac{1}{\sigma} S_1 (T_x - \theta_x) dx = -wsdT \quad (11)$$

But from Peclet's formula

$$\sigma + \sigma_1 = \frac{1}{K\{1 + B(T_x - \theta_x)\}}$$

here

$$\sigma = \sigma_1$$

hence

$$\frac{1}{\sigma} = 2K\{1 + B(T_x - \theta_x)\}$$

Substituting in (11) we get

$$dq_x = (T_x - \theta_x) 2K\{1 + B(T_x - \theta_x)\} S_1 dx = -wsdT \quad (12)$$

and at maximum (9)=(10)=(12), or

$$AS(\theta - \beta) = 2KS_1(T_0 - \theta) + 2KBS_1(T_0 - \theta)^2 \quad (13)$$

Hence if we determine T_0 , all the quantities being known except β , this last may be readily calculated.

The determination of T_0 is attended with some difficulties, which may be avoided by expressing T_0 as a function of the time x_0 required for the contents of the calorimeter to acquire the maximum temperature θ .

The total heat imparted to the water of the calorimeter consists of two parts :

1st. Heat taken from body

$$= (T - T_0)ws, \quad \text{at time } x_0 \quad (14)$$

2d. Heat taken from air

$$= AS \int_0^{x_0} (\theta_x - \beta) dx \quad (15)$$

and since the heat contained in the water is the same at maximum point θ (by assumption) as though all the heat from the body had been communicated to it and no radiation had taken place, we have at the time, x_0 , of maximum

$$(T_0 - \theta)ws = AS \int_0^{x_0} (\theta_x - \beta) dx \quad *$$

or in general at any time, x , from the instant of immersion

$$(T - T_x)ws = (\theta_x - t)(M + W)c + AS \int_0^x (\theta_x - \beta) dx \quad (17)$$

To find an approximate value of $T_x - \theta_x$ for substitution in (12) we may neglect the last term as small compared with the others, and write

$$(T - T_x)ws = (\theta_x - t)(M + W)c$$

whence

$$(T_x - \theta_x) = T_x \left(1 + \frac{ws}{(M + W)c} \right) - \left(T \frac{ws}{(M + W)c} + t \right) = bT_x - a \quad (18)$$

Then substituting in (12), we get

$$-ws \frac{dT}{dx} = 2KS_1(bT_x - a) + 2KBS_1(bT_x - a)^2$$

Integrating we get

$$x \int_0^{x_0} = - \frac{ws}{2bKS_1} \left[\log \frac{bT_x - a}{2KS_1 + 2KBS_1(bT_x - a)} \right]_T^{T_0}$$

or

$$x_0 = \frac{ws}{2bKS_1} \log \left\{ \frac{bT - a}{bT_0 - a} \cdot \frac{1 + B(bT_0 - a)}{1 + B(bT - a)} \right\} \quad (19)$$

or

$$e^{\frac{2bKS_1}{ws} x_0} = \frac{bT - a}{bT_0 - a} \cdot \frac{1 + B(bT_0 - a)}{1 + B(bT - a)} \quad (20)$$

Then solving for T_0 we find

$$\begin{aligned} T_0 &= \frac{a}{b} + \frac{bT - a}{b\{e^{\frac{2bKS_1}{ws} x_0} [1 + B(bT - a)] - B(T - t)\}} \\ &= \theta + \frac{T - t}{b\{e^{\frac{2bKS_1}{ws} x_0} + B(e^{\frac{2bKS_1}{ws} x_0} - 1)\} (T - t)} \end{aligned} \quad (21)$$

* It may be observed that the value of the integral in the second member of this equation is not necessarily zero. In other words the conditions (value of β , etc.), which give the proper value of θ for use in equation (2) are not such as to make the total loss of heat by radiation zero, as assumed by Rumford.

where

$$R = \frac{2bKS_1}{ws} x_0$$

In this equation all the quantities are known, at least approximately, or may be observed or calculated except K , B , and T_0 . The values of the constants K and B for metal plates in contact with water are, according to Peclet (Rankine, p. 260),

$$K = \cdot 00119$$

$$B = \cdot 1044$$

I have not been able to find the data upon which these values are based. They will of course vary with the condition and nature of the cooling surface and will be larger when the water is well stirred than when it is not. The best way is to determine them, for the given body and given calorimeter, by a series of preliminary observations on x_0 , the time required for θ_x to attain its maximum value, θ . In making these observations, t should be made about $\frac{2}{3}(\theta - t)$ lower than β , the temperature of the surrounding air. Three such preliminary observations (made in the same way as they would ordinarily be made to determine s) would suffice (though a larger number reduced by the method of Least Squares would be better) to determine K , B , and T_0 , this last quantity as determined from (21) being practically the same (for such rapid cooling as always takes place in a properly conducted calorimetric experiment) as that which would be determined from the theoretically correct but far more complicated expression (17). Having thus found T_0 , we may then find a first approximation to the value of β from (13); A , the radiation factor of the calorimeter being taken as given by Jamin, or better determined for each calorimeter by experiment.

With this value of β a second set of observations are taken for x_0 and with this new value a second and closer value of β determined as before. Two such successive approximations will suffice to determine β with the desired accuracy.

The use of this method renders any precautions for preventing radiation useless. All that is necessary is to keep the temperature of the surrounding air uniform, and at the determined temperature (practically this is best done by adjusting the initial temperature t of the calorimeter contents), and keep the water in the calorimeter well agitated during the progress of the experiment, while screening the calorimeter from direct radiation from the observer's body. Then the maximum temperature attained will be the theoretical maximum, θ , desired, and radiation, instead of being a disadvantage, will become an advantage inasmuch as it lessens the time of the experiment

and makes the maximum more sharply defined. The greatest drawback to the use of this method is the preliminary labor of observing for and computing T_0 and β . But this preliminary labor is well worth while, when the highest degree of accuracy is aimed at.

Conclusion.—It appears then from the preceding discussion that the greatest possible care should be taken in reading temperatures, and since the errors of these readings are much greater than any others likely to be committed, it is advisable, in order to minimize the effect of these errors, to use

1. A small amount of water in the calorimeter; i. e., a small calorimeter.

2. A large mass of metal having a maximum surface for given weight (sheets or wire);

3. As high an initial temperature, T , as can be conveniently attained.

4. The calorimeter should be surrounded by a water jacket maintained at a constant temperature β , higher than the initial temperature t of the water in the calorimeter by the amount determined by (21) and (13).

Physical Laboratory, Ohio State University,
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NOTES ON CALORIMETRY.

The ordinary method of transferring the hot body from the heating chamber to the calorimeter by allowing it to slide down and out of an inclined tube into the mouth of the calorimeter is open to a number of objections, chief among which is the loss of heat in passing through the air, the loss of water by splashing, etc., and more important than all else, the loss of time in moving the calorimeter up to and away from the heating chamber, and in uncovering and covering the calorimeter at the most critical stage of the operation, when the attention of the observer should be entirely directed to the reading of temperatures, and disturbing influences should be reduced to a minimum. To avoid these difficulties I devised some time ago the arrangement shown in fig. 2. The tube, which forms the heating chamber of a Regnault apparatus, is removed and replaced in a more nearly horizontal position, A, B, fig. 2. A track consisting of two parallel steel wires, tied together at intervals, is laid along the bottom of this tube and continues for some distance beyond the lower end. On this track rolls a square (or cylindrical) double-walled car of sheet copper, mounted on four wheels, two (on one side) with grooved faces, and two (on the other side) with straight faces. In this car is placed, just over a trap door at the forward end, the object whose specific heat is to be determined. When the latter is being heated the car containing it is drawn up into the

heating tube by a silk cord passing over a pulley, and held taut by a mass attached to the free end, whose weight is somewhat less than the component weight along the track, of car and body together, and somewhat greater than that of car alone. The

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car is held in position by a pin *b*, on the steel wire *abc*, which is pivoted at *a* between the rails of the track. A second pin *c* at the lower end of this wire enters a catch on the inside of the door *B* at the lower end of the heating tube and holds it closed against the tension of a coiled spring.

The calorimeter itself is placed under the lower end of the track (six or eight feet distant from the heating chamber) and consists as shown in section in fig. 3 (taken at right angles to the section of the heating chamber fig. 2), of an inner copper chamber which differs from that ordinarily used in being much shorter (diameter=height) and in having a tightly fitting bottle-shaped top, the opening in which is just large enough to admit the heated body. Just under this opening is a wire basket with attached copper paddles, which is hung on three light brass wires, passing freely through tubular holes at the sides of the neck of the opening and on up through the outer double cover of the calorimeter. They are attached above by

hooks to a light brass ring, which in turn is pivoted in the forked end of a long wooden lever *a, b, c*. This lever is hung on a link at *b* and has a pin at *c* which moves in a slot cut in a plate of brass or hard wood of such shape that *a* moves up

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and down in a straight line. The end *c* is so weighted as to slightly overbalance the ring, bracket, etc., hung on the other end. The thermometer, *t*, is read by means of a very short focus telescope, made by slipping over the end of an ordinary reading telescope, a cap carrying a second object glass of about the same focal length as that of the telescope. It is balanced on pivots, *d*, so as to easily follow the movement of the mercury column. The inner calorimeter, which is filled with water almost up to the neck, is completely enclosed in a water jacket whose inner walls are blackened (not left bright as usual). The cover is double, of heavy sheet metal, and the hole in the center through which the body drops into the inner calorimeter has a hinged trap door, *f*, which can be turned back against a step on the calorimeter cover. When a good water supply is available, I have found that the temperature of this water jacket is most easily kept constant by allowing a slow constant stream to flow through it from bottom to top, from a large tank supplied from the city (or building) mains.

The method of introducing the hot body into the calorimeter is almost self-explanatory from what has preceded. The observer at the eye end of the telescope pulls open by aid of a string the trap door in the top of the water jacket, and then by means of a second string pulls down the end of the wire, *ac* (fig. 2), releasing the car and the door, *B*, at the same instant. The car runs rapidly down the track, throwing aside in its course the flaps of woolen cloth which cover the openings in the interposed wooden screens (see fig. 2), and is brought to rest by a rubber buffer which stops it in such a

position that the trap door in the bottom of the car is just over that in the water jacket. A pin fixed in proper position on the track knocks away the catch on the trap door of the car just as the latter comes to rest, and the body falls into the basket (which is held at its highest point by the overweight on the end *c* of the lever), precipitating the latter, both by its momentum and weight, downward into the water in the calorimeter. As the lever goes down the observer lets go the string which holds the trap door *f* open, and it also closes. The car, relieved of the weight of *w*, is pulled back out of the way by the attached weight. The observer himself has then only to observe temperatures while keeping the water in constant and complete agitation by moving the end *c* of the lever up and down.

The calorimeter is readily removed when temperature observations have been completed, by unhooking the wires, sliding the water jacket to one side from under the track, and lifting off the cover of the latter. The thermometer and wire basket remain in the calorimeter vessel, and are weighed with it, thus avoiding any loss of water, etc., consequent upon their removal.

This apparatus, although it may seem at first sight complicated, is in reality very simple, and readily put together by any one having a small shop in his laboratory, in one or two days. The great advantage resulting from its use will be readily appreciated. It enables, in the first place, one observer to do all the work of observation, although it is convenient to have some one to write down the thermometer readings. The use of the wire basket to catch the hot body, rather than allowing it to fall directly into the calorimeter, has three advantages: (1) it prevents splashing the water, and therefore allows the calorimeter to be filled nearly full, thus obtaining a maximum volume with a minimum of radiating surface; (2) it allows of a more thorough agitation of the water, the body itself being moved through it, and hence a more rapid equalization of temperature in the calorimeter; (3) it prevents any danger of breaking the thermometer bulb or injuring the sides or bottom of the calorimeter when a heavy body is dropped into it.

The use of the car to transfer the body from the heating chamber to the calorimeter not only prevents a loss of heat during the transfer, but also enables a number of small fragments, or even a mass of powder of the substance, to be used without the necessity of using an enclosing bulb, a device which always renders the equalization process slower and more uncertain.

Notes on the Bunsen Ice Calorimeter.

Filling.—More or less elaborate directions are generally given for filling the body of the calorimeter with water and mercury. The following process, which I have used for some time, is very simple, direct and efficient. The required quantity of mercury is first poured into the calorimeter through a small glass funnel, whose stem has been drawn out into a long, fine bulb, which will reach to the bottom of the side tube *b*, of

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the calorimeter. The calorimeter is then inverted in a beaker of distilled water deep enough to cover it to above the bend of the side tube, as in fig. 4. The mercury already introduced, which is now in the upper part of the water chamber, will hold the calorimeter down under the water. The beaker containing the water is now heated to boiling and cooled. When the calorimeter chamber *a* has been partly filled with water by the cooling, the whole is raised to boiling again, and kept at that temperature until all the air in *a* has been replaced by steam. On cooling again *a* will be completely filled with hot, air free, water. When cool enough to handle, the

finger is placed over the mouth of *b* and the calorimeter removed from the water and turned into the upright position. The mercury will run down to the bottom of *a*, leaving, however, some water still in *b*. This is then displaced by more mercury introduced through a funnel as before.

Maintaining at Zero Temperature.—In using the ice calorimeter it is necessary, as has been pointed out by Bunsen, to have the calorimeter surrounded by *pure* melting ice or snow of exactly zero temperature. Since perfectly pure ice or snow is difficult to obtain, it occurred to the writer some time ago that the most convenient way of securing the desired result would be to immerse the calorimeter in a vessel (a wide-mouthed bottle has proved very convenient in practice) filled with distilled water, and freeze a shell of pure ice on the inside of this bottle by placing it in a freezing mixture, leaving a space between ice and calorimeter filled with pure distilled water. When this has been done the whole arrangement is then placed in a larger vessel filled with ordinary crushed ice or snow. If this is not exactly at zero temperature (owing to impurities) the only result will be to cause a slow progressive freezing or thawing in the ice shell of the inner vessel. The distilled water being in contact with pure ice will, if occasionally stirred, remain at zero temperature.

Yerkes Observatory, June, 1897.