

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

TWO RAPID AND ACCURATE METHODS IN CALORIMETRY

BY WALTER P. WHITE

RECEIVED OCTOBER 6, 1925

PUBLISHED MAY 5, 1926

I. Avoiding One Rating Period

In calorimetry the total heat is normally determined in two portions; one which remains in the calorimeter and causes a *temperature rise* which is measured directly, and one which leaks away to the environment causing a *temperature loss* which has to be calculated. The chief field for brief and ingenious methods is in dealing with the temperature loss.

The calculation of the temperature loss (the "cooling correction") is generally thought of, probably, as essentially a multiplication of the calorimeter temperature by a factor giving the temperature loss per degree. In some rapid methods it is only that; but the factor is liable to change from day to day, so in accurate work a determination of the factor itself is made along with each experiment. Thus in the classical Regnault-Pfaundler formula

$$\text{t.l.} = \left[V_a + \frac{V_r - V_a}{\theta_r - \theta_a} (\theta_x - \theta_a) \right] T_x \quad (1)$$

where V is rate, T the time, θ the temperature during the periods, and the subscripts denote the three periods; x , the experimental, r , the chief or second rating period, a , the anterior rating period; the fraction is the leakage factor, that is, the change of rate with change of temperature, and the second term gives the change of rate from V_a , that observed in the anterior period, to the rate in the experimental period, which is the thing the experimenter wishes to get. The formula, however, is more useful if the rating periods are exchanged,¹ thus:

$$\text{t.l.} = \left[V_r + \frac{V_r - V_a}{\theta_r - \theta_a} (\theta_x - \theta_r) \right] T_x \quad (2)$$

The advantage depends upon the fact that θ_x and θ_r are usually nearly equal,² so that $\theta_x - \theta_r$ is a small fraction of θ_x . Whenever this is so (a) Formula 2 shows that the temperature loss calculation is not so much a computation of the whole loss as of the small difference between the desired loss and the observed loss, $V_r T$; so that the calculation is really a comparison of two nearly equal things, one of which is very accurately known. Since (1) and (2) are mathematically identical, this is true whenever $\theta_x - \theta_r$ is small; (2) only makes it more evident; (b) since the com-

¹ White, *Met. Chem. Eng.*, 9, 451 (1911).

² If heat is communicated to the calorimeter water from any body the time required for complete equilibrium is necessarily much longer than that in which most of the heat is transferred. Hence the water is near the final temperature during most of the experimental period. This is the case in the great majority of experiments.

puted term in (2) is much smaller than in (1), the multiplication is easier; it can be done by inspection, or with a slide rule, where more effort, time and possibility of error might attend the use of (1). Since (1) has no advantage under any circumstances, and since, when correctly computed, it gives a result identical with (2) it should apparently be altogether superseded by (2).

Formula 2, however, may have a much greater advantage. As the fraction is multiplied by $\theta_x - \theta_r$, its errors are also multiplied by $\theta_x - \theta_r$, and when this multiplier is small the effect of the errors is diminished. But the fraction is an expression for the thermal leakage modulus or factor of the calorimeter (symbol, K), so that (2) is equivalent to

$$t.1. = [V_r + K (\theta_x - \theta_r)] T_x \quad (3)$$

Hence, by so modifying (2) we get a formula and method where a predetermined value of K can be used, practically always in ordinary cases, and usually even for the highest precision. For instance, T_x seldom exceeds ten minutes, K seldom exceeds 0.003, and its variation, or error, should be as small as 2%; $\theta_x - \theta_r$ is often only 0.01 of the temperature rise; if it is taken as that, the whole error is $0.003 \times 0.02 \times 0.01 \times 10$, or 0.000006. This error is evidently quite negligible, even in work of 0.1 per mille precision, if one of its components should have five times the value here given.

There is some reason for thinking that the variations reported in the value of K were really not in that, but resulted from variations in the constant rate, the rate due to the heat of stirring and some other causes. Wherever this is the case Formula 3 appears still more valuable, for the constant rate is taken care of in the direct observation of the rate V_r .

Formula 3, then, saves one out of the usual two rating periods; that is, it gives half the saving that is accomplished by the less accurate and in some ways more troublesome brief methods with no rating period. It does this with no appreciable loss of precision in ordinary work and usually with none in work of the highest precision. It seems legitimate to consider (3) the standard formula, with the original formula (in form (2)) reserved for cases of special difficulty.

II. Diminishing the Experimental-Period Observations

There appears to be some demand for a diminution in the number of observations needed during the temperature rise, in order to calculate the temperature loss. Dickinson³ has suggested a method, whose error under favorable conditions may run from 0.1 to 0.3 per mille,⁴ which reduces the

³ Dickinson, *Bur. Standards Bull.*, 11, or *Bur. Standards Sci. Paper*, 230, p. 233 (1914).

⁴ This estimate is based on a comparison of Dickinson's and Davis and Wallace's reports. J. D. Davis and E. L. Wallace, *U. S. Dept. Interior Tech. Paper*, 91, 42, full line 12 (1918). Dickinson, Ref. 3, lower half of page.

number of observations to one only.⁵ It applies where the whole temperature rise can be taken to be approximately a single exponential curve. In nearly all cases higher precision is attainable by fitting to the observed curve a calculated curve, or a sequence of them, each coinciding at three points. The customary summation of the X-period observations really gives an inscribed polygon. The segments between the polygon and the curve are an error, and must ordinarily be made small by taking the points sufficiently near together. If curves, instead of straight lines, are used to fit the observed curve, a smaller number of points will give greater accuracy.

A convenient means of doing this is found in Simpson's Rule.⁶ All the formulas given by this rule are rigorous for curves whose equations are binomial, and thus come closer to an exponential curve than the ordinary observed curve does to either binomial or exponential. One formula applying to three observations defining two intervals is (calling the observations ABC) $A + 4B + C$. This gives six observations, and divided by three gives one per interval. Another, for four points and three intervals is $A + 3B + 3C + D$. This multiplied by three-eighths gives one observation for each of the three intervals. Another, for three points, each at the middle of one of three intervals, is: $3A + 2B + 3C$.

The possibilities of the method are indicated by a study of an actual temperature-rise curve, where nine observations had been taken over eight 15-second intervals. The results were as follows.

Number of observations used	Sum, as a polygon	Sum by Simpson's rule	Error of polygon	Error of Simpson's rule
9	10,763	10,804	-41	00 ^a
5	10,638	10,848	-166	+44
3	10,016	10,772	-788	-32

^a The 9-point Simpson result was taken as correct.

A comparison of several other similar curves confirmed the indication of this, namely, that the variations in the Simpson's rule results were purely accidental, resulting from the uncertainty of individual observations, and that three points only gave a perfect result by that rule, in striking contrast with the usual method. The sensitiveness of reading is evidently excessive, and the errors by Simpson's rule are far beneath the limit of the negligible.

⁵ The observation is necessarily of the time at which a predetermined temperature is reached, and this feature is a great advantage of the method when that is used with the usual resistance thermometer installations, since these, on account of inconstant galvanometer sensitiveness, are suited for null readings only, especially with changing magnitudes; but this point is of no permanent importance, since the present fashion in resistance thermometer installation is undesirable for several reasons. If the rheostat is put in the same arm of the Wheatstone bridge as the "bulb," an arrangement which much improves the treatment of lead resistance, constant galvanometer sensitiveness follows at once, and hence facility in reading changing temperatures, as well as greater freedom with all.

⁶ "Encyclopedia Britannica," 11th ed., vol. 18, p. 143.

Summary

A new method of calculating the temperature loss in calorimetry is described, in which a predetermined value of the leakage modulus can be used, and considerable time and labor thus saved, yet with no loss of precision in most cases.

By the application of Simpson's rule to the temperature rise observations a method is obtained which requires fewer observations than usual, but gives superior precision.

WASHINGTON, D. C.

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

COPPER COVERS FOR CALORIMETER JACKETS

BY WALTER P. WHITE

RECEIVED OCTOBER 6, 1925

PUBLISHED MAY 5, 1926

The advantage of having a uniform temperature for the surroundings of a calorimeter has doubtless always been seen. But the inconvenience of it led earlier workers to content themselves with a water jacket below and around the calorimeter, where such jacketing was easier, letting the top remain more exposed to the vicissitudes of the room temperature, and modern workers ordinarily pursue the same plan. The introduction of the submarine and the water cap methods of inclosure have made complete inclosure no longer difficult, and have led to its use where high precision is desired. In most cases the experimenter has still been content to supplement the water jacket below with a cover of wood or rubber above. Such covers diminish the effect of room temperature variations. They have, however, as Dickinson has pointed out,¹ a large lag, so that their temperature is uncertain, and often not very constant.

Vastly better is the cover of sheet copper,² bent down around the edge so as to dip into the jacket water. Since it can be satisfactorily constructed with no other tools than a pair of shears and a drill or two, its low cost is evident. Its superiority to mere thermally insulating covers seems equally evident, since thermal insulation from the room can very easily be added to the small lag and uniform temperature of the copper. How efficient it is seemed worth knowing, especially to find out how far it could be used in more accurate work, perhaps in place of the more elaborate water cap and submarine arrangements. An investigation of these questions forms the subject of the present paper.

Copper 0.8 mm. thick was used, and the diameter was 20 cm. The vari-

¹ Dickinson, *Bull. Bur. Standards*, 11, or *Sci. Paper*, 230, 197 (1914).

² Covers of *thick* copper have been mentioned, but without any data as to efficiency; for example (a) White, *THIS JOURNAL*, 40, 1888 (1918). (b) Bichowsky, *ibid.*, 45, 2230 (1923).