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.

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

COPPER COVERS FOR CALORIMETER JACKETS

BY WALTER P. WHITE

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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-

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[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).

ous arrangements tried, and the results obtained, are sufficiently shown in Table I. The discrepancies in this table were in part clearly due to changes in the arrangement of the blanket and, almost as clearly, in part to differences in air velocity. The apparatus was in a thermostated closet, and no pains were taken to maintain constant speed in the stirring of the air.

TABLE I

PERCENTAGE DIVERGENCE OF COPPER JACKET-COVER TEMPERATURE CAUSED BY DIFFERENCE BETWEEN JACKET-WATER AND AIR TEMPERATURES

	With stirring of the water				With no stirring			
	Air warmer		Air cooler		Air warmer		Air cooler	
	Rim	Center	Rim	Center	Rim	Center	Rim	Center
Cover bare	3.5	8.3	4.3	8.4	9	13	7	12
	2.5	7.5	5.7	11	6	9		
	5.7	10.4	6	12				
	5.4	10.1	4.9	10				
	4	6.1						
	4	7.1						
Cover blanketed	0.9	2	3.4	4.8	3.7	5	4.5	5.4
	1	2	2.5	3.2	0	2	6.5	8.3
	1	1	1.8	2.3			10.6	10.4
			2.3	2.6				
			3.2	2.2				
			3.9	4.6				
			2.0	4.1				
With kerosene and blanket	Very small		3.5	6	7.6	7.3	4	6
			2.7	4.5			5	7
							3	5
							2	4
Blanket under outer copper cover			1.3	0				

The variations with bath unstirred were less than some observed between different parts of the water; hence, when there is no stirring the copper cover adds to the uniformity of the whole environment. The stopping of evaporation by kerosene is evidently of little value as far as cover temperature is concerned. Observations not given here showed that the heat loss due to evaporation was about half that due to conduction, convection and radiation. A difference of 18 mm. in the height of the jacket water was tried in three of the stirred arrangements, and made no perceptible difference in the cover temperatures.

Practical Conclusions

The copper cover is more efficient when the air is warmer. Nevertheless, to avoid the necessity of always keeping the air warmer, and also to avoid possible error from the condensation of water vapor, it seems better to employ, or at any rate to provide for, colder air.

Changes in the cover arising from change in the calorimeter temperature will be more important, as a rule, than those due to the outer air, since the calorimeter changes almost suddenly, and no blanket can be interposed below the cover without diminishing the benefit it gives. This cover change, however, will be definitely related to the change in the calorimeter, and hence will cause no error in a calorimeter experimentally calibrated; that is, provided the lag of the cover is not too great. But if this lag is to be kept small, the rather large lag of the blanket should not be included in it. This end can be attained, without sacrificing the benefits of the blanket in shielding against room temperature differences or changes, by putting the blanket farther above the cover. The most effective way is to use a second copper cover with a blanket above that (Fig. 1). The blanket had better not touch the copper except at the rim, but should touch there, and should be of generous diameter, since the experiments reported in Table I indicated that an important service of the blanket is the exclusion of convection currents.

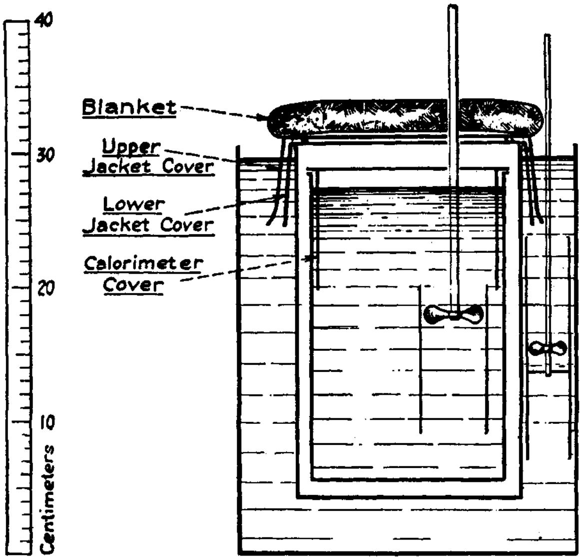

Fig. 1.—Shielded double sheet copper calorimeter jacket cover giving uniform enclosing temperature.

The effectiveness in shielding against room temperature can be quantitatively estimated as follows, according to Table I. The upper, blanketed cover would vary from the rest of the jacket by not over 4% of the jacket-air difference. The lower, unblanketed cover should not vary much more than 10% as much as the upper, that is, not over 0.4% of the jacket-air difference. Assuming, for safety, that the effect of the upper cover on the other, through the water or otherwise, is three times the above estimate.

we get a variation of 1.2% of the jacket-air difference. But the cover is opposite to only the top of the calorimeter, which has one-sixth the whole calorimeter surface, hence this 1.2% is equivalent to an error in the whole jacket of 1.2 ÷ 6 or 0.2% of the jacket-air difference. For calorimeters of the size used in getting Table I, the thermal leakage modulus ("cooling constant") will not be larger than 0.002 (degrees per minute per degree of calorimeter-jacket difference). Hence for a period of ten minutes, the maximum usually employed, the error in calorimeter temperature will be 0.002 × 0.002 × 10 or 0.00004 of the jacket-air difference. And this result, small as it is, contains a very large factor of safety, and is several times what is probable. Moreover, in experiments where the actual cooling rate is observed each time, the error would be only that due to the change of room temperature in the ten minutes intervening, and the final error, therefore, may be dismissed from further consideration. In experiments where a predetermined value of the leakage modulus is relied upon in calculating the amount of leakage, the error would be 0.00004 of the total air-jacket difference. But the uncertainty of such a predetermined value of the modulus at present is at least 2%, which corresponds to an error of 0.0004 times the temperature rise, if the time and modulus are as above, that is, 10 minutes and 0.002. Hence, unless the difference of air and jacket is over three times the temperature rise, the error from the double copper cover is negligible even when all rating periods are omitted.

The change in the lower copper jacket cover due to change in the calorimeter is greater than any ordinarily due to the room. From Table I, 0.12 time the temperature rise seems a generous estimate, but this may be doubled for safety. The lower cover, however, will be somewhat nearer to the upper cover, which is practically at jacket temperature, than to the calorimeter, so the 0.24 may be reduced again at least to 0.12. Since the cover affects only one-sixth of the calorimeter surface, the effective temperature difference is 2% of the rise, which, calculated as above, gives an effect of 0.0004 on the calorimeter. Hence, as far as this particular temperature difference is concerned, its value need be kept constant only to 0.1 of itself to be safely negligible in work of 0.1 per mille precision if the calorimeter is experimentally calibrated. This degree of constancy should be easy to secure, since variations in the height of the two covers or of the water are the only ones likely to affect the temperatures materially.

The lag of the inner copper cover when the calorimeter temperature changes is of the order of one minute, as indicated by experiments not here given. Error from any true lag is completely eliminated in an experimentally calibrated calorimeter,[3] except as the lag may vary. The pro-

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[3] White, Ref. 2 a, p. 1861, lines 7–11. The effect $LK\eta$, mentioned further down the page, is precisely the effect neglected on the preceding page, 1860, as appears from Footnote 1 to that page. If that effect is not neglected, the middle of p. 1861 ceases to be applicable, and the statement of lines 7–11, p. 1861, is absolute.

portional lag effect is fLK, where L is the lag in minutes, K the leakage modulus of the calorimeter and f the fractional part of the calorimeter affected by the lag. In the present case another factor enters, since the lagging change is only one-tenth of the temperature rise. It has been shown above that f is one-sixth, while L is 1. The formula, then, becomes $1 \times {}^1/_6 \times {}^1/_{10}K$ or ${}^1/_{60}K$. That is, the effective lag is one second. The total effect of the lag, then, is negligible in most work, and its probable variations always are.

In adiabatic calorimeters the sheet copper cover might be supposed to be inadmissible because in it the lagging change is larger, being equal to the whole temperature rise. But in other adiabatic systems also the lags in the jacket are relatively large; the equivalent lag of a copper cover is only ten seconds, which is quite of the order of magnitude of stirring lags often encountered; while the variation in this lag, the only thing that causes error, may be absolutely less than that of many a stirring lag. Actually, the total lag effect, fLK, is ${}^1/_6 \times 1 \times 0.002$, or 0.0003, and is, therefore, negligible in the most accurate work unless it varies by more than 10%.

Complete direct tests of the performance of the copper cover in calorimetry are practically impossible, for they would contain other errors larger than those here attributed to the cover. A single unblanketed cover, which has for several years been used with a 3-liter calorimeter, has proved entirely satisfactory. In a dozen runs of from 40 to 70 minutes the leakage modulus as calculated remained constant to 3%, and nearly always within 2%, which was about the variation to be expected from the errors of reading. Even if the error were all attributed to the copper cover, this result with a very crude cover is good enough for most work and indicates that the double cover of Fig. 1 will show sufficient precision in the most accurate work.

It thus appears that a suitable sheet copper jacket cover can be controlled well enough for work of the highest precision ordinarily considered in calorimetry, namely, 0.1 per mille, with the usual period of not over ten minutes, and can be used without hesitation for a precision of 0.3 per mille.

In one respect the copper cover is inferior to the water cap or submarine. Although its own temperature is quite satisfactory, it is much less effective in preventing flow of heat from the room direct to the calorimeter along stirring rod, thermometer or wires.[4] This source of error must beconsidered before the copper cover is adopted in any case. But copper sleeves or shields, the same in principle as the copper cover, can be used to control the temperature of rods or wires.

Summary

Calorimeter jacket covers of sheet copper dipping in the jacket water are altogether better than heat-insulating covers. They can replace the

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[4] Ref. 2 a, p. 1882.

water cap or submarine, even for a precision of 0.1 per mille, with one proviso. They are inferior to these two for preventing the flow of heat along thermometers, rods or wires.

It is necessary, not only for the highest accuracy but for all adiabatic methods and for all rapid methods of fair precision, to have the calorimeter completely surrounded by surfaces of known temperature; the copper jacket cover offers a very easy way of providing such an inclosure.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

THE CRITICAL CONSTANTS AND VAPOR TENSION OF PHOSGENE[1]

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Only one experimental observation of the critical temperature of phosgene is on record, and this is due to Hackspill and Mathieu,[2] who report a value of 183° from a direct observation. Paternò and Mazzucchelli[3] studied the densities of coexisting phases of phosgene, and by comparison of their density curves with Young's curve for pentane deduced the value 187° for this constant and the value 0.5135 for the critical density. No experimental values for the critical pressure of phosgene are on record. Paternò and Mazzucchelli,[3] using the modified van der Waals' relation, $P_c = {}^8/_3\sqrt{2}\ (R/M)\ T_cD_c$, deduced the value 51.5 atmospheres for the critical pressure. The vapor tension of phosgene has been the subject of two published investigations. Atkinson, Heycock and Pope[4] made measurements over a wide range of temperatures, from the boiling point of oxygen to the boiling point of water. Paternò and Mazzucchelli[3] covered a much smaller range, from —19° to +21°; each of two samples used was made the basis of a series of measurements throughout the temperature range studied, the successive series of measurements being made on the residue from the sample used in the preceding series after distilling off a portion of the liquid; in this way any more volatile impurities were progressively removed, and any less volatile impurities were concentrated in the residue. The effect of distillation on the vapor tension at zero of a sample of technical phosgene (prepared from carbon monoxide and chlorine) has been studied by Germann and Birosel;[5] their findings agree excel-

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[1] Part of the material included in this article is from a thesis submitted by Quimby W. Taylor to the Department of Chemistry of Stanford University in partial fulfilment of the requirements for the degree of Engineer in Chemistry, 1923.

[2] Hackspill and Mathieu, *Bull. soc. chim.*, [4] **25**, 482 (1919).

[3] Paternò and Mazzucchelli, *Gazz. chim. ital.*, **50**, I, 30 (1920).

[4] Atkinson, Heycock and Pope, *J. Chem. Soc.*, **117**, 1410 (1920).

[5] Germann and Birosel, *J. Phys. Chem.*, **29**, 1528 (1925).