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A New Bunsen-Type Calorimeter

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A new Bunsen-type calorimeter, using diphenyl ether as the calorimetric substance, is described. Tests of this calorimeter show that it can be used to measure quantities of heat of the order of 38 calories with a precision of about 0.05 percent.

1. Introduction

A new Bunsen-type [1][1] calorimeter for use in measurements of small quantities of heat, such as heats of mixing of polymers and solvents is described. The calorimeter uses diphenyl ether (phenyl ether, phenoxybenzene) as the calorimetric substance instead of water. The data reported in the literature indicate that Bunsen calorimeters using organic compounds as calorimetric substances have considerably higher sensitivity than that reported for the ice calorimeter [2, 3]. The organic compounds that have been used for this purpose include acetic acid [4], anethole [5], diphenylmethane [6, 8, 9] naphthalene [10,11], phenol [7, 12], benzalacetone [13], and diphenyl ether [14, 15, 16, 21]. The last-named substance has the important advantages that it is quite stable, it can be easily prepared in a state of high purity, and its melting point (26.87° C) is conveniently near room temperature.

2. Description of Calorimeter

The calorimeter is shown schematically in figure 1. It is similar in design to the ice calorimeter described by Ginnings, Douglas, and Ball [3], but has a larger central well to accommodate a "reaction vessel" for use in measurements of heats of reaction or heats of mixing.

The central well of the calorimeter was made from a piece of 1¾ in. stainless-steel pipe that was turned down to a wall thickness of 0.02 in. at the upper end to reduce thermal leakage, and is hard soldered to a copper insert in the jacket cover, *K*, and to the brass piece, *I*, which constitutes the top of the calorimeter proper. The brass bottom of the well is hard-soldered to the stainless-steel pipe. The copper fins, *F*, which are soldered to the outer wall of the well are partly to improve thermal contact between the well and the diphenyl ether, and partly for supporting the solid diphenyl ether, which is denser than the liquid. The copper spacers, *C*, between the fins at the lower end of the well are to promote uniformity in the vertical distribution of heat transferred between the well and the diphenyl ether outside of it. The outer shell, *E*, of the calorimeter is of stainless steel $\frac{1}{16}$ in. in thickness and is soft-soldered to the brass piece, *I*. The diphenyl ether occupies the space enclosed by the shell, *E*, the top, *I*, and central well of the calorimeter, with the exception of the space occupied by the pool, *H*, of mercury in the bottom of *E*.

An electric heater having a resistance of about 30 ohms is wound on the outside of the cylindrical part of shell *E* of the calorimeter, and a heater of about 10 ohms is wound on the hemispherical part of the bottom. Both heaters are cemented to the shell with glyptal lacquer, and are covered with aluminum foil to reduce radiation. They can be used separately or in series. The use of these heaters is described in section 4.

When the calorimeter is in use the outer surface of the central well is covered by a mantle of solid diphenyl ether. Heat transferred between the central well and the diphenyl ether causes partial melting or freezing, with a consequent change in volume of the diphenyl ether and a flow of mercury into or out of the calorimeter through the platinum tube, *W*, and the stainless steel tube, *J*, so as to keep the total volume of liquid plus solid in *E* constant.[2] The quantity of heat is measured by the volume or weight of mercury so transferred. If this is small, it can be determined from the displacement of the mercury meniscus in the 40-cm graduated glass capillary, *G*, the steel valve, *V*, being kept closed. If the volume of mercury is large it can be determined from the combination of the change in weight of the contents of the beaker, *B*, and the change in position of the meniscus in the capillary.

The capillary, *G*, is horizontal so that the changes in the position of the mercury meniscus in it do not affect the pressure on the diphenyl ether in the calorimeter. Changes in barometric pressure might be large enough to affect the position of the meniscus significantly. To reduce any such effect the open end of capillary *G* is connected to a 1-liter flask immersed in oil in a Dewar flask. The pressure in this system is adjusted to atmospheric at the beginning of an experiment and has been shown by measurements with a closed-end mercury manometer to remain practically constant during the time of an experiment.

The T-joint in the stainless-steel tube near the valve, *V*, and the connections to the valve and the glass capillary, *G*, are made with Apiezon wax.

The interchange of heat between the calorimeter and its environment is reduced to a minimum by

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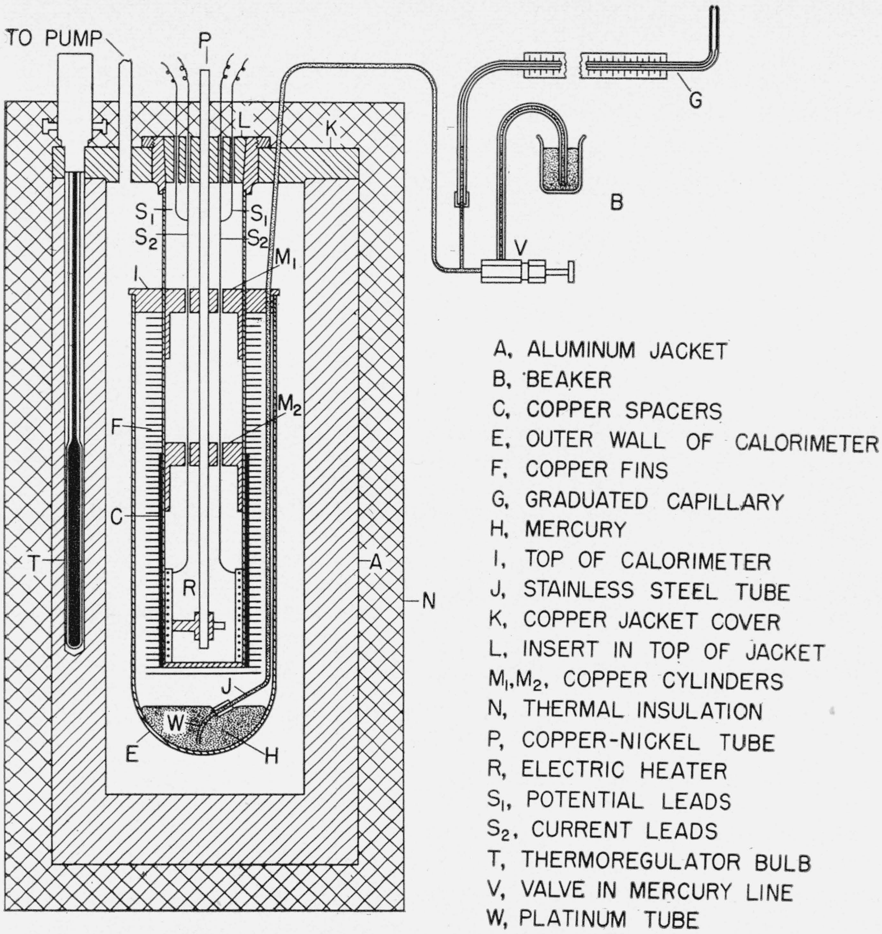
[1] Figures in brackets indicate the literature references at the end of this pape .

[2] The calorimeter was originally constructed with the stainless-steel tube *J*, extending nearly to the bottom of the pool of mercury. Difficulties were encountered due to creeping of the diphenyl ether past the mercury seal between diphenyl ether and the stainless-steel tube. This was overcome by replacing the lower end of the stainless-steel tube with the platinum tube, *W* [17]. The nickel sleeve connecting tubes *J* and *W* is sealed to them with a low-melting-point glass made of equal parts by weight of soda glass, borax, and zinc oxide.



A, ALUMINUM JACKET
B, BEAKER
C, COPPER SPACERS
E, OUTER WALL OF CALORIMETER
F, COPPER FINS
G, GRADUATED CAPILLARY
H, MERCURY
I, TOP OF CALORIMETER
J, STAINLESS STEEL TUBE
K, COPPER JACKET COVER
L, INSERT IN TOP OF JACKET
M_1, M_2, COPPER CYLINDERS
N, THERMAL INSULATION
P, COPPER-NICKEL TUBE
R, ELECTRIC HEATER
S_1, POTENTIAL LEADS
S_2, CURRENT LEADS
T, THERMOREGULATOR BULB
V, VALVE IN MERCURY LINE
W, PLATINUM TUBE

FIGURE 1. *Schematic drawing of calorimeter.*

surrounding the calorimeter with the aluminum jacket, *A*, with its copper cover *K*. The jacket is maintained at the temperature of the calorimeter within ±0.001 deg C by means of thermoregulator T. The temperature difference between the top of the calorimeter, *I*, and the copper jacket cover, *K*, is measured by means of a 10-junction copper-constantin thermocouple (not shown in fig. 1) and a Diesselhorst potentiometer. The coefficient of thermal leakage between calorimeter and jacket is reduced by radiation shields (not shown in fig. 1) of aluminum foil and by evacuating the space between calorimeter and jacket to a pressure of about 1μ.

The 100-ohm electric heater, *R*, the $\frac{3}{16}$-in. copper-nickel tube, *P*, the cylindrical copper pieces, M_1 and M_2, and the conical copper piece, *L*, form a unit, the lower part of which fits closely inside the central well. This unit, which is used only for calibrating the calorimeter, can be removed and replaced by a similar unit having a reaction vessel instead of the heater, *R*, together with suitable tubes for introducing reactants. The purpose of copper pieces M_1 and M_2 is to provide zones of good thermal contact with the wall of the well, and thereby trap heat that would otherwise escape by conduction along the leads, or by radiation and convection. The conical piece, *L*, fits into a conical hole in the jacket cover and forms a part of the jacket cover, and M_1 forms part of the top of the calorimeter proper.

The heater leads are brought out in such a manner that they are in intimate thermal contact with jacket *L* and calorimeter M_1. The potential leads are connected to the current leads midway between *L* and M_1. As the total resistance of the current leads between *L* and M_1 is approximately 0.01 ohm, or 0.01 percent of the heater resistance, the uncertainty in the heat developed between calorimeter and jacket is negligible.

The current through the heater was turned on and off by a double-pole double-throw switch similar to one described by Osborne, Stimson, and Fiock [20]. It is operated by a spring and a release that is actuated by second signals from a standard clock.

3. Filling the Calorimeter With Diphenyl Ether

3.1. Diphenyl Ether

The diphenyl ether used was purified under the direction of F. L. Howard by fractional freezing and distillation in the Engine Fuels Section of the Bureau. The purity was determined by R. E. McCoskey and G. T. Furukawa from measurement of the equilibrium temperature of a solid-liquid mixture for various known values of the mass ratio of solid to liquid. The value reported for the purity is 99.9985 mole percent and that for the triple-point temperature is 300.03° K. It was later found [18] that the purity of this sample of diphenyl ether after heating to about 360° K in a tin-lined calorimeter had decreased to 99.9926 mole percent.

3.2. Cleaning the Calorimeter

Before shell *E* (fig. 1) was soldered to brass piece *I*, it was washed internally, and the central well and attached vanes were washed externally with organic solvents to remove traces of oil or grease. After shell *E* was soldered in place, the interior surfaces were washed repeatedly with boiling distilled water until tests showed only a slight change in the resistivity of the water after such washings. The system was then heated internally and externally to a temperature somewhat lower than the melting point of the soft solder, and was evacuated for about a week at a pressure less than 10^{-4} mm of mercury to remove water and other adsorbed materials.

3.3. Introducing Diphenyl Ether and Mercury into the Calorimeter

The method of introducing diphenyl ether and mercury into the calorimeter can best be explained by reference to figure 2. The liquid diphenyl ether was first put into a 1-liter spherical flask, *F*, and slowly frozen under vacuum. This process was repeated several times until most of the dissolved gas was removed. Then with the diphenyl ether frozen the flask was disconnected from the vacuum system and sealed to the 2-in. glass tube, *T* (fig. 2), and connecting tubing, and connected to a vacuum pump and to the calorimeter as indicated. The system was then evacuated to a pressure less than 10^{-4} mm of mercury.

During this procedure the end of glass capillary *G* (fig. 1) was sealed, and beaker *B* (fig. 1) was replaced by a short glass test tube containing mercury and closed at the top by a rubber stopper with a hole of the proper size to fit the glass capillary leading to valve *V*. This tube was evacuated through a side tube above the mercury surface. Valve *V* was then opened so that the pressure in it and the glass capillary above it was reduced to that in the calorimeter (less than 10^{-4} mm). Valve *V* was then closed, and air admitted to the glass tube, which replaced beaker *B*, thus filling the valve and connecting glass capillary completely with mercury. The beaker, *B*, containing a weighed amount of mercury, was then replaced in its normal position, as shown in figure 1.

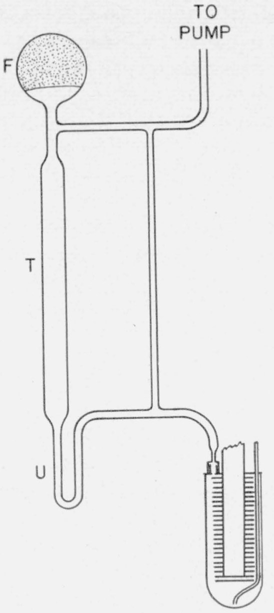


FIGURE 2. *Schematic diagram to illustrate method of introducing diphenyl ether into calorimeter.*

An attempt was made to remove any residual gas in the diphenyl ether before introducing it into the calorimeter, as follows:

With the vacuum pump operating, a small amount of diphenyl ether in flask *F* (fig. 2) was melted and allowed to run down into tube *T*, where it was refrozen by surrounding the tube with ice. The diphenyl ether in *T* was then remelted and allowed to run down into the U-tube at the lower end of *T*. After this the U-tube was kept in an ice bath to prevent any premature flow of diphenyl ether into the calorimeter. The procedure of melting a small amount of the diphenyl ether in *F*, freezing it in *T*, and finally remelting it and allowing it to flow to the bottom of *T*, was followed repeatedly until the entire amount had been transferred from *F* into *T*.

Valve *V* (fig. 1) was then opened, and the desired amount of mercury was introduced into the calorimeter. After this, the temperature of the room was raised above the melting point of diphenyl ether, the entire amount of diphenyl ether in tube *T* (fig. 2) and in the U-tube at the bottom was melted, and the liquid allowed to flow into the calorimeter. When the flow stopped, a small amount of liquid remained in the tube connecting to the calorimeter. Air was then admitted to the system through the line to the vacuum pump, raising the pressure to atmospheric. The connection to the calorimeter was then removed and the small opening into the calorimeter was closed by a conical stainless-steel pin forced into the opening by means of a screwcap. Holes in ths screwcap permitted washing out any diphenyl ether remaining outside the calorimeter proper in the space around the conical pin.

It is believed that by the above procedure the diphenyl ether introduced into the calorimeter was substantially free from dissolved gases. Unfortunately, however, a small amount of air was later introduced into the system due to failure of the room thermostat during a weekend, resulting in an excessively low room temperature and consequent freezing of enough diphenyl ether to draw all the mercury from beaker *B* (fig. 1), together with a small amount of air, into the calorimeter. The part of the air that was trapped in valve *V* and tube *J* was easily removed, but that which actually got into the calorimeter could not be removed without a major operation, which it seemed desirable to avoid. The air is normally dissolved in the liquid diphenyl ether and apparently does not seriously reduce the accuracy of measurements with the calorimeter, but it does cause considerable inconvenience in the use of the instrument.

4. Forming a Mantle of Solid Diphenyl Ether

The inconvenience in the use of the calorimeter resulting from dissolved air in the diphenyl ether has been greatest in attempts to form a satisfactory mantle of solid around the central wall. Because it is not possible to see into the calorimeter, some parts of the following discussion were inferred from the observed behavior of the calorimeter.

Because diphenyl ether may undercool several degrees, it is necessary to cool some part of the material in the calorimeter several degrees below its melting point to start freezing. This is done most conveniently by pressing a piece of ice against the wall of the central well. If any considerable amount of diphenyl ether is frozen in this way, air in the gas phase accumulates in the calorimeter, as shown by the fact that the change with pressure in the position of the mercury meniscus in the capillary, *G*, increases by a factor of as much as five in some cases. The excess sensitivity to pressure disappears due to solution of air in the remaining liquid, but mantles formed entirely by cooling with ice have never given satisfactorily consistent results in calibration experiments. It is inferred that this is due to air entrapped inside the solid in such a manner that it did not contribute appreciably to the apparent compressibility of the diphenyl ether, but that it dissolved in the liquid when the adjacent solid is melted in a calibration experiment, thus causing the observed increase in volume of the system to be low.

In some cases the freezing of the diphenyl ether was started with ice, and the central well was then filled with water and freezing continued slowly by bubbling air through the water. This procedure did not always lead to satisfactory precision in the calorimetric experiments. In some cases it appeared that in this procedure the mantle did not spread uniformly over the central well, but tended to grow over only a small area, and finally to bridge over the space between the central well and shell *E* (fig. 1) of the calorimeter.

The most satisfactory results were obtained with the following procedure: (1) A small amount of diphenyl ether was frozen by cooling with ice, and the calorimeter was left overnight to permit any gaseous air to redissolve. (2) The central well was filled with water, which was stirred by bubbling air through it; heat was supplied by means of the heaters wound on the outer shell *E* (fig. 1) of the calorimeter, and small pieces of ice were added periodically to the water in the central well. By proper adjustment of the heating current and the rate of addition of ice, the rate of freezing of diphenyl ether could be made as low as desired, and the temperature of the water could be maintained from 0.5 to 2 deg below the freezing point. Under these conditions it was expected that the mantle would spread over the central well so as to form a more or less uniform layer.

After the above procedure had been followed for about 1.5 hr, the addition of ice to the central well was stopped, and the current through the heaters was reduced gradually to zero as the temperature of the water in the well rose to the melting point of the diphenyl ether. Slow freezing of the diphenyl ether was then continued over a period of 2 or 3 days by bubbling air through the water in the central well, at first with the well filled with water up to the top of the calorimeter proper, and finally with about half of this amount in order to make the mantle thicker in the lower part where heat was to be added to it. During this slow freezing a small current was passed through the electric heaters on the outside of shall *E*.

Even with a mantle formed in the manner indicated, it was necessary to melt part of it by means of the heater, *R*, before consistent results could be obtained. It seems probable that the part of the solid diphenyl ether which was frozen with ice contained entrapped gaseous air, and this part must be melted and the air dissolved in order to obtain satisfactory results.

It is believed that the difficulties encountered in forming a satisfactory mantle are due to the air in the system, and that if no air were present, a mantle could be formed much more quickly and easily.

5. Thermal Leakage

The results of typical experiments to determine the thermal-leakage coefficient of the calorimeter are plotted in figure 3. The slope of the straight line corresponds to a thermal leakage of 0.0042 j (0.0010 cal) per minute for a temperature difference of 0.001 deg C between calorimeter and jacket. That part of the thermal leakage due to conduction along metallic connections between calorimeter and jacket has been calculated to be approximately half of the observed total, so that the other half may be assumed to be due to radiation.

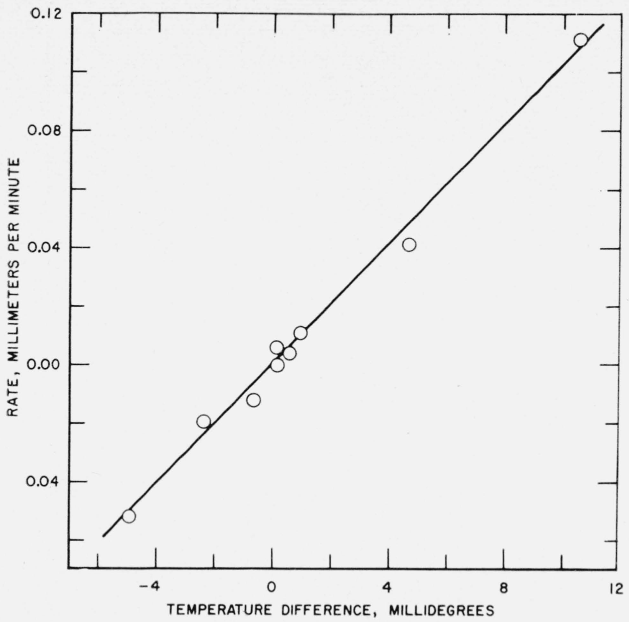


FIGURE 3. *Thermal leakage between calorimeter and jacket.*

Ordinate represents the rate change of position of the mercury meniscus in the graduated capillary tube. (1 mm is approximately equivalent to 0.1 cal) Abscissa represents temperature difference between calorimeter and jacket.

The observed thermal-leakage coefficient is a little larger than is desirable for measurements to a precision of one or two hundredths of a calorie. The "reaction period" for an electrical calibration experiment is about 30 min, and the temperature of the jacket varies in an irregular manner over a range of a few ten thousandths of a degree up to 0.001 deg. It is found, however, that the observed rate of heat transfer remains more nearly constant over periods of 1 or 2 hr than would be expected on the basis of the curve in figure 3 and the observed variation in jacket temperature. This is undoubtedly due to damping of the effect of fluctuations in jacket temperature by the radiation shields between calorimeter and jacket, the relatively heavy calorimeter wall, and the layer of liquid between the calorimeter wall and the mantle of solid diphenyl ether. Although this damping of the effect of fluctuations in jacket temperature probably reduces the uncertainty in the thermal leakage, this uncertainty nevertheless is very probably one of the major sources of error in the calorimeter, particularly in experiments extending over long periods of time.

6. Calibration of the Calorimeter

The graduated capillary, *G* (fig. 1), was calibrated by observing at various points along the capillary the lengths of 2- and 8-cm mercury threads with reference to the scale etched on the capillary, and by weighing the mercury removed from the capillary when the reading of the meniscus changed from 40 cm to zero. Corrections found for nonuniformity of the capillary bore did not exceed 0.2 mm (0.02 cal), and the mass of mercury required to fill the capillary was found to be $0.05239_8 \pm 0.000004_3$ (sdm) g/cm. This corresponds to an average capillary diameter of 0.71 mm.

TABLE 1. *Electrical calibration experiments*

Series	Experiment	Calibration factor	Deviation from mean for series	Deviation from mean of all experiments
		j/cm	*j/cm*	*j/cm*
1	1	4.1435	−0.0021	−0.0012
	2	4.1452	−.0004	+.0005
	3	4.1458	+.0002	+.0011
	4	4.1473	+.0017	+.0026
	5	4.1433	−.0023	−.0014
	6	4.1485	+.0029	+.0038
Mean		4.1456		
Standard deviation of mean			$\pm 0.0008_4$	
2	1	4.1461	+0.0021	+0.0014
	2	4.1438	−.0002	−.0009
	3	4.1418	−.0022	−.0029
	4	4.1421	−.0019	−.0026
	5	4.1444	+.0004	−.0003
	6	4.1450	+.0010	+.0003
	7	4.1443	+.0003	−.0004
	8	4.1449	+.0009	+.0001
Mean		4.1440		
Standard deviation of mean			$\pm 0.0005_2$	
3	1	4.1470	+0.00025	+0.0023
	2	4.1448	+.00003	+.0001
	3	4.1436	−.00009	−.0011
	4	4.1448	+.00003	+.0001
	5	4.1425	−.00020	−.0022
Mean		4.1445		
Standard deviation of mean			$\pm 0.0007_5$	
Mean of all results		4.1447		
Standard deviation of mean				$\pm 0.0004_0$

The calorimeter was calibrated electrically, using the 100-ohm heater, *R*, shown in figure 1, a Wolff-Diesselhorst potentiometer, a Wolff 0.1-ohm standard resistor, a 20000/20-ohm volt box, and a saturated cadmium standard cell maintained at a constant temperature of about 32.8° C by means of a temperature-control box [19]. The potentiometer, volt box, standard resistor, and standard cell were calibrated in the Electricity and Electronics Division of the Bureau immediately following the calibration experiments reported.

The results of three series of calibration experiments are given in table 1, expressed in absolute joules per centimeter displacement of the mercury meniscus in the graduated capillary, *G*. The results of each series were obtained on a separate mantle formed in the manner described in section 5. The amount of heat supplied to the calorimeter in each experiment was approximately 159 j (38 cal).

Table 1 shows that the results of each series of experiments are in satisfactory agreement among themselves, the maximum deviation from the mean in any one series being about 0.07 percent, which corresponds to about 0.11 j (0.02_7 cal) in the 159 j supplied to the calorimeter. However, the mean of the results of the first series differs from the means for the other two series by somewhat more than would be expected in view of the precision attained in the separate series. This suggests that perhaps the method of forming a mantle of solid does not entirely prevent the entrapment of air in the solid, and that the amount entrapped in different mantles may be significantly different, but that in any one mantle it is small enough and distributed uniformly enough through the solid to permit a relatively high precision in measurements with that mantle. It is to be expected, therefore, that to obtain a precision of the order of 0.1 j in the measurement of a small quantity of heat with the calorimeter it will be necessary to make a new calibration of the calorimeter for each new mantle.

If the individual results of all three series are averaged, the maximum deviation from the mean result so obtained of the mean for any one series is about 0.02 percent, corresponding to 0.03_5 j (0.01cal), but the maximum deviation of individual results from this mean is now 0.09_5 percent (0.15 j, or 0.04 cal).

Combination of the calibration factor 4.1447 j/cm with the value 0.05239_8 g/cm for the mercury required to fill the capillary yields the calibration factor 79.10 ±0.010 (sdm) j/g of mercury. This may be compared with the value 270.46 j/g of mercury reported by Ginnings, Douglas, and Ball [3] for the calibration factor of the ice calorimeter. The sensitivity of the diphenyl ether calorimeter is thus about 3.4 times that of the ice calorimeter.

Combination of the value 79.10 j/g of mercury for the calibration factor with the value 300.06° K for the freezing point of diphenyl ether under the pressure (114 cm of mercury) in the calorimeter yields the value $-\Delta H/T\Delta V=35.6_6$ bars per deg C. This value is subject to some uncertainty because of the fact that the observed value of $\Delta H/\Delta V$ may be affected by gaseous air in the solid diphenyl ether.

It is of interest to compare the calibration factor obtained in the present work with those reported by other investigators—who have reported their results in terms of weight (or volume) of mercury expelled per calorie. The results on this basis are as follows:

Author	Calibration factor
	g Hg/*cal*
Sachse [14]	0.0364
Holmberg [15]	.0488
Klemm, Tilk, and Jacobi [16]	.0528
Giguère, Morissette, and Olmos [21]	.05260
Present work	$.05289_5$

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