An Improved Ice Calorimeter—the Determination of its Calibration Factor and the Density of Ice at 0° C

By Defoe C. Ginnings and Robert J. Corruccini

There has been described an improved Bunsen ice calorimeter that has been constructed for measurements of enthalpy at high temperatures by the "drop" method. The calibration factor of the ice calorimeter has been determined electrically to be 270.37 ±0.06 international joules per gram of mercury, equivalent to 64.631 ±0.014 calories per gram of mercury where 1 calorie=4.1833 international joule. Using this calibration factor, it is calculated that the density of ice at 0° C and 1 atmosphere pressure is 0.91671±0.00005 gram per milliliter.

I. Introduction

In 1870 Robert Bunsen devised what is now known as the Bunsen ice calorimeter [1].[1] In this device, the heat to be measured is allowed to melt ice that is in equilibrium with water in a closed system, and the resulting volume decrease is determined by means of mercury drawn into the system. The calibration factor, K, of this ice calorimeter (ratio of heat input to mass of mercury intake) is related to the heat of fusion L of ice, the specific volumes of ice, v_i, and water, v_w, and the density of mercury, d_m, by the equation

$$K=L/(v_i-v_w)d_m. \qquad (1)$$

This type of calorimeter has several advantages. First, no temperature or electrical-measuring instruments are necessary if the calibration factor is constant. Second, its sensitivity is sufficiently high that it may be used in microcalorimetry. Third, when it is properly used in an ice bath, the heat leak is very small. On the other hand, it has the disadvantages that it must always be used at 0° C and that the volume of the calorimeter system must be constant. There has been some question of the constancy of the calibration factor of the ice calorimeter because of the poor reproducibility of measurements of the density of ice [2]. As the calibration factor depends on the difference in the specific volumes of ice and water

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

at 0° C, a variation of 0.01 percent in the density of ice would introduce a variation of 0.1 percent in the calibration factor. Values of the density of ice reported by various observers are rather scattered. The value given in the International Critical Tables [3] is given a tolerance of about 0.05 percent, corresponding to 0.5 percent on the calibration factor of the ice calorimeter. As this tolerance is many times larger than might be expected, the desirability for electric-energy calibration is evident. The calibration factor apparently has not been determined by the electrical method since 1914. It is the purpose of this paper to describe a modern ice calorimeter (developed for use in measurements of enthalpy at high temperatures by the "drop" method), the determination of its calibration factor by measured electric-energy input, and the investigation of the constancy of this calibration factor under various experimental conditions.

II. Experimental Procedure

1. Description of Apparatus

A schematic diagram of the ice calorimeter is shown in figure 1. A central well, A, is provided to receive objects whose enthalpy (heat content) is to be measured. This well tapers in diameter from 1 in. at the top to ¾ in. at the bottom. An electric heater, H, sheathed in a metal tube is soldered on the outside of the well in order to introduce known amounts of heat for calibration

purposes. The lower part of the well is surrounded by two coaxial glass vessels, M, which provide an insulating space between the inner ice-water system and the surrounding ice bath. The vessels are sealed to brass with Apiezon wax. Any change in volume resulting from melting ice in the inner vessel is transmitted to mercury in reservoir R_1 and thence through a valve, V, to a beaker, B, which is weighed to account for the change in the amount of mercury in the calorimeter system. A constant flow of dry carbon dioxide gas up this central well is provided to prevent diffusion of water vapor from above and condensation in the calorimeter. A coil, T, serves to cool the gas to the bath temperature. A specially designed gate, G, prevents transfer of heat from above to the calorimeter along the central well. The apparatus is immersed in an ice bath up to the level, L, in order to minimize heat leak.

2. Filling the Calorimeter with Water

The calorimeter was filled with water that had been distilled in a special still designed to remove about 99.9 percent of the dissolved gases. After the calorimeter system was thoroughly cleaned and evacuated, the air-free water was allowed to flow by gravity down through reservoir R_3, to fill the calorimeter and glass system. After an ice mantle was frozen in the calorimeter, pure mercury was sucked through the mercury valve, V, into reservoir R_3. Melting the ice mantle then brought mercury down into reservoirs R_2 and R_1, while another ice-mantle freezing pushed out any water trapped in R_2. The system above R_3 was then opened to the atmosphere without danger of contaminating the water. The function of R_2 was to trap any air accidentally let into the mercury system and prevent its entry into R_1, where it would contaminate the water. All metal surfaces in the calorimeter were coated with tin so that the water was exposed essentially to Pyrex glass and tin with only a small area exposed to the Apiezon wax. As a check on the upper limit of the amount of impurities in the water in the calorimeter, the water that had been used from July 5 to August 18, 1945, was removed and its electrical conductivity measured. In spite of some contamination during its removal, its electrical conductivity indicated a freezing-point lowering of only a few ten-thousandths of a degree. A check on the purity of the water while it was in the calorimeter was provided by observation of the heat-leak coefficient. As the ice-bath temperature was probably reproducible to a few ten-thousandths of a degree, as indicated by conductivity measurements, any lowering in the calorimeter temperature due to contamination of the water in the inner system would be detected by a change in the heat-leak coefficient. No significant change was observed during the 7-month period one sample of water was in the calorimeter.
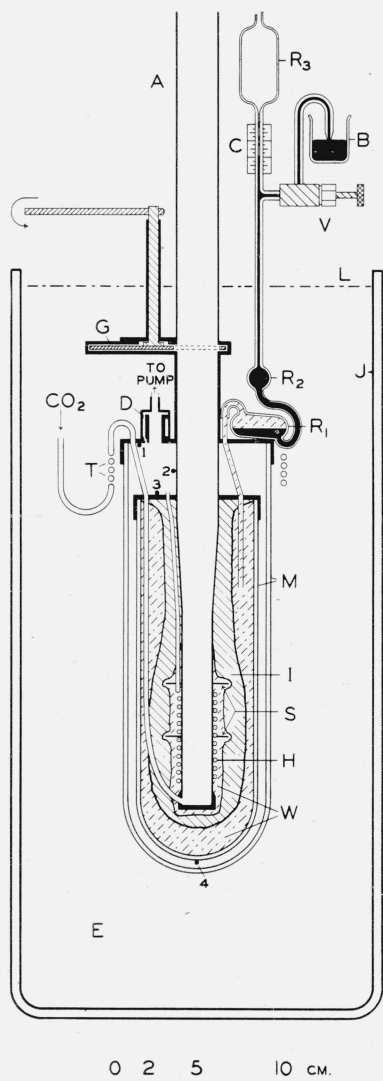

FIGURE 1.—*Diagram of ice calorimeter.*

A, Central well; H, electric heater; R_1, R_2, R_3, mercury reservoirs; V, needle valve; B, weighing beaker; T, cooling coil; G, gate; E, ice bath; L, ice-bath level; I, ice mantle; S, convection shields; 1, 2, 3, 4, thermocouple junctions; W, water; M, Pyrex vessels; D, heat shunt for electric leads; C, glass capillary with scale; J, Pyrex jar.

3. Description of Ice-Mantle Technic

An ice mantle, I, was frozen around the central well in the inner vessel by introducing a tube filled with solid carbon dioxide into the well. The shape of the ice mantle and the rate of freezing were controlled by adjusting the thermal contact between this tube and the well. The ice mantle was usually frozen in about $1\frac{1}{2}$ hr to approximately the configuration shown in figure 1. With this rate of freezing, no visible cracks in the ice developed during freezing, although some very small "filaments" always developed in the ice after the freezing was stopped. These filaments seemed to go all the way through the ice mantle to the central well and apparently [4] are spaces filled with liquid. Microscopic examination of ordinary ice showed similar filaments that were located at intersections of surfaces of individual ice crystals. As shown in figure 1, the tube connecting the calorimeter with mercury reservoir R_1 extended down into the calorimeter far enough to prevent ice closing the end of the tube. For ordinary rates of freezing, the water in this tube, where it was surrounded by ice, subcooled sufficiently to avoid freezing. Usually, an ice mantle was frozen and allowed to stand overnight before being used, although experiments have shown that this is not necessary if certain precautions are taken. The dimensions of the ice mantle around the lower part of the central well, where most of the heat is dissipated, permit the measurement of about 5,000 calories before the mantle melts through. Once the ice mantle has melted through, the calorimeter no longer accurately accounts for heat supplied to it as the warm water escaping to the outside of the pierced mantle then loses some of its heat to the outer ice bath.

The shields, S, served to reduce convection in the liquid water next to the central well and thereby distribute more evenly the melting of the ice. It would be advantageous to utilize a system of heat-diffusing metal vanes in the calorimeter so that the heat might travel more quickly to the inner ice surface. As the calorimeter is now constructed, the time required for the calorimeter to come to equilibrium varies from a few seconds when the ice mantle is very close to the central well to about 25 minutes after 4,000 calories have been absorbed. This latter time could probably be reduced to less than 5 minutes with a heat-diffusing system.

With the intent of establishing a fluid connection from the inside to the outside of the ice mantle, it was the usual practice to "premelt" a little ice along the central well and next to the brass lid of the inner system by introducing a tube with warm water into the central well. However, experiments made with no intentional premelting indicate that the response of the mercury meniscus to heat input is immediate in spite of no apparent liquid connection between the inner and outer water. This might possibly mean that the ice has been pulled away from the metal or that there is a liquid connection through the filament-like openings in the ice. It is believed that after "premelting", the calorimeter may be used for precise measurements as soon after freezing the ice mantle as thermal and mechanical equilibria are attained, and the calorimeter "drift", or heat leak, has been established. With the present apparatus, the calorimeter seems to be at equilibrium within 1 to 2 hr after freezing the mantle and packing the ice bath, provided no recent mechanical strain has been imposed on the system. An example of such a strain is a change in pressure of 1 atmosphere on the calorimeter system; equilibrium was attained only after at least 2 hr.

4. Description of Accounting for Mercury

The amount of mercury drawn in during an experiment is accounted for mainly by weighing the beaker of mercury. When the valve, V, is closed, the beaker may be removed for weighing and any small change in the amount of mercury measured in a calibrated-glass capillary. The observation of the position of the mercury meniscus in the capillary tube, C, is much easier than weighing mercury when changes are small. The position of the mercury meniscus in this capillary is usually made essentially the same at the end of an experiment as at the beginning. The capillary tube was calibrated in place by weighing the increase in the amount of mercury in the beaker as the mercury meniscus in the tube was lowered. This duplex system of measuring large energies by weighing mercury, and measuring small energies by observing the mercury meniscus in a glass capillary has proved very satisfactory. Before replacing the beaker of mercury, a slight

pressure is applied above R_3 with the valve open, thereby pushing out a small globule of mercury on the end of the tip of the capillary tube. In this way, no air is trapped when the beaker of mercury is brought up around the capillary tip. The glass capillary, which has a bore of about 0.6 mm, is constricted slightly at the tip. The valve consists of a hard steel needle seating upon a soft steel seat, using a paraffin-impregnated leather packing. The valve is designed to contain a minimum of mercury and is always in the closed position when the accounting for mercury is made. Precaution was taken to avoid an air bubble in the valve, which would cause the mercury column in the capillary to break above the end of the capillary as the beaker of mercury was removed. The amount of mercury in the glass capillary and steel valve was small enough so that changes in room temperature would not introduce appreciable error. Experiments described later indicate that the system of mercury accounting was sensitive to the equivalent of a few hundredths of a calorie, corresponding approximately to the precision in observing the position of the mercury meniscus in the glass capillary. In order to utilize this precision, proper precaution must be taken that the ice calorimeter and its mercury connections are rigidly mounted so that there is no appreciable variation in volume of the mercury and water systems due to any other cause than the melting of ice.

5. Heat-Leak Control

The heat leak was maintained small by keeping the temperatures of the calorimeter and the ice bath nearly the same. While barometric pressure was maintained on both the ice bath and the insulating gas space around the calorimeter, the pressure in the calorimeter was about 0.2 atmosphere higher than the barometric pressure due to the head of the mercury column between mercury reservoir R_1 and the mercury meniscus in the glass capillary. The excess pressure about compensates for the elevation of the temperature of the calorimeter due to the absence of air in solution so that the calorimeter is very close to 0° C. The temperature of the ice bath was maintained as close to 0° C as possible by using clear ice and pure water to make up the bath. It was found satisfactory to use the water from the melted ice to make up the bath from day to day.

The ice bath was contained in a large Pyrex jar with insulation, part of which could be removed for observation during the freezing of the ice mantle. One packing of the ice bath was sufficient for at least 12 hr, except for the top inch or so, which was repacked frequently. Several thermocouples were installed for detection of temperature changes. One thermocouple, having a principal junction (4 in fig. 1) on the bottom part of the inner-glass container, proved to be useful in detecting if the protecting ice mantle melted through because the warmer water quickly settled to the bottom. This same thermocouple served as a check on the proper maintenance of the top part of the ice bath as the reference junction (1 in fig. 1) of this thermocouple was located on the top lid of the outer vessel. Under actual working conditions, with dry carbon dioxide in the insulating space around the calorimeter, heat was lost from the calorimeter at the rate of about 0.3 cal/hr, corresponding to about 5 mg of mercury, or 0.7 mm change in the mercury height in the capillary. In order to insure dryness, the insulating space was evacuated once a day through a pump connection near D (fig. 1) and filled with dry gas.

In the evaluation of heat leak when the electric heat is on, it is necessary to consider the possibility of heat loss from the calorimeter by conduction, radiation, or convection up the central well. The heat loss by conduction was made negligible by using a central well made of thin (0.25 mm) copper-nickel for low thermal conductivity. This central well was tempered satisfactorily by the ice mantle, so that the temperature of the well at the top of the calorimeter was not affected by heat input at the bottom of the well. The radiation loss was made small by making the well relatively deep. Experiments described later proved that heat loss by radiation and convection was negligible.

As the calorimeter was devised for use in experiments where an object would be dropped into the central well, it was necessary to provide a gate that could be opened for a short time for the dropping, but which normally is closed exposing a surface near 0° C to the central well so that no heat would be radiated down to the calorimeter. The gate, G, consists of a copper disk (about 3 mm thick) that may be rotated inside a brass housing with only a few tenths of a millimeter spacing between the disk and the housing. Any heat received by

the part of the copper disk which is blocking the central well is dissipated through the gas space and housing to the outer ice bath. In this way, the temperature of the copper disk is maintained sufficiently close to 0° C so that there is no appreciable radiation down to the calorimeter. The copper disk is coated with a surface of polished tin to lower its emissivity. Experiments indicated that the gate is completely effective in dissipating radiation energy even when a furnace at 900° C is used above the calorimeter.

6. Electric-Energy Measurement

The electric heater used in the calibration experiments consisted of 10 ohms of glass-covered No. 34 AWG constantan wire, joined to No. 26 AWG silk-covered enamelled copper wire for current leads, all snugly contained in a thin copper tube about 1.3 mm in outside diameter. The constantan part of the heater was located in a coil, H, wound around the bottom 6 cm of the central well; the current leads extended up along the central well through the top lid of the inner vessel to the insulating space between the two vessels where the potential leads were attached. One potential lead was attached close to the inner lid and the other close to the outer lid on the assumption that one-half of the energy developed in the current leads in the space between the lids would pass to the calorimeter. From the resistance of the current leads, it was computed that about 0.05 percent of the total energy input to the calorimeter came from heat developed in the current leads in the insulating space. Both power and thermocouple leads going to the insulating space from the outside were brought through a tube to a heat shunt, D, where they were wound in good thermal contact with the metal for a length of 10 cm. In this way, any heat conducted from room temperature was dissipated to the ice bath. The measurements of electric power and time were made similar to those of Osborne, Stimson, and Ginnings [5].

III. Results

1. "Apparent" Calibration Factor

The results of the electric-calibration experiments made from July 28, 1945, to May 21, 1946, are given in table 1. In column 3 the mass of mercury listed is the difference in the weights of the beaker of mercury at the beginning and the end of the experiment, corrected for buoyancy, and also corrected for the heat leak and change in the position of the mercury meniscus in the glass capillary during the experiment. This last correction averaged only about 0.5 j and is not listed separately. In column 5, is given the total time of the experiment, that is, the time between the observation of the amount of mercury just before the start of the experiment and the similar observation when the calorimeter is considered to be at equilibrium. In column 6 is given the calibration factor, that is, the electric energy divided by the corrected mass of mercury. In column 7 are given any changes in experimental manipulation that were made to detect experimental errors and to determine if the calibration factor of the ice calorimeter was independent of certain variables. If nothing is given in column 7, the usual experimental manipulation was followed, consisting in freezing the ice mantle in about 1.5 hr, premelting a little ice around the central well, and using an electric power of about 7 w and a carbon dioxide flow rate up the central well of about 0.1 ml/sec.

Examination of table 1 shows that there are two main types of experiments, those with energies from 8,000 to 17,000 j, and those with energies of about 800 j. The large-energy experiments were made to minimize small absolute errors in energy and therefore give the best value of the calibration factor, while the small-energy experiments were made to detect any small absolute error that might be significant only in this type of experiment. The small-energy experiments of March 13, 14, and 15 gave the same result as the average of the large-energy experiments of February and March, indicating that no significant error of this type existed. It is interesting to note that the average deviation from the mean for these 800-j experiments was about 0.04 j/g, or about 0.1 j, which corresponds to about 0.02 mm on the height of the mercury meniscus in the capillary tube. No attempt was made to observe the position of this meniscus closer than the nearest 0.05 mm. It should also be noted that all small-energy experiments were made by using the part of the ice mantle close to the central well. Under these conditions, the time for the calorimeter to come to equilibrium is only a few minutes.

TABLE 1.—*Results of electrical calibration experiments*

Date	Heat leak	Mass of mercury	Electric energy	Time	Calibration factor	Variations in experimental manipulation
1945	*Int. j*	*g*	*Int. j*	*min*	*Int. j/g*	
July 28	4.6	45.3045	12249.1	63	270.37	
Aug. 1	0.6	45.5712	12319.2	66	270.33	
3	1.7	39.4351	10660.2	59	270.32	
4	0.6	60.5326	16367.9	64	270.40	
11	.0	51.1239	13823.0	62	270.38	
20	.6	60.1702	16267.5	69	270.36	Water in calorimeter changed.
Oct. 16	1.0	33.0416	8933.0	46	270.36	Water in calorimeter changed again.
16	1.2	33.0227	8927.1	64	270.33	
Nov. 2	1.3	55.7218	15064.9	85	270.36	Electric power input 1.7 larger than usual.
13	0.6	56.3255	15231.5	70	270.42	Ice 40 hr old instead of usual 17 hr.
15	3.6	52.4115	14169.7	101	270.35	Extra time due to capsule in calorimeter.
19	1.2	61.5785	16650.9	92	270.40	Ice mantle 5 hr old.
20	1.3	61.6041	16655.7	105	270.37	Ice mantle 3 hr old.
Dec. 18	0.4	61.9147	16739.6	75	270.37	
21	1.0	62.0205	16765.4	69	270.32	Ice mantle 60 hr old.
1946						
Jan. 5	0.06	3.0834	833.85	10	270.43	Ice mantle 4 hr old—no premelting around well.
5	.06	3.0834	833.80	11	270.42	Do.
5	.06	3.0828	833.80	14	270.47	Do.
5	.06	3.0841	833.79	16	270.35	Do.
5	.4	46.2425	12502.6	53	270.37	Do.
9	.10	3.0816	833.55	10	270.49	Do.
9	.10	3.0819	833.49	10	270.45	Do.
9	.10	3.0829	833.49	11	270.36	Do.
9	.10	3.0818	833.40	15	270.43	Do.
9	1.0	46.2339	12499.7	57	270.36	Do.
30	0.9	62.3932	16867.9	69	270.35	Froze ice mantle 5 times usual rate—no premelting.
Feb. 21	.3	61.9732	16752.2	68	270.31	Cotton in central well in calorimeter.
25	.5	59.0118	15951.9	80	270.32	Do.
26	1.0	61.0743	16509.9	76	270.32	Reduced CO_2 flow by one-half—cotton in central well.
28	0.9	44.5959	12058.4	62	270.39	Froze ice at one-fifth usual rate—cotton in well.
Mar. 4	.5	59.4616	16072.3	80	270.30	Cotton in central well.
5	.5	58.8596	15911.1	75	270.32	Reduced CO_2 flow rate to one-third usual rate.
6	.0	60.5402	16366.5	73	270.34	Increased CO_2 rate by factor of 2 (0.16 ml/sec).
8	.4	29.6909	8026.0	45	270.32	Froze ice at one-fifth usual rate—cotton in well.
9	.2	61.9352	16742.4	80	270.32	Low mercury level in reservoir—cotton in well.
11	.5	59.8744	16184.8	75	270.31	Froze ice under less pressure—cotton in well.
12	.6	59.3499	16043.8	79	270.33	CO_2 rate high (0.2 ml/sec)—shine light on ice.
13	.10	2.9555	798.96	10	270.33	
13	.12	2.9558	799.09	12	270.35	
13	.12	2.9565	799.11	11	270.29	
13	.15	2.9567	799.15	15	270.28	
13	.3	44.3087	11976.9	53	270.31	
14	.00	3.0846	833.56	10	270.23	
14	.02	3.0821	833.44	10	270.41	
14	.04	3.0827	833.35	13	270.33	
14	.06	3.0825	833.26	13	270.32	
14	.1	46.0957	12458.9	44	270.28	Electric power 1.7 higher than usual. No premelting around well.
15	−.10	2.9840	806.83	11	270.39	
15	−.08	2.9847	806.79	11	270.31	Do.
15	−.04	2.9853	806.83	11	270.27	Do.
15	.00	2.9844	806.77	12	270.33	Do.
15	.8	47.0496	12716.8	79	270.28	Electric power input 0.56 of usual—no premelting.
Apr. 22	.5	60.8200	16444.8	72	270.39	New power—measuring instruments used.
23	.2	60.6033	16387.1	71	270.40	Do.
May 14	.3	57.4830	15544.7	72	270.42	Do.
17	.4	63.9209	17283.3	70	270.39	Do.
20	−.2	63.7193	17229.2	72	270.39	Do.
21	.0	63.6903	17222.9	73	270.42	Do.

The small-energy experiments of January 5 and 9 were made with the ice mantle frozen only about 4 hr before the experiment and with no previous melting of the ice mantle next to the central well. These experiments indicated that about 0.02 percent error might be introduced under these conditions in the first few thousand joules of energy input. It should be noted that in the small-energy experiments of March 15, where no ice was previously melted next to the central well, the time interval after the freezing of the mantle eliminated most of this small error.

Of the large-energy experiments, those of November 2, March 14 and 15 were made varying the electric power by a factor of about 3. In the experiments of November 13, 19, 20, December 21, January 5 and 9, the age of the ice mantle was varied from about 3 to 60 hours. In the experiments of January 30, February 28, and March 8, the rate of freezing of the ice mantle was varied by a factor of about 25. From February 21 to March 6, a study was made of the possibility of loss of heat from the calorimeter up the central well, either by the carbon-dioxide flow or by radiation. The carbon-dioxide flow was varied from about 0.03 to 0.2 ml/sec, and any radiation was blocked by introducing a plug of cotton down the central well in the region just above the heater. The effect of not premelting a little ice around the central well was studied on January 5, 9, and March 15. On March 13 an experiment was made with a mantle that had been exposed to bright light for about 15 minutes, on the possibility that melting between crystals in the ice might affect the calibration factor. The experiments were made with three different charges of water in the calorimeter, the first in the calorimeter from July 4 to August 18, the second from August 19 to September 12, and the third from September 13 through the end of the experiments. On March 11 an experiment was made with an ice mantle frozen under about 0.2-atmosphere pressure instead of the usual 1.2 atmospheres. On March 9 an experiment was made with the level of mercury in reservoir R_1 much lower than usual in order to check that the change in level of the mercury during an experiment was sufficiently constant.

It is believed that none of the experimental variations described had any significant effect on the calibration factor, with the one exception previously mentioned that when an ice mantle is used within a few hours after being frozen, it may be desirable to premelt some of the ice around the central well. This is in contrast with Stern [6], who reports that it was about 4 days after freezing the mantle before the calorimeter was at equilibrium.

In connection with the experiments with old ice mantles, there should be mentioned a few experiments made in July 1945, in which quantities of heat from 800 to 2,400 j were put into the calorimeter in "drop" experiments by using ice-mantles that were 2 and 3 days old. These experiments gave results that were about 0.2 percent lower than experiments with ice mantles that were 1 day old. However, observations of the thermocouple (No. 3) on the upper part of the calorimeter, as well as observations of the time for the calorimeter to come to equilibrium in the morning, indicated that the reason for this behavior lay in the failure to maintain a protecting ice mantle in the upper part of the calorimeter. Because of the hot weather, one overnight packing of the ice bath did not prevent considerable heat flow to the top of the calorimeter. This melted so much of the ice in the top part of the calorimeter overnight, that during the experiments there was not enough ice to prevent loss of some of the heat at the top. In the electric-calibration experiments, precaution was taken that the part of the ice mantle in the top of the calorimeter was still intact.

It will be noted that the results show a downward trend in February and March. The explanation of this trend was found in tests on March 19 to 21, which showed that the calibration of the potentiometer used to measure power had changed since the last determination in November 1944 by about 0.013 percent, affecting the power readings by 0.026 percent. After adjusting the values in table 1 for July 28, 1945, through March 15, 1946, to allow for the potentiometer recalibration, the results prior to April 1946, gave an "apparent" calibration factor of 270.38 int. j/g of mercury. In April and May 1946, experiments were made by using different power-measuring instruments, including a new and more dependable potentiometer. These experiments gave an "apparent" calibration factor of 270.40, which was considered more reliable than the earlier value.

2. "Ideal" Calibration Factor

In the ice calorimeter described the level of mercury in reservoir R_1 rises slightly during each experiment, thereby lowering the pressure on the calorimeter. As the calorimeter system is not ideally noncompressible, this change in pressure produces a change in volume that must be accounted for in order to obtain the "ideal" calibration factor where the pressure remains constant. By observing the response of the meniscus to changes in pressure above R_3, it was found that a change in pressure on the system of 1 mm of mercury changed the height of the mercury in the capillary by 0.27 mm. Taking this compressibility and the observed change in level of the mercury in R_1 during an experiment (about 3 mm for 16,000 j), it is computed that the value of the calibration factor should be reduced to 270.37 int. j/g of mercury. The effect of the small accidental variation of the height of the mercury meniscus in the glass capillary is negligible as the method of calibrating the capillary takes into account the compressibility of the system, and the change in temperature of the calorimeter is negligible for the small pressure changes. Also the calibration factor for 1.0-atmosphere pressure would be essentially the same as for 1.2 atmospheres. Therefore the final value for the calibration factor of the ice calorimeter is taken as 270.37 int. j/g of mercury (equivalent to 64.631 cal/g of mercury when 1 cal=4.1833 int. j). The authors estimate the uncertainty in this value to be about ±0.06 int. j/g. This estimate is based mainly on the uncertainty in the accounting for heat developed in the calorimeter heater leads.

IV. Comparison of Results With Others

Prior to 1900 most experimenters determined the calibration factor of the ice calorimeter in terms of the heat capacity of water. The results of these determinations are not given here as they are not as accurate as those from electric calibration experiments. In recent years most experimenters in ice calorimetry have been satisfied with moderate accuracy in the measurements of small amounts of heat. These experimenters have therefore accepted the calibration factors given in earlier work. The most trustworthy of the determinations of the calibration factor appear to be those of Dieterici [7] in 1905 and Griffiths [8] in 1913, both made by electrical means. Dieterici made 10 calibration experiments of about 300 j each, with an average deviation from the mean of about 0.07 percent. After correction for changes in electrical standards to those now in use, his calibration factor is 270.49 int. j/g ±0.14. Griffiths made 12 experiments of about 1,000 j each with an average deviation from the mean of about 0.09 percent. His calibration factor was 270.18 int. j/g, which he regarded to have a probable error of 0.08 percent (±0.22 int. j/g). The value of 270.37 int. j/g from the present report is within the respective tolerances of both Dieterici and Griffiths.

V. Density of Ice

Using eq 1, the density of ice at 0° C and 1-atmosphere pressure may be calculated from the calibration factor of the ice calorimeter, the heat of fusion of ice, and the densities of water and mercury. Using 270.37 int. j/g of mercury for the calibration factor, 0.999868 g/ml for the density of water, 13.5955 g/ml for the density of mercury, and 333.5 int. j/g [9] for the heat of fusion of ice, the density of ice at 0° C and 1-atmosphere pressure was calculated to be 0.91671 g/ml. The largest uncertainty in this calculation is believed to be caused by the uncertainty of 0.06 percent in the heat of fusion of ice, which is equivalent to 0.00005 g/ml in the density of ice.

The numerous measurements of the density of ice have been reviewed by Dorsey [2]. The results of these measurements have been so scattered that some observers have believed the density of ice to be not strictly constant. The value given in the International Critical Tables [3] for the density of ice at 0° C and 1-atmosphere is 0.9168 ±0.0005 g/ml. It is believed that the ice calorimeter method provides the most accurate determination of this constant since this method is free from many of the difficulties inherent in other methods. On account of the filaments and cracks that all samples of ice appear to have, any experimental method that measures the "bulk" density of ice will obviously give a different result from methods, such as the present one, which determine the true density. Finally, no evidence has been obtained with the ice calorimeter that the true density of ice is anything but constant.

VI. Summary

1. There has been described an improve ice calorimeter that has been used in determinations of enthalpy at high temperatures by the "drop" method.

2. Electric-calibration experiments with this calorimeter indicate that the ice-calorimeter calibration factor is constant within the precision of the experiments under a variety of experimental conditions.

3. The calibration factor of the ice calorimeter has been determined to be 270.37 ± 0.06 int. joule per gram of mercury, equivalent to 64.631 ± 0.014 cal/g of mercury, where 1 cal=4.1833 int. j.

4. From this calibration factor, the densities of water and mercury, and the heat of fusion of ice, it is calculated that the density of ice at $0°$ C and 1 atmosphere pressure is 0.91671 ± 0.00005 g/ml.

VII. References

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