Journal of Research of the National Bureau of Standards Vol. 60, No. 4, April 1958 Research Paper 2848

An Adiabatic Calorimeter for the Range 30° to 500°C [1, 2]

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An adiabatic calorimeter accurate to 0.1 percent and suitable for heat capacity measurements of solids and liquids over the the temperature range 30° to 500° C is described. Factors affecting the design and accuracy are discussed. Automatic controls permit one-man operaion of the apparatus. Measurements of the heat capacity of Al_2O_3 agree to 0.1 percent with earlier measurements made with other calorimeters at the National Bureau of Standards.

1. Introduction

An ideal adiabatic calorimeter may be defined as one which has no heat transfer to its environment. As commonly used for the measurement of heat capacities, an adiabatic calorimeter is one which is heated over a small temperature interval, keeping the temperature of the environment as near as possible to the temperature of the calorimeter. This type of calorimeter has been used extensively at moderate and low temperatures. However, at high temperatures, the large coefficient for heat transfer by radiation increases the difficulty of avoiding heat transfer between the calorimeter and its environment. Only a few adiabatic calorimeters have been used above 500° C and even at this temperature, an accuracy as high as 1 percent is unusual [1, 2, 3, 4].[3] Consequently, at the high temperatures, the "drop" method has been more commonly used for the determination of heat capacities [5]. Although the drop method can reduce uncertainties due to increased heat transfer by radiation, it has one basic limitation which prevents its universal application This limitation is that the method can be used only for materials which reach a thermodynamically reproducible state at the temperature of the calorimeter. With certain materials having slow transitions, this reproducible state may not be reached. The element sulfur is such a material, because it has slow transitions which make accurate measurements impossible by the drop method. The calorimeter described in this report was developed for the temperature range 30° to 500° C with the intention that it would be used first to measure the heat capacity of sulfur.

2. Principles of Design

This adiabatic calorimeter was designed primarily to be accurate to 0.1 percent in measuring heat capacity up to 500° C. In order to attain this accuracy, a number of factors were considered. The evaluation of electric energy input to 0.01 percent is relatively easy with modern techniques. The use of a platinum resistance thermometer for measurement of the temperature change in the calorimeter makes possible an accuracy comparable with that of the electric energy. The largest uncertainty in measuring heat capacity with adiabatic calorimeters in this temperature range is believed to be the uncertainty in "heat leak" (heat transfer between the calorimeter and its environment) which results from experimental departures from the ideal adiabatic condition. Two steps are taken to approach the ideal condition. First, the heat transfer coefficient between the calorimeter and its environment is made small. Second, the temperature of the environment is kept as close as possible to the temperature of the calorimeter. This second step is much more difficult because the surfaces of the calorimeter and its environment are not isothermal, especially during a heating period. Consequently, in many calorimeters thermocouple junctions are distributed over the surfaces to "integrate" the temperature gradients and obtain mean surface temperatures. This procedure introduces difficulties because the mechanism for heat transfer may be different over the various parts of the surface. For example, a part of the calorimeter having a metallic connection to the environment may lose heat mostly by metallic conduction. Another part may loose heat primarily by radiation or conduction through gas. The amount and proportion of heat transferred by various means change with temperature or other circumstances, so that the ideal distribution of thermocouples for proper integration is difficult to achieve.

In adiabatic calorimetry, one of the best procedures is to make two types of heat capacity experiments, one with an empty calorimeter (or with a small amount of sample) and one with the calorimeter filled with the sample. The purpose of the experiments with the empty calorimeter is twofold. The first purpose is to account for the heat capacity of the empty calorimeter by taking the difference in the results of the two experiments. A second purpose, which is sometimes overlooked, is to eliminate heat leak errors and certain other errors which have the same absolute value in the two types of experiments. This procedure can be extremely useful in the elimination of the effect of some unknown heat leaks. However, the procedure does not eliminate heat leak errors which are different in the two types of experiments. Unfortunately, the very existence of the sample in the calorimeter during the heating interval makes the temperature distribution in the full calorimeter different from that in the empty calorimeter. It is therefore vital, for high accuracy, to design a calorimeter having essentially the same temperature dis-

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[1] This work was supported in part by the Allied Chemical and Dye Corporation and American Petroleum Institute Project 48A on the "Production, Isolation, and Purification of Sulfur Compounds and Measurement of Their Properties."

[2] This paper includes material from a thesis submitted by E. D. West to the University of Maryland in partial fulfillment of the requirements for the degree of Master of Science.

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

tribution over its outer surface in the two types of experiments. This has been accomplished in the present calorimeter by using a series of thin silver shields as described later.

In addition to high accuracy, the calorimeter was designed to require only one person for its operation. Adiabatic calorimeters capable of 0.1 percent accuracy over a moderate temperature range usually have required at least two operators. One of these operators has had to devote most of his time to controlling and recording the various temperatures pertinent to heat leak evaluation. The present calorimeter has been designed to use automatic equipment to make it possible for one person to operate the calorimeter without difficulty. The calorimeter was also designed to incorporate a sample container which could be removed from the calorimeter with a minimum of disturbance to the electrical system. To accomplish this, the calorimeter was designed in two parts, a sample container and a shield system surrounding and attached to the sample container.

3. Calorimetric Apparatus

Figure 1 is a schematic diagram of a vertical section of the apparatus. The calorimeter, defined as that part of the apparatus where energy changes are measured, is made in two main parts: (1) a sample container C surrounded by (2) a shield system consisting of the silver ring R_1 to which are attached two sets of silver shields S_1 and L_1. Surrounding the calorimeter is the adiabatic jacket which consists of the silver ring R_2 to which silver shields S_2 and L_2 are attached. Between the jacket ring R_2 and the calorimeter ring R_1 are two ten-junction thermopiles T_1 which indicate the vital temperature difference between the calorimeter and its jacket. Figure 2 is a photograph of the top of the calorimeter and jacket with lids L_1 and L_2 removed.

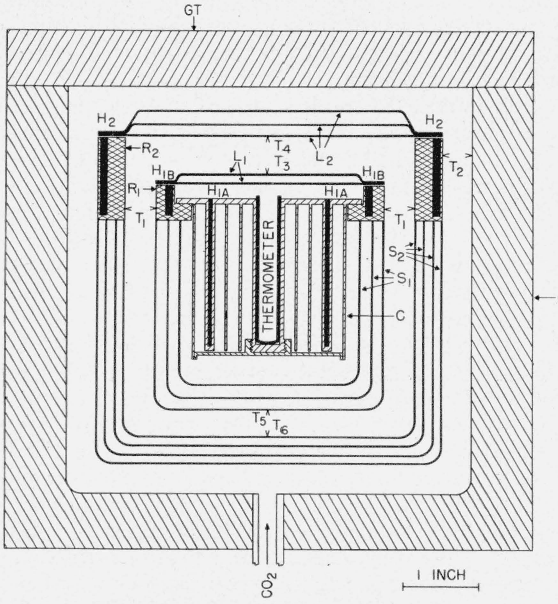

FIGURE 1. *Vertical cross section of the apparatus.*

C, sample container; G, GT, aluminum; H_2, jacket heater; H_{1A}, H_{1B}, calorimeter heater; L_1, L_2, silver lids; R_1, R_2, silver rings; S_1, S_2, silver shields; T_1, thermopile; T_{2-6}, thermocouples.

Surrounding the jacket is a "guard" G whose temperature is controlled a few tenths of a degree below that of the jacket to reduce the power required in the jacket and the consequent temperature gradients. It also guards the jacket from effects of changes in ambient conditions and in the temperature gradients in the glass fiber which is used for thermal insulation of the apparatus.

3.1. The Calorimeter

An essential requirement underlying the design of the calorimeter is that the temperature distribution on its outer silver surface must be independent of the amount of material in the sample container so that the empty calorimeter experiments will properly account for the exchange of small amounts of heat with the jacket. As a practical matter, it is important that the container be easily removed for filling. Consequently, the additional requirement must then be imposed on the design that the temperature distribution on the outer surface also be independent of variations in thermal contact due to differences in the way the sample container is installed. It is apparent that success in meeting these requirements will depend to a great extent on minimizing changes in temperature gradients on the container itself and between the container and ring R_1. It is desirable that these gradients be small so that their changes will be small. For control purposes, the design must meet the further requirement that the calorimeter must reach thermal equilibrium quickly.

The sample container C, figure 1, is a cylinder 2 in. high and 2 in. in diameter made from aluminum alloy 1100 (99+ percent pure) with a stainless steel cover screwed on the bottom. Aluminum was used here so that the container could later be adapted to the measurements on sulfur. In order to distribute heat quickly to the sample and keep gradients small, the

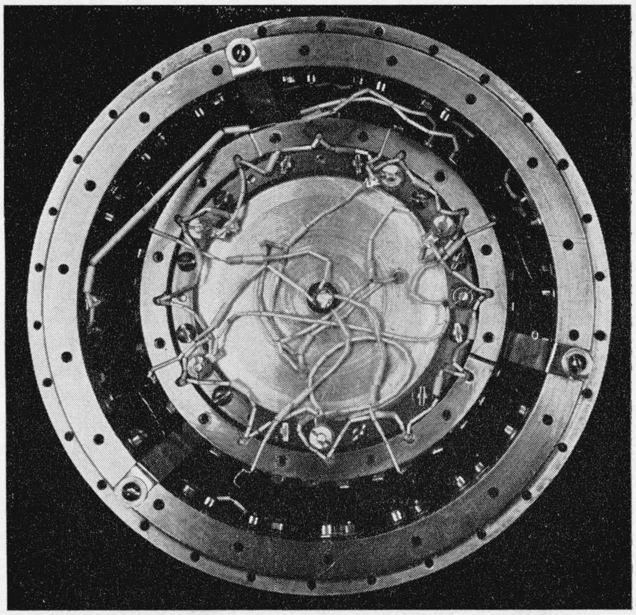

FIGURE 2. *Top view of the calorimeter and jacket.*

container is made from a solid cylinder of aluminum by boring many holes 2 to 5 mm in diameter and leaving a web of metal between holes so that no part of the sample is more than 2.5 mm from a good thermal conductor. The container has an internal volume of 70 cm ^{3} and a mass of about 112 g. In a central well in the container is a platinum resistance thermometer enclosed (but not sealed) in a Vycor tube which is ground cylindrical to permit a good fit in the well. Also inserted in the top of the sample container are three coils (H_{1A}, fig. 1) of the calorimeter heater. This placement of the heaters permits observation of the calorimeter temperature within a few hundredths of a degree while heating.

The sample container is held against the silver ring by a thin stainless steel ring and twelve stainless steel screws. To avoid contact of aluminum with silver, another thin stainless ring is silver-soldered to the ring where it is in contact with the sample container. This second stainless ring also provides a strong material for attaching the screws.

The ring R_1 is made of pure silver 0.8 cm^2 in cross section to reduce temperature gradients due to circumferential heat flow. It provides space for 12 short heater coils and 20 junctions of the thermopiles which measure the effective temperature difference between the calorimeter and its jacket. Silver-soldered to the ring are three silver shields each 0.25 mm thick. The function of the shields is to provide an external surface on which the effect of the gradients on the sample container and between the sample container and the ring is greatly attenuated. It is calculated that the attenuation by one shield is a factor of about 8, so that the attenuation by three shields should be about 500. The temperature differences on the surface of the sample container are significant only during the heating interval. They are calculated to be not greater than 0.02° C when empty and 0.04° C when full. The temperature difference between the sample container and the ring is made small by distributing the calorimeter heater between them approximately in proportion to their heat capacities. By various combinations of the heating coils allowance is made for the full or empty sample container. During heating, the temperature difference between the sample container and the ring is calculated to be about 0.05° C, which is less than 10 percent of what it would be if the heater were all in the ring. Assuming the uncertainty in the reproducibility of this gradient is as much as the calculated gradient, the variation in the average temperature of the outer surface of the calorimeter due to variations on the sample container is estimated to be only about 0.0001° C.

More critical than the thermal contact between the container and the ring is the contact between the lid L_1 and the ring R_1, because variations in this contact are not attenuated and directly affect the temperature over almost one-sixth of the outer surface of the calorimeter. This contact is made between the soft silver lid screwed down against a stainless steel ring. Although the heat capacity of the lid is small, all the heat required to raise its temperature during the heating interval must come from the heaters in the ring through this mechanical contact. In disassembling the calorimeter, this contact is usually found to be so good that the lid and ring must be forced apart, indicating that some heat is transferred by direct metal-to-metal conduction. However, to arrive at an estimate of how large the temperature difference between the ring and the lid may be, it is assumed that heat transfer is only by gaseous conduction through an effective spacing of 0.0002 in. With these assumptions, the temperature difference between lid and ring is calculated to be 0.001° C. The single-junction thermocouple T_3 is not sensitive enough to determine variations in this thermal contact, but it does set an upper limit of a few thousandths of a degree.

The calorimeter heater was designed to have large electrical resistance and small heat capacity. The coils for this heater (and also for the jacket heater) are made by winding helices of oxidized 38 Nichrome V wire to fit inside porcelain tubes 1 mm i. d. The lead from the lower end of each coil is brought up through a smaller porcelain tube inside the helix. To reduce the heat developed in the leads between coils, the helices are arc welded in helium to larger nickel leads. The total resistance of all calorimeter heaters in series would be 640 ohms, but the sections are connected in two series-parallel combinations to give 77 ohms for the empty calorimeter and 60 ohms for the full calorimeter. The heat capacity of the heater is about 1 j deg^{-1} C, which is less than 0.3 percent of the heat capacity of the full calorimeter.

3.2. The Adiabatic Jacket

The main purpose of the adiabatic jacket is to minimize heat transfer from the calorimeter. To accomplish this purpose, both the heat transfer coefficient and the temperature difference between the jacket and the calorimeter are made small. The jacket is adiabatic if its effective temperature is equal to that of the calorimeter. At equilibrium, this equality can be checked by following the calorimeter temperature. However, during the heating interval, no such check on the heat transfer is available. In place of effective temperature equality, the more feasible requirement has been substituted that temperature inequalities and the corresponding small heat losses be the same in the two experiments—one with the calorimeter full and one with it empty. If this substitute requirement is satisfied, then, when the empty heat capacity is subtracted from the full heat capacity, allowance is automatically made for those small heat losses which are the same in the two types of experiments. The uncertainty in the equality of these small heat losses is frequently the chief limitation on the accuracy of the heat capacity measurements.

In order that heat losses compensate, any errors in measuring the temperature difference between the calorimeter and its jacket must be the same in the two types of experiments. These errors are greatest during the heating interval. To make them the same in the empty and full experiments, the thermopile junctions must have the same thermal lags and the gradients on the outer surface of the calorimeter and the inner surface of the jacket must be the same. The temperature difference between the jacket ring and the calorimeter ring is measured by means of two ten-junction Chromel-Alumel thermopiles (T_1, fig. 1) connected so that their emf's are additive. These two thermopiles are compared frequently by opposing their emf's to detect circumferential gradients on the silver rings. The junctions are made at "thermal tiedowns" which consist of small gold tabs sandwiched between mica washers for electric insulation and squeezed against the silver rings by stainless steel nuts. These thermal tiedowns are similar to, but larger than, those used previously in this laboratory [6]. At the usual heating rate of 0.5° C min^{-1}, tests indicate the junctions of the thermopile lag about 0.02° C below the rings. The lag in junctions on the calorimeter is compensated for by the lag in those on the jacket, so that the error in the observed temperature difference will be considerably less than 0.02° C. However, it is necessary to have this temperature difference reproducible to better than 0.001° C between the full and empty measurements. To insure maximum reproducibility, the thermopile junctions are not disturbed when the sample container is removed for filling. To prevent cooling of the thermopile junctions by conduction along the leads an extra thermal tiedown was installed in each of the four leads to bring them to the jacket temperature.

In addition to making the thermal lags the same, the gradients on the inner shield of the jacket must be reproducible, just as the gradients on the outer surface of the calorimeter must be reproducible. However, the variations to be attenuated by the jacket are due to disturbances on the outside and are considerably larger. The attenuation at 400° C has been determined by altering the guard temperature 0.75° C and observing the effect on the calorimeter. The change in the rate of heat transfer corresponds to an offset of the jacket temperature of 0.0056° C, an attenuation of 130. The attenuation is much greater at lower temperatures. The uncertainty in the guard temperature, estimated from observations of time and circumferential variations of thermocouples is less than 0.3° C. From this estimate the uncertainty in reproducing the temperature distribution inside the jacket is calculated to be about 0.002° to 400° C.

During the heating period, there are gradients on the shields S_1 and S_2 due to heat flowing from the rings R_1 and R_2 to raise the temperature of the shields. When the calorimeter is being heated at 0.5° C min^{-1}, the temperature difference between the ring and the center of the bottom of the corresponding shield is about 0.1° C. The maximum temperature difference between the outer shield of the calorimeter and the inner shield of the jacket occurs between the centers of the shield bottoms and is about 0.05° C. The gradients in these two shields and therefore the effective temperature difference between them are very nearly proportional to the rate of heating. Consequently, the rate at which heat is lost from the calorimeter by transfer between these shields is directly proportional to the rate of heating. On first thought, it may appear that the rate of heating in the empty experiment would have to be made the same as in the full experiment. That this is not the case may be seen from the following considerations: In any given experiment, the heating rate is virtually constant, so that energy lost from the calorimeter is directly proportional to the product of the heating rate and the time of heating. Since this product is equal to the change in the calorimeter temperature, the energy lost is the same in the empty and full experiments if they have the same initial and final temperatures. The rate of heating in both full and empty experiments was adjusted to 0.5° C min^{-1} within 3 percent, but, to establish the validity of the above conclusion, two experiments in which the heating rate was one-half the usual rate were carried out at 660.05 and 669.75° K. The data for these two experiments are given in table 1 (see note b). At these temperatures the large heat transfer coefficient would result in the largest effect on the heat capacity values, but no such effect is apparent.

In addition to reproducing the errors in measuring the temperature difference, it is necessary to avoid changes in the heat transfer coefficient between the empty and full experiments. During the heating interval, the gradient on the inner jacket shield is different from that on the outer calorimeter shield, resulting in a net temperature difference even when the ring temperatures are matched. If the heat transfer coefficient were to change between the empty and full measurements, there would be a systematic error equal to the product of this change and the average temperature difference between the shields, which is calculated to be about 0.026° C at the normal heating rate.

To avoid large absolute changes in the heat transfer coefficient, it has been made small by using silver for the outer surfaces of the calorimeter and the inner surfaces of the jacket. The silver surfaces were clean, but not polished. Silver loses its polish when heated, but the heat transfer by radiation is not changed much because the orientations of the new crystallite faces are at small angles with the average plane of the surface. The coefficient for heat transfer by radiation is calculated to be 0.10 w deg^{-1} C at 400° C. The coefficient for heat transfer by CO_2 gas conduction across the 1-cm space is calculated to be 0.07 w deg^{-1} C at 400° C. Although the heat transfer coefficient could be reduced by the amount of the gas conduction if the system were evacuated, the gain would be more than offset by the adverse effects where good thermal contact is desired, i. e., at the lids, heaters, thermocouple junctions and the thermometer.

Heat conduction along leads and supports is minimized by using small wires and poor conductors whenever possible. The thermopile is made of No. 36 AWG Chromel P and Alumel wires. The seven heater and thermometer leads are No. 32 AWG gold between the calorimeter and the jacket. The three supports for the calorimeter are Nichrome V, 6 mm wide and 0.1 mm thick. The total metallic conductance is about 0.006 w deg^{-1} C. The leads

TABLE 1. *Heat capacity of aluminum oxide* [a]

Temperature	Empty Calorimeter		Calorimeter+Al_2O_3		C_p° of Al_2O_3 This work	Standard deviation	C_p° of Al_2O_3 Ref. 5	Difference This work—Ref. 5
	Date	Heat capacity	Date	Heat capacity				
°*K*(*Int. 1948*)		*abs j deg*$^{-1}$		*abs j deg*$^{-1}$	*abs j deg*$^{-1}$ *mole*$^{-1}$	*abs j deg*$^{-1}$ *mole*$^{-1}$	*abs j deg*$^{-1}$	%
311.92	9-9-55 9-13-55 --------	221.64 221.59 --------	10-27-55 10-28-55 11-3-55	318.82 318.79 318.79	81.91	±0.019	81.90	+0.01
321.65	9-9-55 9-13-55 --------	222.83 222.78 --------	10-27-55 10-28-55 11-3-55	322.23 322.23 322.25	83.80	.019	83.82	−.02
331.35	9-6-55 9-9-55 9-13-55	224.17 224.17 224.15	10-27-55 10-28-55 11-3-55	325.81 325.79 325.82	85.66	.017	85.64	+.02
341.05	9-6-55 9-9-55 9-13-55	225.35 225.38 225.31	10-28-55 11-3-55 --------	329.04 329.05 --------	87.38	.019	87.36	+.02
350.65	9-6-55 9-9-55 9-13-55	226.47 226.48 --------	10-28-55 11-3-55 --------	332.06 332.09 --------	89.01	.019	88.99	+.01
360.35	9-6-55 9-9-55 9-13-55	227.54 227.57 227.57	10-28-55 11-3-55 --------	335.05 335.06 --------	90.58	.019	90.58	.00
515.15	9-15-55 9-16-55 1-27-56	241.94 241.90 241.92	11-16-55 11-17-55 1-11-56	369.35 369.34 369.34	107.36	.022	107.19	+.16
524.95	9-15-55 9-16-55 1-27-56 2-7-56	242.66 242.66 242.69 242.67	11-16-55 11-17-55 1-11-56 --------	370.92 370.91 370.90 --------	108.05	.020	107.89	+.15
534.55	9-15-55 9-16-55 1-27-56 2-7-56	243.49 243.47 243.52 243.46	11-16-55 11-17-55 1-11-56 --------	372.52 372.52 372.55 --------	108.72	.020	108.57	+.14
544.15	9-15-55 9-16-55 1-27-56 2-7-56	244.28 244.25 244.30 244.21	11-16-55 11-17-55 1-11-56 --------	374.05 374.04 374.04 --------	109.34	.020	109.20	+.13
553.85	9-15-55 9-16-55 1-27-56 2-7-56	245.08 245.02 245.10 244.98	11-16-55 11-17-55 1-11-56 --------	375.55 375.53 375.55 --------	109.96	.020	109.83	+.12
563.55	9-15-55 9-16-55 1-27-56	245.82 245.80 245.80	11-16-55 11-17-55 1-11-56	377.04 377.02 377.03	110.56	.022	110.42	+.13
660.05	1-30-56 1-31-56 2-2-56 2-3-56	253.75 253.79 253.73 [b] 253.76	12-30-55 1-4-56 1-6-56 --------	390.56 390.59 390.66 --------	115.29	.053	115.39	−.09
669.75	1-30-56 1-31-56 2-2-56 2-3-56	254.62 254.55 254.58 [b] 254.58	12-30-55 1-4-56 1-6-56 --------	391.90 391.80 391.97 --------	115.68	.053	115.81	−.11
679.35	1-31-56 2-2-56	255.31 255.41	1-4-56 1-6-56	393.11 393.21	116.09	.065	116.20	−.09
689.05	1-30-56 1-31-56 2-2-56	256.27 256.19 256.32	12-30-55 1-4-56 1-6-56	394.58 394.48 394.65	116.52	.053	116.59	−.06

[a] Molecular weight 101.96.

[b] Values obtained at one-half normal heating rate not included in heat capacity calculations.

are brought to the temperature of the rings by the same tiedown technique used for the thermopile junctions. The leads and supports are not disturbed when the container is removed. Calculations indicate that heat transfer by convection is wholly negligible, so that the over-all heat transfer coefficient for flow from the calorimeter is calculated to be about 0.18 w deg^{-1} C at 400° C.

By controlling the jacket temperature about 0.01° C hot or cold, the change in heat flow from the calorimeter leads to an experimental evaluation of the heat transfer coefficient. At 400° C, the mean value of this coefficient is 0.23 w deg^{-1} C, with a standard deviation of ±0.02 which is in reasonable agreement with the calculated value above. Estimating the average uncertainty in the temperature difference from all causes to be 0.001° C at 400 and considering a typical 40-min experiment, the heat loss due to this uncertainty is equivalent to 0.08 percent of the heat capacity of the Al_2O_3. This 0.08-percent uncertainty is comparable to the scatter of the heat capacity results around 670° K (table 1). This considerable heat effect from such a small temperature difference is indicative of the difficulties of adiabatic calorimetry at elevated temperatures.

3.3. Guard System

The guard G is made from aluminum 2 cm thick. The heaters are in three sections distributed over the surface. The guard temperature is automatically controlled about 0.3° C below the jacket temperature using a single junction Chromel-Alumel thermocouple between the jacket ring and the cylindrical section of the guard. This temperature difference permits sufficient cooling to maintain automatic control of the jacket. The temperature of the top and bottom sections are controlled to the temperature of the cylindrical section by means of differential thermocouples. After temperature gradients in the guard were found to cause appreciable gradients in the jacket ring R_2, a series of thermocouples was installed to measure circumferential gradients in the guard. These gradients amounted to several degrees and were highly dependent on the variations in packing the glass fiber insulation around the guard. To reduce these gradients, which caused significant circumferential gradients on the jacket ring R_2, a heated aluminum cylinder was placed around the guard.

At the bottom of the guard is a connection to the CO_2 supply. Carbon dioxide is kept flowing into the calorimeter at all times at a rate of about 1 cm^3 sec^{-1}. A fraction diffuses through small holes in the various silver shields and lids to insure a uniform atmosphere throughout. Changing the CO_2 flow by tenfold does not affect the heat transfer from the calorimeter.

4. Energy and Temperature Measurements

The power to the calorimeter is obtained from large capacity storage batteries. It is evaluated in the conventional way by determining the current through the calorimeter heater and the potential drop across it. The current is determined by the potential drop across a 1-ohm series resistor (certified to 0.005%). The potential drop across the calorimeter heater is divided by a 20,000-ohm volt box which has a 100:1 ratio certified to 0.01 percent. The current through the volt box is accounted for in evaluating the true calorimeter current. The potential across the 1-ohm resistor and across 1 percent of the volt box is determined by means of a Wenner potentiometer certified to 0.01 percent and standardized against a saturated standard cell which is accurate to 0.002 percent.

To allow for the small amount of heat generated in the current leads between the calorimeter and its jacket, one potential lead is brought from a terminal on the calorimeter, the other from a terminal on the jacket. If the current leads are alike, this procedure accounts for that part of the heat generated in them which flows to the calorimeter. All leads are brought to the temperature of the jacket and the calorimeter by means of thermal tiedowns like those used for the thermopile. The resistance of the leads is approximately 0.03 ohm, so that only about 0.02 percent of the heat to the calorimeter is generated in the leads. A very small correction is applied for heat generated in the resistance thermometer.

The heating interval (about 1,200 sec) is measured to about 0.02 sec with an electric timer synchronized with an accurate crystal oscillator. The interval is held to integral seconds by synchronizing the heater switch with a relay which closes once each second. The coincidence of these second signals is checked daily against standard time signals from WWV.

The 25-ohm platinum resistance thermometer was calibrated at the Bureau. The resistance at the ice point is checked each time the sample container is removed. A thermometer current of 2 ma was used. The resistance is measured with a Mueller bridge calibrated in this laboratory. Temperatures are reported in degrees Celsius as obtained by use of the International Temperature Scale (1948). Temperatures on the Kelvin scale were obtained by adding 273.15°.

5. Jacket Control System

Precise control of the temperature difference between the jacket and the calorimeter is essential for accurate measurements. The apparatus has been designed with low thermal lags in the thermopiles and heaters to facilitate precise control. A commercially available servo system, used in conjunction with the thermopiles, controls the jacket temperature more precisely and for longer periods than is possible for a human operator. The servo system consists of an amplifier, a recorder and a control unit. A few refinements have been added to permit closer control at the beginning and end of the heating period. The details of the control system are described elsewhere [7].

The control system holds the temperature difference within $\pm 0.001^\circ$ C on the average. This control is much better than that obtained by manual operation, which was attempted in some preliminary experiments. Deviations from ideal control are integrated electronically over the time of an experiment and a small correction is applied. Frequent checks of the amplifier and recorder indicate that the indicated zero is stable to $\pm 0.2\ \mu v$, which corresponds to 0.0002° C. Random variations of the control zero will appear in the data; long-term changes will be taken into account by the operating procedure.

6. Experimental Procedure

In a normal day's work one operator can obtain the data for six to nine experiments, depending on how much time is required to adjust the apparatus to the desired initial conditions. So that the apparatus will not be too far from these conditions, its temperature is held overnight about 10 deg below the desired initial temperature by automatic control of the guard heaters. Prior to starting a series of experiments, the temperatures of the jacket and guard are brought under automatic control. The calorimeter is then heated to the initial temperature, adjusting the number of cells in the storage battery and a resistance in series with the calorimeter heater to give a heating rate of 0.5° min^{-1}. This series resistance is kept about equal to the resistance of the calorimeter heater so that the change in heater resistance with temperature will produce only a very small change in the power level [8]. Whenever current is not desired in the calorimeter heater, it is switched to a "dummy" resistor which has about the same resistance as the calorimeter heater. This procedure keeps the external circuit at operating temperature and avoids most of the change in external resistance which would otherwise occur when the current is turned on. From 7 to 10 minutes after the power is shut off, the temperature of the calorimeter (with the Al_2O_3 sample) can be determined. The temperature is obtained from four readings on a Mueller bridge taken at 30-sec intervals. After another 10-min period, the temperature is again observed to determine the initial temperature "drift", i. e., the rate of change of the calorimeter temperature with time. At 300° K this drift is only 0.005° hr^{-1}, but at 700° K it amounts to 0.03° hr^{-1}.

About 30 sec after the last temperature reading, the current from the storage batteries is switched from the dummy resistor to the calorimeter heater on an integral second. The emf's corresponding to the heater current and voltage are each read on the potentiometer at 3-minute intervals. The operator also has time during the heating period to check the operation of the automatic control equipment and read the various auxiliary thermocouples. About a minute before the end of the heating period, the resistance thermometer current is turned on and the temperature is observed continuously until it is a few hundredths of a degree below the desired final temperature. The power is then switched back to the dummy resistor on the nearest integral second.

The temperature is observed after the calorimeter reaches equilibrium and again after a 10-min interval to obtain the final temperature and its drift. Based on the final and initial drift experiments a correction for drift during an experiment is applied to the apparent heat capacity. This correction makes an allowance for a number of factors which change from one experiment to the next, such as changes in the control point of the jacket control system or changes in spurious emf's of the thermopile. In the time between heating periods, the apparent heat capacity is calculated, so that comparison with previous results can be made before the next experiment is begun.

To obtain the small correction for deviations of the jacket temperature from that of the calorimeter, the electronic integrator is read each time the calorimeter temperature is observed. Each day, the factor for converting the integrator readings to energy correction is evaluated by changing the jacket control point 0.01° C for 10 min and observing the corresponding integrator readings and temperature changes on the calorimeter.

After completion of a series of experiments with the empty container it is removed, filled with a sample, and replaced. When it is not necessary to seal the sample container (as with Al_2O_3) the time required for this operation is about 2 days. After filling the calorimeter, a second series of measurements is made.

7. Heat Capacity of Aluminum Oxide

The heat capacity of the Calorimetry Conference sample of Al_2O_3 [5] has been measured in this calorimeter from 305° to 365°, from 510° to 570°, and from 655° to 695° K, using a 120-g sample. The data are summarized in table 1. The data shown for the empty and full calorimeter have been corrected to the average temperature shown in the first column. The heat capacities calculated from these data have been corrected for the curvature of the heat capacity-temperature function, for buoyancy in weighing, and for the heat capacity of CO_2 displaced by the Al_2O_3. The experiments were carried out at a constant pressure of 1 atm so that C_p is determined directly. Included for comparison are smoothed data taken from earlier work in this laboratory with two different calorimeters [5]. In the last column are shown the percentage differences between the new data and the earlier work. The estimated uncertainty in the earlier data obtained in an adiabatic calorimeter is ±0.1 percent from 90 to 373° K; the uncertainty in the data obtained by the drop method increases from ±0.2 percent at 373 to ±0.4 percent at 1073° K. The agreement with the earlier data is well within these estimated uncertainties.

8. Analysis of Errors

The random errors associated with the results in table 1 have been estimated by ordinary statistical methods, using all the data in each temperature range to estimate the standard deviation of individual measurements in that range. This "pooled estimate" of the standard deviation is then used to compute the standard deviations of the heat capacity of Al_2O_3 at each temperature. These standard deviations are given in table 1. Confidence limits (99% level) for the heat capacity of Al_2O_3 are ±0.05 percent for the two lower ranges and ±0.14 percent for the highest range. These limits would include the average of an infinite number of observations 99 percent of the time, but they do not include an estimate of systematic errors.

It is believed that the variations in the data in table 1 are mainly due to heat transfer from the calorimeter which is not accounted for by the correction for the calorimeter drift experiments. This correction averages 0.05 j deg^{-1} in the lowest range, 0.12 j deg^{-1} in the middle range, and 0.50 j deg^{-1} in the highest range. The magnitude of the drift decreased with time after the heating interval in a manner which is nearly exponential with a time constant of 2 or 3 hr and probably results from thermal lags in the glass fiber insulation. The magnitude of the correction will accordingly depend on when the drift is determined. In general, the drift has been determined as described in section 6. The validity of corrections based on these drift experiments can be judged by the sets of data taken in the middle temperature range on November 16 and 17, 1955, and January 11, 1956 (table 1). These sets of data had very different drift corrections averaging respectively −0.15, +0.13 and +0.09 j deg^{-1}, yet the apparent heat capacities in the three sets agree on the average to 0.01 j deg^{-1}. By contrast, the sets of data taken in the highest range on December 30, 1955, January 4, 1956, and January 6, 1956, had corrections averaging respectively 0.55, 0.39 and 0.49 j deg^{-1}, and the average difference between the heat capacity data of January 4 and those of

January 6 is 0.14 j deg^{-1}. It is obvious that not only are the drift corrections larger at high temperatures, but they are also relatively more uncertain.

The variations in drift seem to be random in nature, not differing significantly between the empty and full calorimeter experiments. Therefore no allowance for errors in drift corrections has been made other than that for the random errors which appear as scatter in the data.

The systematic errors discussed below are estimated to be on about the same probability basis as the confidence limits given above for random variations.

An estimate of the over-all systematic error from the measuring instruments of ±0.02 percent is obtained by taking the square root of the sum of the squares of the individual estimates in section 4. There is also a possibility of systematic errors in accounting for heat lost from the calorimeter. These errors might arise either from changes between empty and full experiments in the heat transfer coefficient or in the temperature distribution on the outer surface of the calorimeter or the inner surface of the jacket.

An estimate can be made of the systematic error which may be due to a change in the heat transfer coefficient. The error is possible because, during the heating interval, the gradient on the inner jacket shield is different from that on the outer calorimeter shield, resulting in a net temperatue difference even though the thermopiles indicate zero. If the heat transfer coefficient changes between the full and empty measurements, the empty measurement will not make the proper allowance for the small heat loss. It is therefore necessary to consider possible changes in the heat transfer coefficient.

The reproducibility of heat transfer by gas conduction depends only on the composition of the gas. The CO_2 is kept flowing through the system at all times so that a significant change in composition due to diffusion of air is unlikely. It has already been pointed out that conduction along leads and supports is the same in the full and empty experiments. It is therefore unlikely that the heat transfer coefficient might change because of changes in metallic or gas conduction.

There remains the possibility of a change in heat transfer by radiation due to a change in the emittance of the silver surfaces. This change might come about, for example, by the formation of a sulfide layer, although no such corrosion was discernible on the several occasions when the calorimeter was opened. The uncertainty in the observed heat transfer coefficient is too large to permit a significant statement about any systematic change between empty and full experiments. However, in the middle temperature range, empty experiments were made both before and after the full experiments. If there is a significant change in the heat transfer coefficient between the two series of empty measurements, it should result in a constant difference between the averages of the heat capacity values. It is apparent from table 1 that there is no evidence of such a difference.

Apart from the variation in the heat transfer coefficient, systematic error can be introduced if there is a change (between empty and full experiments) in the temperature distribution on either the outer surface of the calorimeter or the inner surface of the jacket. In section 3.1, the effect on the outer shield of the calorimeter due to loading the sample container and changing the gradient between the container and the ring is estimated to be about 0.0001° C. Taking the heat transfer coefficient at 400° C to be about 0.23 w deg^{-1}, the error in a 20-min heating period on a sample of 130 j deg^{-1} heat capacity is 0.002 percent. Also in section 3.1, the temperature drop from the ring R_1 to the lid L_1 is estimated to be 0.001° C. If the irreproducibility in squeezing the silver against the stainless steel is 50 percent, the systematic error may be 0.005 percent. A similar estimate applies to the jacket lid L_2. Both lids were removed several times during the measurements to allow work on the electrical system so that the error due to the lids appears to a considerable extent as a random error in the data.

One further possibility of error is in the reproducibility of a circumferential gradient in the silver rings which might arise from a large change in contact between the sample container and the ring, or from a change in the technique of packing the insulation around the guard. If this gradient is properly averaged around the ring by evenly spacing the thermopile junctions, no error results even if it is not reproducible; however, the thermopiles are distributed around only three-fourths of the circumference, so that one-fourth of the circumference is not included in the average. At equilibrium the thermopiles indicate a difference of less than 1 μv, and there is no apparent variation between the full and empty experiments. If a possible change in this gradient between the full and empty measurements is no greater than the limit of sensitivity of the temperature difference measurement, the resulting error is about 0.005 percent of the heat capacity of the Al_2O_3.

Taking into consideration the random and systematic errors, the error in the heat capacity of Al_2O_3 is estimated to be less than 0.1 percent in the lower ranges and less than 0.2 percent in the upper range.

The interest and cooperation of Professor William J. Svirbely is gratefully acknowledged.

9. References

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WASHINGTON, May 16, 1957.