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MEASUREMENTS OF HEAT CAPACITY AND HEAT OF VAPORIZATION OF WATER IN THE RANGE 0° TO 100° C

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ABSTRACT

The present series of measurements of heat capacity and heat of vaporization of water in the range 0° to 100° C have been made to provide greater certainty in the values of the specific heat of water for calorimetric purposes and also to provide greater reliability in the values of enthalpy and the other derived properties for use in steam tables.

To insure the desired accuracy in the specific-heat determinations, complete new calorimetric equipment was designed and built. The same fundamental principles of fluid calorimetry by the electric-heating method were used as in previous measurements extending from 0° to 374° C. In the present case, the limited range of temperature and pressure allowed greater freedom of design to provide for higher accuracy in measurements. Heat leak was accounted for by observation, although it was kept practically nil by insulation and by thermal control of the envelope.

Temperature uniformity in the calorimeter was secured by an efficient circulation pump. Temperature uniformity in the envelope was secured by a controllable saturated-steam bath. Temperatures were measured by platinum resistance thermometers supplemented with numerous thermoelements. Heat added was measured electrically. The process of evaporation was closely controlled by manipulation of a sensitive throttle valve.

From 256 heat-capacity experiments and 152 vaporization experiments, as finally reduced and formulated, there was obtained a group of properties of water comprising specific heat, enthalpy of both liquid and vapor, heat of vaporization, and specific volume of saturated vapor in the range 0° to 100° C.

The values of specific heat have been compared with values from several important researches by both the mechanical and the electrical method. This comparison shows a more satisfactory accord of the present results with the results of Rowland, of Laby and Hercus, and of Jaeger and von Steinwehr, than with those of Callendar and Barnes.

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Part 1. A Calorimeter for Measuring the Heat Capacity and Heat of Vaporization of Water in the Range 0° to 100° C

I. INTRODUCTION

The principal purpose of the calorimeter described here was to provide for a systematic determination of the heat capacity of water from 0° to 100° C. A secondary purpose was to provide for a determination of the heat of vaporization over the same range. It was desired to obtain new experimental data on these properties to remove, if possible, some of the existing uncertainty. Of the earlier determinations of the specific heat of water, some are limited in range and the degree of accord is unsatisfactory. The measurements which have been completed, and which are described in part 2 of this report, were in part repetitions of previous measurements made in this laboratory. These previous determinations of the heat capacity of water were made for the purpose of obtaining data on the properties of saturated steam, using a calorimeter designed to operate at pressures up to 1,200 lb/in². While the values obtained for enthalpy of liquid water were of adequate precision for use in compiling steam tables for engineering purposes, the derived values of specific heat in the range below 100° C were not sufficiently accurate for use as calorimetric standards.

In providing apparatus for a resurvey of the heat capacity, the moderate range of pressure between 0° and 100° C allowed more freedom of design to avoid sources of experimental error. The design also provided for the determination of the heat of vaporization from 0° to 100° C. The results of these measurements are given in part 3.

II. GENERAL DESCRIPTION OF METHOD AND APPARATUS

The principles of the method used in the measurements have been described in previous publications [1],¹ and therefore are not repeated in detail in this report. This method was applied previously [2, 3] to measurements on saturated water and saturated steam from 0° to 374° C. The description given here includes mention of both the heat-capacity and the vaporization measurements.

The apparatus consists essentially of a calorimeter in which a sample of water may be so isolated from other bodies as to enable its amount, state, and energy to be accounted for. The sample may be made to pass through a chosen definite change in state while the accompanying gain or loss of energy is being determined.

A quantity of water, part liquid and part vapor, is enclosed in a metal calorimeter shell. An electric heater immersed in the water provides a means of adding measured energy to the calorimeter and its contents. Outlets with valves provide for filling and emptying the calorimeter and for withdrawing vapor. Detachable receivers suitable for weighing are connected to the outlets to hold the samples of water transferred.

For confining the energy, the calorimeter is well insulated from the influence of external sources of heat. In operation, the temperature of an enveloping shell is kept very close to that of the calorimeter shell. The small amount of heat which passes by leakage to or from the calorimeter is taken into account.

Two general types of experiments were made with this calorimetric apparatus. In the first type (heat-capacity measurements) the calorimeter with a sample of water was heated over a measured temperature range. By making some experiments with the calorimeter nearly full of liquid water and others with it nearly empty of liquid, it is possible to account for the tare heat capacity of the calorimeter, and to obtain the change of a quantity called alpha, α , which is a property of the water alone. It previously has been shown in the theory [1] that this quantity, α , differs from the enthalpy, or heat content, H , of saturated liquid water by another quantity beta, β . In other words,

$$\alpha = H - \beta.$$

The quantity β has been shown to be

$$\beta = L \frac{u}{u' - u} = T u \frac{dP}{dT},$$

where L is the heat of vaporization, u is the specific volume of saturated liquid, u' is the specific volume of saturated vapor, T the absolute temperature, and dP/dT is the vapor-pressure derivative. In the previous experiments the quantity β was measured calorimetrically at higher temperatures, but between 0° and 100° C it is so small that its value can be calculated from liquid-volume and vapor-pressure data with greater accuracy than can be obtained by calorimetric measurements.

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

The second type of experiment (vaporization) made with this calorimeter is virtually an isothermal process. Heat is supplied to evaporate a sample of water which is withdrawn from the calorimeter at a controlled rate, collected, and weighed. From this experiment, there is obtained a value of a quantity γ , which differs from the latent heat of vaporization, L , by the same quantity, β , mentioned above. In other words,

$$\gamma = L + \beta.$$

III. APPARATUS

The essential features of this calorimeter may be explained by reference to a schematic diagram, figure 1, which shows the metal calorimeter shell, C , containing a water sample; an electric heater, H ;

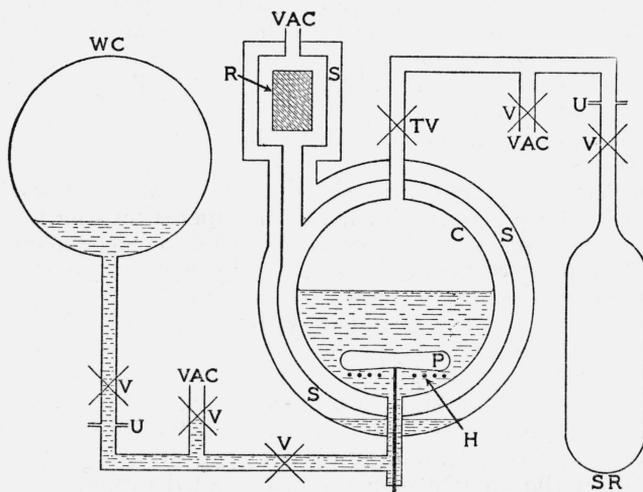


FIGURE 1.—Schematic diagram of calorimetric apparatus.

C , calorimeter shell; H , electric heater; P , water circulating pump; R , reference block; S , saturated steam bath; SR , steam receiver; TV , throttle valve; U , union; V , valve; VAC , vacuum line; WC , water container.

and a water-circulating pump, P . This shell is supported within an evacuated space which is surrounded by a controlled bath, S , of saturated water vapor, hereafter called the steam bath, which shields it against heat exchange with the surroundings. Provision is made for the introduction of a water sample from the water container, WC , into the calorimeter, or the withdrawal of saturated vapor through the throttle valve, TV , into the glass receiver, SR . The calorimeter and flow lines may be evacuated through lines VAC . The reference block, R , provides a temperature datum determined by a platinum resistance thermometer. Auxiliary thermoelements are used for measuring temperatures on the calorimeter shell and its surroundings, relative to this datum. The reference block is located in an inclosure surrounded by an extension of the steam bath. The calorimeter and the essential parts are shown in detail in the scale drawings, figures 2 and 3. Figure 2 shows more of the calorimeter detail, whereas figure 3 shows more of the accessory parts.

1. CALORIMETER SHELL AND INCLUDED PARTS

The purpose of the calorimeter shell shown at *C* is to hold the sample of water whose thermal properties are being determined. The shell was made nearly spherical in shape for compactness and calorimetric efficiency. It was spun from pure copper and has a thickness of about 0.55 mm. The two hemispherical ends were joined by solder,

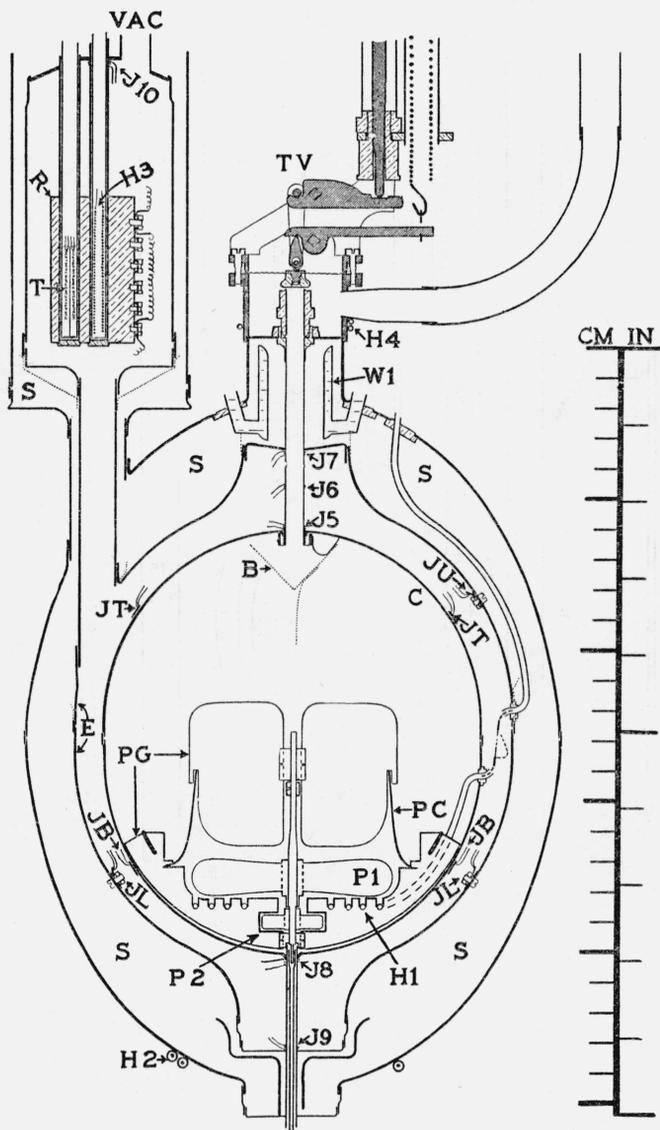


FIGURE 2.—Scale drawing of calorimeter.

B, gauze baffle; *C*, calorimeter shell; *E*, envelope shell; *H1*, calorimeter heater; *H2*, steam bath heater; *H3*, reference block heater; *H4*, throttle valve heater; *JT*, *J5*, etc., thermoelement principal junctions; *P1*, *P2*, pump propellers; *PC*, pump casing; *PG*, pump guides; *R*, reference block; *S*, saturated steam bath; *T*, resistance thermometer; *TV*, throttle valve; *VAC*, vacuum line; *W1*, condenser.

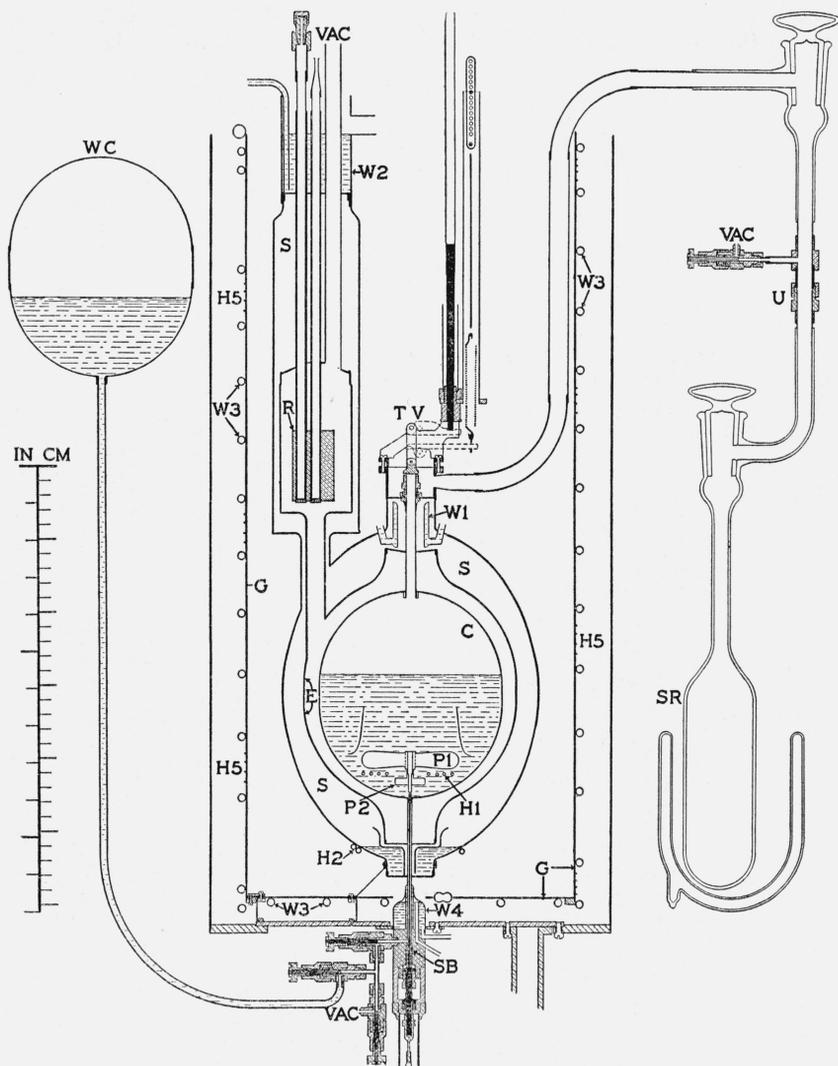


FIGURE 3.—Scale drawing of calorimetric apparatus.

C, calorimeter shell; *E*, envelope shell; *G*, guard; *H1*, calorimeter heater; *H2*, steam bath heater; *H5*, guard heater; *P1*, *P2*, pump propellers; *R*, reference block; *S*, saturated steam bath; *SB*, stuffing box; *SR*, steam receiver; *TV*, throttle valve; *U*, union; *VAC*, vacuum line; *W1*, condenser; *W2*, condenser; *W3*, cooling water tubes; *W4*, cooling water chamber; *WC*, water container.

with a narrow cylindrical copper band at the equatorial zone. As assembled with the various parts in place, the shell has a capacity of 1,190 cm³.

Two tubes connected axially at the top and bottom of the calorimeter shell are designated as the "upper tube" and "lower tube", respectively. These tubes serve for the transfer of fluid to and from the calorimeter and to hold the calorimeter shell in place.

All surfaces of the calorimeter shell and the parts inside were gold-plated. The outer surface of the shell was polished to reduce heat transfer by radiation. Eight thermoelement junctions, *J*, distributed over the outer calorimeter surface were used in the evaluation of calorimeter temperature, as described later in the section "Thermometric installation."

The circulating pump consists of two screw propellers, shown at *P1* and *P2*, and a system of guides to direct flow. The larger propeller, *P1*, performed most of the work in circulating water, while the smaller propeller, *P2*, was used to avoid stagnation in the extreme bottom of the calorimeter. The specially designed blades of the larger propeller were formed from sheet copper and soldered to a hub of brass, all plated with gold and polished. The two propellers were fastened to a phosphor-bronze pump shaft, which was squared at its lower end so that it could be engaged from below by a shaft extension.

In addition to the propellers, there is a system of guides designed to direct flow and increase the pumping efficiency. The liquid water flows downward next to the inner surface of the calorimeter shell and is directed by radial guides at the bottom so that the water flows without swirl past the heater into the propellers. The water from the propeller is guided upward by a casing, *PC*, and by guide vanes *PG*, curved to remove the swirl imparted to the water by the propeller.

The pump guides form a rigid framework which supports the two pump bearings and the electric heater, *H1*. The downward thrust on the pump shaft is taken on a copper-nickel washer located just below the small propeller, *P2*. This whole pump framework is held down against the calorimeter shell by a threaded connection to a short piece of the lower outlet tube which extends into the calorimeter.

The electric heater shown at *H1* is an insulated resistor encased in a coiled metal tube sealed hermetically through the shell. It consists of about 107 ohms of a chromium-nickel-alloy wire, 0.2 mm in diameter with 0.4-mm copper leads. This resistor was wound in helical form, 0.6-mm outside diameter, and embedded in magnesia for insulation. The resistor with leads was sheathed in a copper tube drawn down tightly on the magnesia to an outside diameter of about 2 mm. This sheathed resistor was then bent to form a flat spiral of five turns, the largest being 6 cm in diameter. This coil was fastened in slots in the metal guides just below the large circulating pump propeller, *P1*. The resistor is so located as to concentrate the heating in the region just below the large propeller. The leads extending out from the envelope shell, both for current and potential connections, were made like the leads of the sheathed resistor.

For measuring the potential drop in the calorimeter heater, two potential leads were joined to the current leads where they cross the vacuum space between the calorimeter shell and the envelope. These junctions were located to include in the measured electric-energy input that part of the heat developed in the leads, which went to the calorim-

eter. Choice of suitable proportions of the leads in this boundary region of the calorimeter was a compromise between thermal conductance, electrical resistance, and convenient battery voltage. As made, the two current leads contributed but little to the total heat-leak transfer, and their combined electrical resistance was only $1/3000$ of the calorimeter heater resistance of 107 ohms. Therefore, only $1/3000$ of the energy input was developed in the current leads between the calorimeter and envelope shells, and so a small inequality in the eventual distribution of this extraneous heat was negligible.

To minimize the uncertainty of the accounting for the heat developed in this small resistance, the current leads, their insulation, and their sheaths were all made as much alike as possible on both sides of the vacuum space. The sheaths were soldered into the shells similarly, and the leads extended about 3 mm beyond their sheaths. In this way, the two electric connecting links had equal thermal connection with the calorimeter and the envelope shells. The current links were made of 0.3-mm gold wire about 4 cm long. One potential lead was connected to the calorimeter end of one link. The other potential lead was connected to the envelope end of the other link. In this way, the electric power developed in one link was apportioned to the calorimeter, and the power developed in the other link was apportioned to the envelope. Thus it was not necessary to connect potential leads within the vacuum space to the midpoints of the links, where the temperature of the wire rose above the calorimeter temperature during the heating period. These potential leads were made small and long to keep their thermal conductance negligible.

In order to prevent passage of liquid drops during the vapor withdrawal experiments, a baffle, *B*, shown in figure 2, made of conical-shaped wire gauze, was installed near the vapor outlet tube.

2. THERMAL-PROTECTING ENCLOSURE

In an ideal calorimeter no unmeasured heat would be gained or lost. This ideal may be approached by three means: First, the calorimeter may be thermally insulated from its surroundings. Second, the surroundings may be kept approximately at the temperature of the calorimeter. Third, the heat transferred may be accounted for by observation. In the present calorimeter, all three means were provided by use of a protecting enclosure for the calorimeter. This thermal-protecting enclosure will next be described.

The enclosure which surrounds the calorimeter is used to control heat leak to or from the calorimeter and to provide for determining the correction for the small unavoidable heat leak. The inner wall of the enclosure is a shell called the envelope, shown at *E*. It is a closed copper shell made in the same manner as the calorimeter shell, but larger. At the bottom of the envelope, the seal to the lower tube was made with a thin copper disk to accommodate differential expansion. The copper envelope shell is 0.55 mm thick, gold-plated and the inside surface polished to reduce heat transfer by radiation to the calorimeter. The space between the calorimeter shell and the envelope was evacuated for improving the insulation, leaving radiation between the polished gold surfaces as the chief path for heat leak. In the preliminary cooling of the calorimeter, this space was filled with helium to promote heat removal. Eight thermoelements on the inner surface of the envelope are used in the control and evaluation of

heat leak, as described later. To provide a space for the reference block, *R*, described later, an extension to the envelope is located as shown.

Control of the envelope temperature is an important factor in the operation of the calorimetric equipment. Upon this control depends not only the magnitude of the heat leak, but also its correct evaluation. In the calorimetric measurement, it is important that the envelope temperature be kept uniform and close to the average temperature of the calorimeter, not only when at the initial and final steady states, but also during the heating period. Another function of the envelope is the cooling of the calorimeter as a preliminary to a series of measurements. In consideration of the several functions of the envelope, a saturated-steam bath was chosen to control its temperature. An electric heater for vaporizing water and water-cooled condensers furnished the means for controlling the steam bath. The saturated steam furnished the medium for distribution of heat or refrigeration to the parts of the envelope, and thus automatically provided the desired uniformity of temperature distribution and the desired responsiveness in temperature regulation.

The saturated-steam bath, *S*, occupies the space between the envelope and a third shell of brass. This shell, or steam jacket, as it is called, is entirely closed except for small tubes for introducing or removing liquid water and vapor. A flexible copper disk was used to join the brass shell to the axial lower tube. The volume of this steam space between the steam jacket and the envelope was about 2,000 cm³. The sheathed heater, *H2*, soldered to the outside of the steam jacket just below the level of the pool of water inside, furnished the controlled source of heat input. The vapor spaces were sufficiently open so that only negligible pressure differences could exist, even when there was flow of vapor to the remote parts.

The action of this vapor bath depends upon the latent heat of the water vapor and upon the principle that the temperature of a wet surface is determined by the vapor pressure. It therefore follows that the temperature of the entire envelope responds to any increase in saturation temperature of the vapor. In other words, the saturated steam acts as an automatic thermodynamic distributor of heat and equalizer of temperature for the space which it occupies. In heating, the saturation temperature of the vapor is raised above that of the metal, and condensation takes place, using up the latent heat of the vapor to add heat. The heat flows to the shells through whatever condensed liquid is on the metal. Gravity tends to make the condensed water run down to the pool at the bottom, where it receives heat and goes through the cycle again. Since the entire mass of fluid in this space is small and the metals of the envelope and jacket are thin, the temperature of the envelope is quickly responsive to changes in power imparted to the heater.

For the purpose of initial cooling preliminary to a day's experiments, or for a steady heat drain to be compensated by heat for regulation, two condensers are provided in the steam bath, as shown at *W1* and *W2*. Cooling was supplied to these condensers by water, regulated in flow and temperature. The water condensed within the steam bath was directed by wire-gauze leaders to parts which needed to be kept wet. The surplus returned by gravity to the pool at the bottom.

It is possible that the surfaces are not always completely wetted,

but even so, large temperature gradients could not be produced in the well-conducting envelope shell. The steam-bath enclosure was found to have a very small air leak, which made it necessary to purge it of air occasionally to secure the best operation. This was done by drawing off a small amount of steam from the region of the condenser, *W2*.

In order to protect the steam bath from the influence of the outside temperature, it was surrounded except at the top by a controlled metal casing called the "guard", shown at *G* in figure 3. This guard was a sheet-copper cylinder with a plane bottom. It could be cooled by means of a system of cooling-water tubes, *W3*, distributed over its surface. Heat could be supplied by an electric heater, *H5*, distributed over the surface. By thus controlling the temperature of the guard, the operation of the steam bath was improved.

Outside the guard there is another shell made of aluminum, for a cover. For the purpose of insulation, the blank spaces inside the cover and the guard were filled with insulating material consisting of wool and kapok.

3. CONNECTIONS TO THE CALORIMETER

The calorimeter shell is held in place by two tubes of copper-nickel alloy. In addition to furnishing a firm support for the shell without too great heat conduction, these tubes serve also for the transfer of fluid to or from the calorimeter. The "upper tube," which has an outside diameter of 6.35 mm and a wall thickness of 0.25 mm, connects to the vapor throttle valve, *TV*, which permits control of the rate of flow of outgoing steam in the evaporation type of experiments. The diameter of this upper tube was large enough to allow for adequate rates of withdrawal of steam at the lower temperatures. Near 0° C, where the specific volume of saturated steam is over 200,000 cm³/g, it was possible to withdraw about 0.63 g/min.

During the heat-capacity experiments, which preceded the vaporization measurements, the upper tube was sealed at both the bottom and top by disks across the ends. This was to exclude water which might distill from end to end and thereby transfer unmeasured heat. These disks were removed prior to the vaporization experiments.

The "lower tube", which has an outside diameter of 3.0 mm and wall thickness of 0.35 mm, encloses the propeller drive shaft of the circulating pump. It also connects to the valve through which the calorimeter is filled or emptied.

The container, *WC*, for storing and transferring water samples was a copper shell similar to but slightly larger than the calorimeter shell, tinned on the inside to avoid contamination of the water sample, and with a tubular stem ending in a valve. It was connected to the calorimeter by a union. The long stem was to give head for running the water in or out when the vapor pressure was low.

4. STUFFING BOX AND PUMP DRIVE

The calorimeter circulating pump is driven from a 1/75-hp synchronous motor, using controlled-frequency alternating current to provide a constant speed. The drive is transmitted through a speed-reducing gear train to a vertical shaft running in a stuffing box below the calorimeter. From this shaft, a tubular extension with squared

ends transmits the rotation to the bottom of the calorimeter pump shaft.

The stuffing box, shown at *SB* in figure 3, was taken from an older calorimeter and has been more fully described in a previous publication [2]. The shaft through this stuffing box is of hardened tool steel 1 mm in diameter where it runs in the packing. A packing material of soft kid leather impregnated with a mixture of paraffin and vaseline was found to be satisfactory. This packing is kept compressed to the proper tightness around the shaft by a spring acting between the retaining ring and the threaded cap. Clearances were made small to avoid exuding the packing. The agreement of the amounts of water put in and taken out of the calorimeter was a check on the satisfactory tightness of the stuffing box.

The stuffing box was cooled with water circulating in a chamber, *W*₄, around the shaft tube at the top of the stuffing box. In experiments at temperatures near 0° C, this cooling was found necessary to prevent transfer of unmeasured heat to the calorimeter by boiling in the lower tube, whereas in experiments at higher temperatures, it was necessary to keep the packing cool to prevent leaking.

5. VAPOR LINE AND THROTTLE VALVE

The vapor throttle valve used in the vaporization experiments is an extremely vital part. On it depends the precision with which the experimental process of evaporation can be controlled. The valve opening must necessarily be large enough to allow sufficient flow of vapor when the specific volume is large at temperatures near 0° C. It should also be capable of closing tightly in order to permit accurate accounting for mass and energy. It should also allow steady, continuous adjustment, so that the evaporation temperatures can be controlled by regulating the flow.

The vapor throttle valve is shown at *TV*. It is made as a cylindrical cell joined to the top of the steam jacket, capped by a flexible corrugated-copper diaphragm, clamped tightly to the upper rim of the cell. This diaphragm seals against the atmosphere and carries a short valve stem at the center. The stem projects above and below the diaphragm, to which it is sealed by hard solder. The flexibility of the diaphragm permits about 1-mm linear motion of the stem to open or close the flow aperture. The outflow tube ends in a brass plug, which forms the seat. The actual seat (6.1-mm diameter) is merely a 45° sloped ridge rising about 0.15 mm above the plane end of the brass plug. The part of the stem which bears on the seat has a flat face and is fastened to the diaphragm with a threaded stud. The stem face was covered with a thin film of soft rubber, applied by dipping in latex and vulcanizing. The performance of this soft-rubber coating exceeded all expectations. It enabled the valve to be closed tightly with no perceptible leak and permitted fine regulation of throttling. One application of rubber served for the entire series of evaporation experiments.

The valve stem is operated by two levers acting axially on the stem outside the diaphragm. One lever thrusts a strut against the stem to close the valve, and the other lifts it by a stirrup to open the valve. These levers act on knife-edges to avoid any irregularity in their motion. The closing lever is actuated by a spring which not only removes any backlash but keeps a steady moderate force against the

seat of the valve when closed. The opening lever with a mechanical reduction of motion of 4 to 1 is operated by a screw with a pitch of 32 threads per inch. The shaft of this screw extends up to a grooved pulley above the calorimeter and is driven by remote control with a wire belt from a small pulley over the observing bench. A shaft from this pulley extends down to a handwheel and lever easily accessible to the operator. Using an additional lever 20 cm long, which could be clamped to the handwheel, there was a total reduction of motion of over 30,000 to 1 from the end of this lever to the valve stem. In spite of this large reduction, there was no detectable backlash in the operation of the valve. The nicety of the mechanical operation of the throttle, and the consequent excellent control of evaporation conditions amply repaid for the effort expended on the refinement of this throttle valve.

A sheathed heater, shown at H_4 in figure 2, was soldered to the body of the throttle valve to maintain both the valve and the upper tube warmer than the calorimeter. This was to prevent water from condensing in the upper tube during the evaporation experiments.

The outlet tube from the throttle was made larger than the inlet to accommodate the larger specific volume of vapor after throttling. The vapor line from the throttle to the receiver is nowhere less than 1 cm in diameter. The vapor line extends up and out of the guard space, through copper and copper-nickel tubes to a glass stopcock. Beyond the stopcock, a union, U , provides for the attachment of either of two Pyrex-glass containers for collecting the samples of vapor by condensation in liquid air. A side tube with valve permits evacuation of the vapor line. The glass containers, of about 225-cm³ capacity, are provided with unions and stopcocks so that they can be detached and weighed for determining the amounts of samples.

6. THERMOMETRIC INSTALLATION

Platinum resistance thermometers and thermoelements were used in the control and measurement of temperature in this apparatus. A resistance thermometer, T , placed in the copper reference block, R , determines a reference datum on the International Temperature Scale, from which small temperature differences to the calorimeter or other points are measured by means of thermoelements. Thermoelements were also used differentially for the survey of temperature distribution and for regulation of the calorimetric processes.

The reference block, R , is located in a space somewhat apart from the calorimeter to avoid direct interchange of heat but is connected to it through a tube for evacuation and for installing differential thermoelement wires. The surrounding steam jacket maintains the temperature of the enclosure approximately at the temperature of the calorimeter. The reference block was designed to give adequate thermal connection between the resistance thermometer and the reference junctions of the thermoelements. It is of copper in the form of a right hexagonal prism, 5 cm tall, with three broad vertical faces on which the reference junctions of the thermoelements and attachments for the leads are located. These attachments are for intercepting heat conducted along the leads and will be referred to as "thermal tie downs."

Four vertical round holes in the reference block are the sockets into which fit the several tubes containing resistance thermometers

and the tube containing an electric heater, *H3*. The heater socket is at the axis and the thermometer sockets are located symmetrically. Tubes of thermally resistant Cu-Ni alloy extend up from these four sockets successively through the envelope, the steam space, the outer wall of the steam jacket, and the water in the condenser, *W2* in figure 3, to the outside. A length of 4.5 cm was allowed in the vacuum space to give thermal separation from the envelope and a length of 12 cm in the steam space permitted a resistance thermometer coil to be placed there for automatic regulation of the steam-bath temperature.

The platinum resistance thermometer used as a working standard for the temperature measurement was of the four-lead potential-terminal type described by C. H. Meyers [4]. The windings were of pure platinum wound on a mica cross, and the initial strains were relieved by annealing the completed thermometer at 660° C. The thermometer was then sealed in an atmosphere of helium in a tubular sheath of copper-nickel, 6.3-mm in diameter and 46 cm long. The calibration was made according to the specifications for the International Temperature Scale [5], using the fixed points of ice, steam, and boiling sulphur as 0°, 100°, and 444.6° C, respectively. The thermometer fulfilled the requirements of the specifications for the International Temperature Scale and was recalibrated several times during the calorimetric experiments.

There are, in all, 22 thermoelements within the vacuum space, all having their reference junctions on the reference block. Some of the thermoelement principal measuring junctions are shown at points labeled *J* in figure 2. Eight of these thermoelements have their principal junctions uniformly spaced on the outer surface of the calorimeter so as to evaluate the average temperature. Four of these on the bottom hemisphere are connected in series and designated as *JB*. The other four on the top hemisphere, which have separate leads to allow for examining temperature uniformity in azimuth, are also connected in series and designated as *JT*. All eight in series may be used to refer the average temperature of the calorimeter to the reference block, i. e., to the standard thermometer. Similarly, eight principal junctions on the inside surface of the envelope evaluate its average surface temperature; four of these on the lower part are designated as *JL*, and four on the upper part as *JU*. All eight on the envelope may be opposed to the eight on the calorimeter for heat-leak control and measurement.

In addition to the 16 thermoelement junctions located on the surfaces of the calorimeter and envelope shells, there are five more located on the connecting tubes between the shells. These thermoelements are used in the control and measurement of heat leak by metallic conduction along the tubes. The three principal junctions on the "upper tube" are shown at *J5*, *J6*, and *J7*. Junction *J6*, located midway between *J5* and *J7*, was used for determining the temperature of the steam withdrawn in the evaporation experiments. The two junctions on the "lower tube" are shown at *J8* and *J9*.

One thermoelement, shown at *J10*, is placed near where the tubes from the reference block pass through its envelope. This thermoelement is useful as a detector or purge indicator, since it quickly shows local temperature differences when enough air eventually leaks into the steam jacket to interfere with the free transfer of heat by the steam. For the purpose of regulating the temperature of the guard

shell, one thermoelement was placed near the top of the guard. During the evaporation experiments, a thermoelement was used on the outside of the throttle valve for regulating the heat applied.

The thermoelements used in this apparatus were made of No. 32 (0.20-mm) Chromel *P* wire containing about 90 percent of Ni and 10 percent of Cr, and No. 34 (0.16-mm) constantan wire containing about 60 percent of Cu and 40 percent of Ni. These wires, which gave about $60 \mu\text{v}^\circ\text{C}$ for single elements, were insulated with silk and covered with Glyptal lacquer. The junctions of these elements were made in three different ways, depending on the way the thermal contact had to be made to acquire the temperature of the surface where they were placed.

The usual type of junction was on a copper terminal made in the form of a narrow washer with a radial tag to which the wires were soldered with the least bit of solder. These terminals were clamped with a screw stud and nut between thin mica washers to the metal whose temperature they were to acquire. They were somewhat larger but made according to the same principles as those described in previous reports [2, 3]. These terminals were used on the reference block for the "reference junctions" and for the first "tie-downs," and for the eight principal junctions on the envelope shell.

A second type of junction, used on the outside of the calorimeter shell, was made by soldering the two wires to larger plates of copper. These plates were insulated with thin sheets of mica and lacquer and held down with two narrow thin bands of copper extending around the shell in great circles.

The third type of attachment was used on the tubes between the calorimeter and envelope shells. In this type, the two wires were soldered together end to end, reinsulated with silk, and bound and lacquered to the tube for several turns away from the junction to insure that the junction was at the temperature of the tube.

Each thermoelement had two reference junctions on the reference block, although in cases where the elements were connected in series, some of the reference junctions were common to several elements. Eighteen copper leads from reference junctions sufficed for all of the temperature exploration it was desired to make. Their leads were carried in coils from the reference junction terminals near the bottom of the reference block to "thermal tie-downs" with similar terminals near the top of the block. From these tie-down terminals, the wires led up through a flat copper-nickel sheath which extended through the steam jacket to above the liquid in the condenser. These silk-insulated wires were in a single layer and sealed into the flat copper-nickel sheath with Glyptal for electric insulation and thermal contact. The length in thermal contact with steam sufficed to bring the temperature of the wire at the envelope boundary very close to the steam temperature. The tie-downs on the upper part of the reference block still further eliminated any temperature gradients on the lead wires toward the reference junctions.

Various combinations of the thermoelements for the several functions mentioned above were provided for by connections to specially built all-copper distributing switches. By manipulation of these switches, the observer could quickly shift from one to another combination, with little more delay than for galvanometer response.

The electromotive forces of the thermoelements were measured on a Wolff potentiometer designed by F. Wenner. The potentiometer

measurements were referred to a standard cell, described in part 2 under "Accounting for energy." The electromotive forces measured were so small that the potentiometer calibration errors were negligible.

The eight thermoelements used to measure the temperature of the calorimeter and contents were calibrated in place against the resistance thermometer in the reference block. This calibration procedure was first to observe the resistance thermometer and thermoelements, when the reference-block temperature was very close to that of the calorimeter. The reference block was then heated for a few seconds, keeping the calorimeter temperature constant, and the thermometer and thermoelements observed again. The change in the electromotive force of the thermoelements was then given directly in terms of the change in temperature by the resistance thermometer. No evidence was found that the calibration of any of the other thermoelements differed at all from this one and furthermore, even moderate differences could have had no significant effect on the results.

The resistance of the thermometer was measured with a Mueller bridge [6] built by O. Wolff and calibrated several times during the experiments. The addition of a commutator with normal (*N*) and reverse (*R*) positions adapts the bridge for measuring the resistance between the branch points of a four-terminal resistance thermometer. A bridge current of 5 ma was used, half of which passed through the resistance thermometer. The bridge current could be quickly reversed by a double-pole tapping switch. This automatically compensates for a drifting bridge zero and doubles the bridge sensitivity. To further increase the sensitivity, a special galvanometer arrangement was used. A stationary mirror inside the galvanometer case was so placed that the beam of light from the movable galvanometer mirror was reflected back to the movable mirror before emerging to the scale. This arrangement doubles the deflection with less loss in light intensity than doubling the scale distance. With these arrangements, a sensitivity of 0.0001° C was attained.

For the purpose of automatic regulation of the envelope temperature, one resistance thermometer was inserted only to the region between the reference block envelope and condenser so that its temperature was quickly affected by the steam bath. This resistance thermometer was connected in a simple Wheatstone bridge and was used with a galvanometer, photoelectric cell, and amplifier to automatically maintain constant temperature of the steam bath.

7. AUXILIARY COOLING APPARATUS

Cold water was used for cooling the apparatus in the experiments below room temperature. About 30 liters of water circulating in a storage reservoir was cooled by an electric refrigerating unit and the temperature was controlled by a kerosene-filled thermostat. The cooled water from the reservoir was led by gravity through several different flow lines on the apparatus and emptied into a small centrifugal pump which returned it to the reservoir. The reservoir and flow lines were insulated with wool to avoid dew and excessive loss in refrigeration.

In all experiments starting near 0° C, the cooling water was maintained at a constant temperature by circulating over a layer of ice frozen to the refrigerator unit. In order to have the cooling water

temperature somewhat below 0°C to compensate for heating in the flow lines, enough ethyl alcohol was mixed with the water to lower the freezing point in the reservoir by the required amount. A special device was used for maintaining a covering of ice on the cooling unit. This device consisted of a straight tube with a small open end which rested against the unit. This tube was filled with water from the reservoir and the end sealed shut with ice as soon as ice began to form on the unit. Further freezing displaced the water in the tube and actuated the thermostat in the usual manner.

8. MEASURING INSTRUMENTS AND CALIBRATIONS

The water samples were weighed by the method of substitution, using a balance having a capacity of 2 kg. Below the balance pans there was a closed cabinet in which the water containers, tare containers, and counterpoises were suspended. The platinum-plated brass weights used were calibrated at this Bureau. Corrections were made for buoyancy of the air on the brass weights. Since the water sample is in a closed container, no correction for the air buoyancy on the sample is necessary. Correction for air buoyancy on the container was avoided by using counterpoises having approximately the same displacement as containers.

A Wolff-Diesselhorst potentiometer was used for measurements of current and potential drop in the calorimeter heater. A 0.1-ohm four-terminal resistor in series with the heater was used for the current determination and a 1,000 to 1 ratio volt box for the potential drop. Correction was made for the fraction of the main current shunted through the volt box, whose resistance was about 20,000 ohms. The potential drop in the calorimeter heater was measured by means of the two potential leads which join the current leads at points which had been chosen to account properly for the heat developed in the current leads between the calorimeter shell and envelope.

All electrical-measuring instruments were carefully calibrated several times during this series of experiments. The standard resistors and the volt boxes used were calibrated before, during, and after the series of measurements and showed no significant changes. The potentiometric measurements of power input were referred to a group of three cadmium standard cells. These cells were of the saturated type and were maintained at a constant temperature in a special temperature-controlled box described by Mueller and Stimson [7]. Frequent calibration of the standard cells proved their reliability to about a microvolt.

The Wolff-Diesselhorst potentiometer which was available for this work was not ideally adapted to these measurements. The calibration of the potentiometer showed a seasonal variation of nearly 1 part in 10,000 and a smaller daily variation. A scheme was devised using two permanent standard resistors to calibrate the potentiometer in place. By making this calibration two or three times a day, errors due to changes in the potentiometer were avoided.

The potentiometer was intended for use with standard cells having voltages between 1.01800 and 1.01930. The saturated standard cells at the temperature used in these experiments, however, gave about 1.01762 v. It was necessary, therefore, to set the potentiometer arbitrarily for some voltage in its range of adjustment and to correct for the true standard-cell voltage. In practice, the potentiometer

was set for a standard-cell electromotive force of 0.0005 v higher than that of the standard cells used, thereby giving a correction to each potentiometer reading of about 1 part in 2,036. This correction appears in the sample computation sheet as "correction for potentiometer ratio."

The description of the temperature-measuring instruments and their calibrations is given in the preceding section, "Thermometric installation."

Part 2. Heat Capacity of Water in the Range 0° to 100° C

I. INTRODUCTION

The heat capacity ² of water has been the subject of various experimental determinations extending back to the time of Regnault. Some of them have been inspired by the usefulness of water as a calorimetric medium and definitive standard for determining heat capacities, while others have had for their objective the evaluation of the "mechanical equivalent of heat." The study of these past measurements for appraisal and correlation of results has been the subject of many reviews and reveals diligent effort to overcome inherent obstacles to accuracy in heat measurements by developing refinements of laboratory technique. During this development, the art of calorimetry has been far advanced by the evolution of standards and technique in electrical measurements of temperature and energy.

Notwithstanding all the advances in the laboratory arts, the appraisal of past experimental results has been unsatisfactory because so many uncertain factors have been involved regarding former units, standards, and calorimetric technique. Consequently, any interpretation of past results is subject to some arbitrary choice, and the various reviews have failed to bring the results into the accord to be expected from the accounts of the experimenters.

In 1921 the Cambridge, Mass. [8], conference on the properties of steam, as their first recommendation, made the proposal "the specific heat of water should be determined with the greatest possible accuracy up to the boiling point of water at atmospheric pressure for the more accurate determination of the mechanical equivalent of the mean heat unit."

Measurements made at the National Bureau of Standards and published in 1930 included data on the heat capacity of saturated water between 0° and 100° C., from which the specific heat at one atmosphere pressure could be derived. Since the experiments were not made especially for establishing accurate specific heats, the derived values were of only moderate precision. They have nevertheless been used in preference to earlier data as a basis for measurements of the enthalpy of superheated steam by several of the laboratories cooperating in the international steam research project. Recognizing that the accord of steam data was limited by the uncertainty in the values of the specific heat of water, the Third International Conference on Steam Tables [9], held in America in 1934, adopted a recommendation "that new measurements of the enthalpy or total heat of water between 0° and 100° C be undertaken by the National

² The expression "heat capacity" is used in this paper in the general sense of the energy required to produce a change of temperature, without necessarily restricting its application to unit mass, to unit temperature change, or to derivatives only.

Bureau of Standards to provide greater accuracy in these values for use in other calorimetric measurements." The present series of measurements was undertaken in response to this request and in extension of the program of steam research already completed.

In planning the work, it was the aim to provide for refinement of the technique of heat-balance accounting comparable with the accuracy of the temperature and power measurements, and if possible, to avoid an error of more than 1 part in 5,000 in the final results. To do this, it was necessary to design the new calorimetric equipment described in part 1 of this report.

II. METHOD AND APPARATUS

The method and apparatus have been described in detail in part 1 of this report, and therefore will be given only very brief mention here. The apparatus consisted essentially of a metal calorimeter shell containing a quantity of water, part liquid and part vapor. Immersed in the water are an electric heater and a circulating pump. Valves provide for filling and emptying the calorimeter. The calorimeter is well insulated from its surroundings, which are controlled to its temperature. Resistance thermometers and thermoelements are used in measuring temperatures.

In the measurement of heat capacity, the calorimeter with a sample of water was heated over a measured temperature range. By making some experiments with the calorimeter nearly full of liquid water, and others with it nearly empty, the tare heat capacity of the calorimeter was accounted for and there was obtained the change of a quantity called alpha, α , which is a property of the water alone. This quantity alpha differs from the enthalpy, or heat content, H , of saturated liquid water by another quantity beta, β . In other words,

$$\alpha = H - \beta$$

The quantity beta, β , had been measured calorimetrically in previous experiments at higher temperatures. However, between 0° and 100° C, it is so small that its value can be calculated from other data with greater accuracy than can be obtained by calorimetric measurements.

In addition to the enthalpy, H , of saturated liquid, values of specific heat, etc., may be derived.

III. EXPERIMENTAL PROCEDURE

In the heat-capacity measurements it was necessary to measure the amount of water subjected to the process, the amount of energy exchanged, and the change in state produced. It was the aim to account accurately for all three of these main factors. The following description of the experimental procedure indicates how these essential accountings were made.

1. ACCOUNTING FOR MASS OF WATER

The mass of water subjected to a change of state enters as a direct factor in the reduction of the data. The results, therefore, would be no more reliable than the determinations of the masses. Special care was therefore taken that the weighings were accurate and free from systematic errors. An account was kept of the amount in the calorim-

eter at any time and a check made by completely exhausting and weighing each charge before refilling with a new one.

The water used in these experiments was purified by preliminary distillation and then redistilled in a specially designed still under a pressure of about 0.1 atmosphere for the purpose of removing dissolved gases. These gases were removed by continuously withdrawing a part of the mixture of gas and water vapor from the condenser of the still. This kept the partial pressure of the gas at the condensing surface less than 0.001 atmosphere. The fraction of gas dissolving in the condensing water at this low pressure was too small to have any significant effect on any of the measurements.

The purified sample of water was then transferred from the still to an evacuated container, which was then weighed. When filling the calorimeter, this container was connected to the evacuated calorimeter, as shown in figure 3, and the connecting line evacuated. The water was transferred by gravity from the container to the calorimeter, leaving only a few grams in the container and line. The water in the line was collected and weighed by pumping through a detachable liquid-air trap in the vacuum line. The container with the water remaining in it was then reweighed. From the weights of the container before and after filling the calorimeter, and the weight of the water from the line, the amount of the water in the calorimeter was obtained by differences. When emptying the calorimeter, a similar procedure was followed, except that the water container was placed below the calorimeter, so that the water would flow from the calorimeter down to the container. The water remaining in the line and calorimeter was accounted for by condensing in liquid air and weighing as before.

The same charge of water was usually left in the calorimeter for several days' experiments. Comparison of the amount put in with the amount taken out was a check on the accuracy of accounting for the mass. Such a sum check was carefully kept in this work, and when the accounts did not agree, the results were discarded. Usually the check was to about 0.020 g, which amounts to about 1 part in 50,000 in a 1-kg water sample.

2. ACCOUNTING FOR ENERGY

Measured energy was supplied electrically to the calorimeter and contents by means of the calorimeter heating coil installed within the calorimeter shell and immersed in the water sample. Power was supplied by a separate storage battery of large current capacity. Potentiometer readings of current and potential drop across the calorimeter heater were made periodically for obtaining the energy added electrically, as described later. Reduction of these readings took account of the timing of the readings and of the slight gradual change in power which sometimes occurred.

In order to avoid too rapid an initial change when the current was switched to the calorimeter heater at the start of an experiment, a substitute resistor was used to steady the battery output. Between heating periods, the battery current was adjusted to a selected value to make the final temperature of the calorimeter come close to the desired even temperature after the power had been on an integral number of minutes. It was usually possible to adjust the current,

so that the final temperature would be within 0.01° C of the desired temperature.

The resistance of the calorimeter heater increased, during the first few seconds after the power was switched on, until the resistor temperature had reached a steady value. Since this change was practically completed before the first current reading was made ($\frac{1}{2}$ min after the start), the correction for it was determined by separate experiments. The correction for the current change was found by leaving the galvanometer connected when the current was shifted to the calorimeter and observing the deflections periodically for 15 sec. The integral of the galvanometer deflections over this time was used to compute the starting correction to the current. The starting correction for the potential drop, which is of the opposite sign, was obtained in a similar manner. These corrections were then combined to get the energy correction. This amounted to only 1 part in 10,000 of the whole energy input, even in the extreme case.

The shift in current from the substitute resistor to the calorimeter heater, was made automatically by means of double-pole double-throw switch, which was actuated by a tensed spring and released by the electric seconds-signals furnished by the standard clock. Since the heating periods were integral numbers of minutes, no significant errors have been attributed to the mechanism for transmitting the electric signals from the clock. Some experiments made to determine the time error due to the switch showed it to be 0.002 sec. or less and therefore insignificant.

The auxiliary electrical-measuring apparatus used in the measurement of the power and its calibration have been described in part 1. The routine of current and potential-drop observations for evaluating the power input are described later in the description of heat-capacity measurements.

The small amount of energy transmitted to the calorimeter by the pump and appearing as heat added was included in the accounting for total energy added in any experiment. The pump speed was kept constant at approximately 70 rpm, by a geared drive from a synchronous motor. Determinations of the pump power thus dissipated as heat were a part of the regular routine of the entire experimental program. These determinations were made calorimetrically by observing the rise in temperature produced in the calorimeter by running the pump alone with no electric-power input, keeping control and account of heat leak just as in a heat-capacity measurement. These pump-power experiments usually lasted for half an hour and the energy per minute was derived for each.

About 70 pump-power determinations were made during the series of heat-capacity experiments. Pump-power determinations were made with both large and small masses of water in the calorimeter and, at one time or another, at most of the even temperatures where stops were made in the experiments. These determinations gave values of pump power about 0.2 to 0.3 j/min. After a study of the resulting values of pump power, simple formulas were derived for use in calculating pump energies in the heat-capacity experiments.

The accidental variation of the observed pump power from the general mean was larger than could be accounted for by the uncertainty of the temperature measurement, but this was usually not more than would correspond to about 1 part in 20,000 in the value of α .

The characteristics of the pump, i. e., speed, power input, and corresponding heat-distributing effect, had been investigated by preliminary measurements before installing the pump in the calorimeter shell and served as a guide in choice of speed for the most advantageous operation in the final measurements.

The control and evaluation of heat leak is a vital part of any calorimetry when high precision is sought. The means provided for this purpose have been described in part 1. In operation, there were usually slight deviations from the ideal control which would nullify heat leak. The small corrections for this remaining heat leak were evaluated with the aid of the differential thermoelements, which indicated temperature differences between the calorimeter and its envelope by the number of microvolts. These differences were observed every minute and added algebraically to give sums in microvolt-minutes, called "heat-leak factors." These factors, when multiplied by "heat-leak coefficients," give the heat-leak corrections for the individual experiments. As previously stated in another way, the calorimeter was designed to make the coefficient small by construction and by evacuation of the insulating space, and means were provided to make the factor small by manipulation of the envelope temperature.

The total heat leak as determined experimentally consists of several parts, designated as "envelope," "upper-tube," and "lower-tube" heat leaks. The envelope heat leak is the chief part and results mainly from radiation between the surface of the calorimeter and of the envelope. The two tube heat leaks account for the heat transfer by metallic conduction along the tubes between the calorimeter and envelope. These tube heat leaks were nearly proportional to the envelope heat leak but not always exactly so for all experimental conditions, and therefore they were corrected for separately. Their coefficients were computed with sufficient accuracy from the knowledge of their dimensions and the thermal conductivity of their material.

The envelope heat-leak coefficient (in joules per microvolt-minute) was determined experimentally during the early part of the program and were checked occasionally later. This was done by exaggerating the temperature difference between the envelope and the calorimeter for a suitable time, observing this temperature difference and the two tube-temperature gradients every minute by means of the thermoelements, and summing these thermoelement indications (in microvolt-minutes) for the whole period to give the heat-leak factor. The total energy change in the calorimeter was computed from the measurements of the calorimeter temperature before and after this exaggerated heat leak. This energy, when corrected for the pump energy and the upper- and lower-tube heat leaks, was divided by the heat-leak factor, to give the envelope heat-leak coefficient, in joules per microvolt-minute, at the mean temperature of the experiment. This coefficient included, beside the radiation, any conduction (except by the two tubes) which was proportional to the temperature difference between the shells. This accounted for conduction through the heater and thermoelement wires. The gaseous conduction between these shells was probably negligible with the evacuation (less than 0.000,001-atmosphere pressure) maintained during all the experiments.

The factors of the three heat leaks were determined from observations made every minute during the experiments and were summed

algebraically for the whole periods. The experimental manipulation was usually such as to make the envelope heat-leak factor very small. During the heat-capacity experiments, the entire heat-leak correction would seldom affect the individual results by as much as 1 part in 50,000. It might be thought that corrections as small as these could have been disregarded, but had they not been regularly observed there would be no assurance that they were always insignificant.

The lower tube was always full of liquid, and precautions were taken to keep this tube always cool enough to prevent boiling, which might have caused transfer of heat to the calorimeter.

In addition to the various heat leaks mentioned, there is the possibility of a residual heat leak which could have been overlooked in the accounting for energy. This residual heat leak would be one which still occurred when everything else was eliminated and could be observed during periods when the pump was stopped and all other heat-leak factors kept as near zero as possible. A few such experiments were made but gave little more than a detectable coefficient. These experiments were discontinued, because whatever this residual heat leak was, it was included always in determinations of the pump power and therefore not neglected.

In the heat-capacity experiments, the usual procedure was to start observing the calorimeter temperature at 3 min after the end of the heating period. Investigation showed that thermal equilibrium was not complete in that time and that a small correction should be made if that temperature were used. This correction was found to be a function of the amount of water in the calorimeter and the temperature of the experiment. Although it was very small, it was applied to all heat-capacity experiments.

3. ACCOUNTING FOR CHANGE IN STATE

The temperature of the calorimeter and contents was measured by a platinum resistance thermometer used in conjunction with thermoelements, as previously described. The temperature change of the calorimeter and contained water sample was thus accurately observed in all experiments. All observed temperatures are expressed on the International Temperature Scale.

For determining either the initial or final temperature, each temperature reading consisted in simultaneous observations of resistance thermometer and thermoelements. The eight thermoelements on the calorimeter were connected in series to indicate the mean temperature of the calorimeter with respect to the reference block. Four successive temperature readings were made at half-minute intervals. This method of making several successive temperature readings is desirable for several reasons. The four-lead potential-terminal resistance thermometer requires at least two observations to eliminate the lead resistance from the measurement. Increasing the number of readings decreases the accidental error of observation. A regular schedule of readings takes account of slight drift in temperature.

A change in the proportion of liquid and vapor in the calorimeter occurs in the experiments. This change is analyzed in the theory of the method and is accounted for by use of the supplementary quantity, which is designated as β .

Special details of the experimental procedure that apply to the carrying out of the calorimetric measurements will next be described.

4. DESCRIPTION OF HEAT-CAPACITY MEASUREMENTS

It will be recalled that these experiments yield values of the change with temperature of the quantity α . Combined algebraically with corresponding changes of the quantity β , obtained from calculations, the data suffice to determine the change in enthalpy, H , of the saturated liquid.

The procedure in these heat-capacity experiments consisted essentially in heating a sample of water, part liquid and part vapor, over an accurately measured temperature range and in accounting for the energy added in the process. Two such heat-capacity determinations, a gross and a tare, are required for an evaluation of the change in α . These two determinations over the same temperature interval are made with different amounts of water, always maintaining the saturation condition. One determination, made with a large charge, yields a gross value of energy added. The other, made with a small charge, yields a tare value. The difference, or net value, of energy added, divided by the net mass, gives the value of the change in α for that temperature interval. This method of differences avoids the necessity of determining the heat capacity of the empty calorimeter.

In an experiment starting, for example at 0° C, the calorimeter is first cooled by the following procedure. The cold water from the cooling tank, where the temperature is a few tenths of a degree below 0° C, flows through the condenser ($W1$ in fig. 3) located at the top of the main steam jacket, the condenser, $W2$, located at the top of the reference block steam jacket, the guard cooling coil, $W3$, and the stuffing-box cooling cell, $W4$. The space between the envelope and calorimeter is filled with helium to increase heat transfer between the two. Heat from the calorimeter and contents is transferred to the colder surroundings until the temperature of the calorimeter and contents is about 0° C. This process took many hours when the calorimeter contained a large charge and was usually done overnight. In a few of the experiments starting near zero the temperature of the calorimeter and contents was reduced to a few hundredths of a degree below zero. At no time was there any evidence of freezing in the calorimeter.

The envelope and the reference block are then brought to the temperature of the calorimeter. The helium is then pumped out of the envelope space to reduce heat transfer. The circulating pump is started at the desired speed, and the apparatus is ready for the beginning of an experiment.

The equilibrium temperature of the calorimeter and its contents is observed as described in section 3. The storage battery is connected to the calorimeter heater by the switch actuated by the time signals. At about the same time, the power is supplied to the envelope heater and reference-block heater. The currents in these heaters are adjusted so that the temperatures of the envelope and reference block stay very close to the temperature of the calorimeter. The differential thermoelement indications for determining the heat leak are observed almost continuously and recorded once each minute. One or more complete surveys with all thermoelement combinations are usually recorded in each individual experiment. The current and potential drop in the calorimeter heater are observed on alternate minutes starting with the first half-minute of the interval. The calorimeter heating

is continued for an integral number of minutes and stopped when the desired temperature interval has been completed.

The rate of heating was chosen as $0.5^{\circ}\text{C}/\text{min}$, and the calorimeter heater current was adjusted before the beginning of each experiment, so that after the integral number of minutes, the calorimeter temperature ended very close to the desired even temperature. The envelope and reference-block heater currents were adjustable to keep the temperatures of the envelope and reference block very near that of the calorimeter at all times. After several minutes, to allow the calorimeter and contents to come to temperature equilibrium, the final temperature was observed. This completed the heat-capacity experiment.

Two groups of such experiments were made, one with large charges of water in the calorimeter and the other with small charges. The experiments with small charges may be regarded as determinations of the tare-heat capacity of the calorimeter. Choice of the extent of the temperature intervals was governed by the rate of change of heat capacity with temperature. It was found that 10° intervals were suitable to determine the trend over most of the temperature range. Toward 0°C , where the change was increasingly rapid, the shorter intervals of 5° , 2.5° , and finally 1°C , gave more convincing evidence about this rate of change, even at the cost of some loss in the percentage of accuracy of the intervals.

During the heat-capacity experiments, the upper tube was closed at both its upper and lower ends by metal disks. In this way, possible error from condensation of water in the upper tube was avoided.

IV. RESULTS OF HEAT-CAPACITY EXPERIMENTS

The observations made during the experiments were recorded on separate laboratory-data sheets as soon as they were made. The computations from these sheets were often begun before all of the day's data sheets had been completed, and it was the rule to have preliminary results of the data for one day before the experiments of the next day were under way. This made it possible to arrange the day's observations with the full knowledge of what was most needed and what special precautions, if any, needed to be taken in observing. As more data were collected, it was possible to get and use more complete knowledge of contributory results, such as pump power, heat-leak coefficients, etc., that enter into the final reductions. Lastly, corrections were made for all known factors. The energies thus determined for the actual temperature intervals were then interpolated to even temperature intervals. These were reduced to determinations of the change of α over separate temperature intervals. These data were then formulated for use in the computation of tables and for computations involving the heat capacity of water.

In table 1, a typical data sheet is shown for a "large-mass" experiment made with 1,093.647 g of water in the calorimeter. The observations recorded under "Power" consist of the potentiometer readings of potential drop and current in the calorimeter heater after applying the decimal factors for standard resistor and volt box to reduce the readings to volts and amperes. Under "Thermometer" are given both "normal" (N) and "reverse" (R) bridge readings of the resistance of the thermometer in the reference block. The remaining observations are thermolement readings, in microvolts. The column "Calorimeter minus reference block" shows the thermolement readings of the eight

thermoelements (*JT+JB*) used in the measurement of the average temperature of the calorimeter. Under "Envelope minus calorimeter" are recorded the readings of the eight thermoelements on the envelope (*JU+JL*) opposed to the eight on the calorimeter (*JT+JB*). The column "Lower tube" shows the indications of the thermoelements (*J9-J8*), while the column "Upper tube" shows (*J7-J5*). In the last column, a survey of thermoelement indications is shown, starting just after the routine observations at 11:57. At least one such survey, taking less than a minute, was made in each experiment.

TABLE 1.—*Sample data sheet*

[Temperature interval 25° to 30° C ----- October 27, 1937]

Time	Power		Thermometer, Bridge readings	Thermoelement readings				
	Potential drop	Current		Calorimeter minus reference block	Envelope minus calorimeter	Lower tube	Upper tube	Survey of other thermoelements
	<i>v</i>	<i>amp</i>	<i>Ohms</i>	μv	μv	μv	μv	μv
11:53	-----	-----	30.41524 N	-0.4	1	-1	0	
53.5	-----	-----	30.41517 R	- .5				
54	-----	-----	30.41516 R	- .5	2			
54.5	-----	-----	30.41524 N	- .6				
55	On	-----	-----		1	-1	0	
55.5	-----	.60268	-----		2	-3	5	
56.5	65.965	-----	-----	0	0	-3	5	
57.5	-----	.60269	-----		0	-3	5	JU 1
58.5	65.965	-----	-----		-1			JL 1
59.5	-----	.60274	-----		-1	-4	5	JT 0
12:00.5	65.964	-----	-----		0			JB -1
01.5	-----	.60278	-----		0	-3	5	J1 0
02.5	65.963	-----	-----		-1			J5 -12
03.5	-----	.60283	-----		-1	-3	5	J8 -2
04.5	65.963	-----	-----		-1			J10 -3
05	Off	-----	-----		-2			
06	-----	-----	-----		0			
07	-----	-----	-----		2			
08	-----	-----	30.96171 N	-0.3				
08.5	-----	-----	30.96162 R	- .3				
09	-----	-----	30.96165 R	- .4	0	-1	0	
09.5	-----	-----	30.96171 N	- .5				

Table 2 shows a computation sheet, using the data given in table 1. The first step is the calculation of the temperature of the calorimeter. The average of the first four bridge readings is taken as the resistance of the thermometer at the mean time. Using the thermometer and bridge calibrations, the temperature of the reference block corresponding to this resistance value is obtained. Likewise, the average of the first four readings of the thermoelements (*JT+JB*) is found and from this and the calibrations, the difference in temperature called "temp. cal. minus temp. ref. block" is obtained at the same mean time. Combination of these temperature measurements gives the initial temperature of the calorimeter at that time, considered as the beginning of the experiment. The same method is used in the computation of the final temperature.

TABLE 2.—*Sample computation sheet, using data shown in table 1*

[Temperature interval 25° to 30° C October 27, 1937]

Steps in computations	Temperature	
	Initial	Final
Average of bridge readings..... (ohms)	30.41520	30.96167
Temperature of reference block..... (°C)	25.0034	30.0036
Average thermoelement reading..... (μv)	-0.50	-0.38
Temp. cal. minus temp. ref. block..... (°C)	-0.0010	-0.0008
Temperature of calorimeter..... (°C)	25.0024	30.0028
	Energy	
	Potential drop	Current
	<i>v</i>	<i>amp</i>
Average of potentiometer readings.....	65.9640	0.602744
Correction for timing of readings.....	0.0001	.000009
Potentiometer calibration correction.....	.0090	.000090
Correction for potentiometer ratio.....	-.0324	-.000296
Volt-box current.....		-.003298
Correction for volt-box factor.....	.0011	
Correction for standard resistance factor.....		-.000086
	65.9418	0.599163
	<i>int. j</i>	
Electric energy for 600 sec.....	23,705.9	
Pump energy for 15 min.....	3.7	
Envelope heat leak (for -2 μv min).....	0.0	
Lower tube heat leak (for -36 μv min).....	-.1	
Upper tube heat leak (for 50 μv min).....	0.3	
Starting correction.....	2.3	
Equilibrium correction.....	-0.2	
Energy added to calorimeter and contents.....	23,711.9	
Energy to correct initial temp. to 25° C.....	11.4	
Energy to correct final temp. to 30° C.....	-13.3	
Energy for even temp. interval, 25° to 30° C.....	23,710.0	

The next step is the computation of the electric-energy input to the calorimeter during the heating period, 11:55 to 12:05. The potential drop across the calorimeter heater is calculated from the average of the five potentiometer readings of potential drop. Since these potentiometer readings are not distributed symmetrically about the middle of the heating period, a small correction is made to account for the drift during the experiment. This is recorded as "correction for timing of readings." The "potentiometer calibration correction" is computed, taking into account the calibrations made during the day of the experiment. The "correction for potentiometer ratio" has been explained in part 1 of this report under "measuring instruments and calibrations." The correction for the volt-box calibration factor is also recorded. Applying all of these corrections to the average of the potentiometer readings, the average calorimeter potential drop, expressed in international volts, is computed.

Likewise, the average calorimeter heater current (international amperes) is computed. In this case, corrections must be made for the current through the volt box and for the standard 0.1-ohm calibration factor. By multiplying together the current, the potential drop, and the time of electric heating (600 sec), the total electric energy (international joules) is computed.

The next step is the computation of the total energy added to the calorimeter and contents during the experiment. This is obtained by adding to the total electric energy the following small energy corrections. The pump energy is calculated from the value of power formulated from pump-power experiments. This pump power was multiplied by the time of the experiment (15 min) to give the pump energy. The three heat leaks (envelope, upper tube, and lower tube) were computed by summing the thermoelement readings from table 1 to give heat-leak factors in microvolt-minutes. These factors were multiplied by their respective heat-leak coefficients to give the heat-leak corrections. The "starting correction" and "equilibrium correction," which have been described in the previous section, were calculated from the results of the special experiments. The sum of the electric energy and all the energy corrections gives the entire energy added to heat the calorimeter and its contents from the initial temperature, 25.0024° C, to the final temperature, 30.0028° C.

In the reduction of the results, it was convenient to use the even temperature interval 25° to 30° C. Therefore, corrections were made for the small deviations of the measured temperatures from the intended even temperatures. Only approximate values of the heat capacity of the calorimeter and contents were necessary to make these corrections. The resulting energy is recorded as "energy for even temperature interval," and will be referred to as ΔQ .

The sample computation just described is one of the 256 assembled in table 3. This table contains the substance of the principal data and preliminary reductions of the heat-capacity experiments made with a large mass of water in the calorimeter. Table 4 contains a similar assembly of the principal data of the 137 experiments made with a small mass of water. These two tables comprise an abstract of the record of all the experimental data which were accepted as trustworthy. Only those experiments in which the technique was faulty or the record incomplete were excluded. Further reductions of these data are included in these tables, as next described.

Each experiment for the temperature interval Δt gives a value of ΔQ which, according to the theory [1], should satisfy the equation

$$\frac{\Delta Q}{\Delta t} = \frac{\Delta Z}{\Delta t} + \frac{M\Delta\alpha}{\Delta t},$$

where M is the mass of water in the calorimeter, $\Delta Z/\Delta t$ is a property of the calorimeter independent of the amount of water in it, and $\Delta\alpha/\Delta t$ is a specific property of the water. By taking all the equations for one temperature interval for both the large- and small-mass experiments, it is possible to solve for the $\Delta\alpha/\Delta t$ and $\Delta Z/\Delta t$ for that interval by the method of least squares, as was done in previous publications. Actually, however, since approximate values of $\Delta\alpha/\Delta t$ were available from previous researches, it was found expedient to solve for preliminary values of $\Delta Z/\Delta t$ as the experimental work progressed, using these tentative values of $\Delta\alpha/\Delta t$ together with the data from experiments with small mass. These values of $\Delta Z/\Delta t$ were smoothed by formulating dZ/dt and were then used with the large-mass data to compute corresponding values of $\Delta\alpha/\Delta t$. Successive substitutions of these tentative values of $\Delta Z/\Delta t$ and $\Delta\alpha/\Delta t$ gave rapid approach to the limiting mean values, since the ratio of the large to the small masses was usually about 8.6. This method of reduction facilitated

the preliminary survey of results as the experimental data accumulated and served as a guide in the choice of temperature intervals best suited to determine the trend of the heat-capacity curve.

As finally reduced and recorded in table 4, the result of each experiment with small mass constitutes a separate determination of $\Delta Z/\Delta t$, and the entire series of these results is a calibration of the calorimeter. Similarly, the result of each experiment with large mass, as reduced by use of the calibration results and recorded in table 3, constitutes a separate determination of $\Delta\alpha/\Delta t$, and the entire series is a determination of the heat capacity of water in the range 0° to 100° C.

A comparison of the individual results with the average values indicates the degree of consistency of the measurements, and comparison of the averages with the formulated values indicates the degree of consistency of the trend with temperature. The manner of formulation of these results will next be described.

Since all experiments are necessarily made over finite temperature intervals, the results, in terms of increments $\Delta\alpha/\Delta t$ and $\Delta Z/\Delta t$, differ slightly from the corresponding derivatives, $d\alpha/dt$ and dZ/dt . These differences were computed by use of preliminary approximate equations and were used to get the corresponding values of $d\alpha/dt$ and dZ/dt^0 at the mid temperatures to be fitted by formulas.

The empirical formula chosen for dZ/dt has the following form:

$$dZ/dt = A + Bt + C(t+60)^{5.14}.$$

The final coefficients determined from the average values of $\Delta Z/\Delta t$ listed in table 4 are $A=168.69$, $B=0.089$, and $C=68.85214 \times 10^{-10}$, where t is in degrees centigrade and dZ/dt is in international joules per degree centigrade. Values of $\Delta Z/\Delta t$ calculated from this formula are given in table 4 as formulated values of $\Delta Z/\Delta t$. It appears that a further adjustment of the dZ/dt formulation by another approximation would have changed the final value of $d\alpha/dt$ by about 1 part in 80,000 at 0° C and by successively smaller amounts up to 100° C. This change was considered as sufficiently insignificant to be neglected.

The formulation for $d\alpha/dt$ was based on the values of $\Delta\alpha/\Delta t$ given in table 3. The average values of $\Delta\alpha/\Delta t$ were computed for each of the 20 temperature intervals and then corrected for deviations from the derivatives to get corresponding mean values of $d\alpha/dt$. It is obvious that some of these experimental means should have more weight than others. For example, the 19 experiments over the 10° interval from 40° to 50° C should have more weight than the 4 experiments over the 1° interval from 0° to 1° C. The means were therefore weighted approximately proportionally to the number of experiments times the number of degrees in the interval. A least-squares solution was then made for the constants in the following empirical equation:

$$d\alpha/dt = A + Bt + C(10)^{-0.036t}.$$

The constants were found to be $A=4.1699$, $B=0.000\ 015\ 27$, and $C=0.0467$, where t is in degrees centigrade, and $d\alpha/dt$ is in international joules per gram-degree centigrade. Using this equation, the values of $\Delta\alpha/\Delta t$ for each of the intervals have been computed and are recorded in table 3 for each interval. The deviations from these formulated values are tabulated in the last column of table 3.

It may be seen from table 3 that in the later experiments there is a trend to lower values of $\Delta\alpha/\Delta t$. The experiments above 5° C made after October 28, 1937, show values of $\Delta\alpha/\Delta t$ which average about 1 part in 10,000 less than those before that date. No explanation is offered for this change, and the fact is taken merely as evidence of the limitation of accuracy due to unknown systematic causes.

Since the specific heat at ordinary atmospheric pressure is the property of water most commonly utilized for calorimetric purposes, this property was determined by further reduction of the experimental average values of $\Delta\alpha/\Delta t$ given in table 3. This computation will next be described.

The reduction may be considered in three steps, which are indicated in table 5, starting with the average of the measured values of $\Delta\alpha/\Delta t$. At saturation pressure, the mean enthalpy change, $\Delta H/\Delta t$, exceeds $\Delta\alpha/\Delta t$ by the quantity $\Delta\beta/\Delta t$, as shown in the theory. The values of this reduction term, as given in column 3, were calculated by the relation $\beta = T u dP/dT$, as explained in part 1 of this report. Values of the specific volume, u , were obtained from the density data of Chappuis [10] up to 50° C and of Thiesen [11] up to 100° C, and the compressibility data of Smith and Keyes [12]. Values of dP/dT were obtained from an unpublished formulation of the vapor-pressure data of the Reichsanstalt as reformulated by Harold T. Gerry and used for the saturation pressure table by the International Steam Conference of 1934 [9, 36].

Next, values of the term for reduction to mean enthalpy change at 1-atmosphere pressure, $(\Delta H/\Delta t)_{p=1} - (\Delta H/\Delta t)_{sat.}$, as given in column 4, were calculated by the relation

$$\left(\frac{dH}{dP}\right)_T = V - T\left(\frac{dV}{dT}\right)_P,$$

using the same data as above. There is still the difference between the mean value of the change of enthalpy per degree at 1 atmosphere and the derivative, $C_{p=1}$, the desired specific-heat value at the mid-temperature of the interval. This reduction term, $C_{p=1} - (\Delta H/\Delta t)_{p=1}$, given in column 5, was computed by using a preliminary approximate equation for C_p .

The 20 experimental values of C_p in column 6, which were obtained by applying the three reduction terms just described, were then formulated, using the same weighting factors previously used in the formulation of $d\alpha/dt$. After tests of types of functions to represent the experimental data, the empirical equation finally chosen was

$$C_p = A + B(t+100)^{5.26} + C(10)^{-0.036t}.$$

The coefficients were determined by least squares to be $A = 4.169\,036$, $B = 0.000\,3639(10)^{-10}$, and $C = 0.0467$, when t is expressed in degrees centigrade, and C_p in international joules per gram-degree centigrade at 1-atmosphere pressure. Both the formulated and the experimental values of C_p are given in table 5, together with the deviations. The midtemperatures of the temperature intervals are given also.

Figure 4 shows graphically the comparison of the experimental values with the formulated values of C_p . In this figure the areas of the circles representing the observed means are made proportional to the weights assigned in the formulation. In other words, the larger

circles indicate that more experiments or larger temperature intervals are represented. The degree of accord of the formulation with the experimental results shows that this fairly simple empirical equation is adequate to represent the results over the entire 100° C range. However, this agreement must not be taken as an estimate of the accuracy of the results, since it takes no account of unknown systematic errors, which may well be larger than the accidental errors.

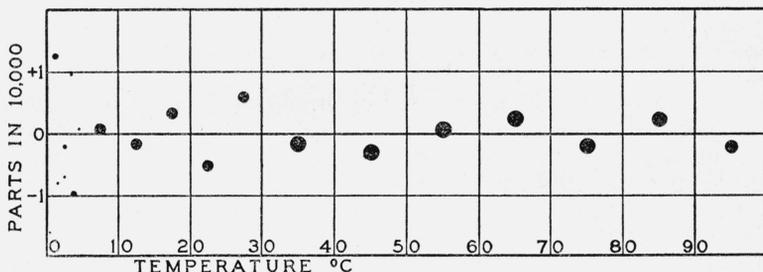


FIGURE 4.—Deviations of mean measured C_p from formulation. Areas of circles are proportional to the weights assigned to the mean values.

Figure 5 shows a comparison of the heat capacities. It should be noted from the figure that the scale of the heat capacities is very much exaggerated and that the extreme range of the values of C_{p1} between 0° and 100° C is only about 1 percent. The $d\alpha/dt$ line gives essentially the measured values of heat capacity. The departure of the $(dH/dt)_{\text{sat}}$ line from the $d\alpha/dt$ line represents the magnitude of the $d\beta/dt$ reduction. The difference between the C_p line and the

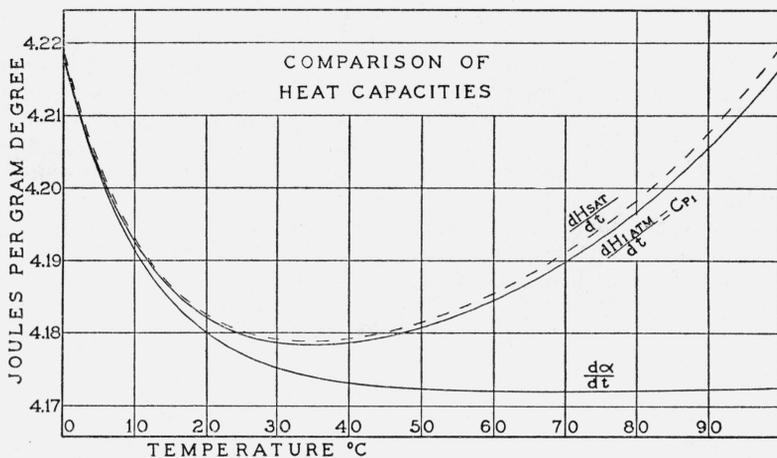


FIGURE 5.—Comparison of heat capacities.

$(dH/dt)_{\text{sat}}$ line shows the magnitude of the reduction to 1-atmosphere pressure. The experimental values have not been plotted on this figure, because only one or two values would fall outside the width of the line in spite of the exaggerated scale.

Water is often used as a calorimetric medium and also as a standard of heat capacity, as, for example, in a condensing calorimeter for measuring the enthalpy of superheated steam or for measuring

specific heats by the method of mixtures. For such purposes, it is useful to know the integral of the specific heat (C_p) function, since these calorimetric measurements must necessarily apply to finite temperature intervals. A table of values of the integral, giving the heat content, or enthalpy, from 0 to each temperature at intervals of 1° from 0° to 100° C has been prepared for this use. This table has been compiled in terms of absolute joules per gram and international steam-table calories per gram instead of any of the numerous heat units which have been used in the past, and defined variously in terms of the heat capacity of water.

Since the absolute practical electrical units are expected to replace the present international units on January 1, 1940, it seems desirable to use the absolute joule rather than the international joule which has been used in the measurements, but which is likely so soon to be obsolete. Also since the international steam-table calorie (IT Cal), defined as 1/860 int. whr, has now become the basis of heat units used in steam tables, values are included in this unit.

The conversion factor from international joules to absolute joules, being based on measurement, can not be exactly known, but the uncertainty has been greatly reduced by the more recent measurements of the absolute ohm and absolute ampere in terms of the electrical standards maintained in National laboratories. Since a final official figure for this factor has not yet been announced, the value 1 int. j = 1.00019 abs. j used here was an estimate of the probable value of the absolute joule in international joules as derived from electrical standards maintained in this laboratory and was based on recent measurements, partly unpublished. It is believed that this value expresses the equivalent of the units actually used within 1 or 2 units in the last place.

The equation for C_p in international joules per gram-degree centigrade has been converted to absolute joules per gram-degree by multiplying the coefficients by the factor 1.00019, giving the new equation

$$C_p = 4.169828 + 0.000364(t + 100)^{5.26} \times 10^{-10} + 0.046709(10)^{-0.036t},$$

where t is in degrees centigrade and C_p is in absolute joules per gram-degree centigrade at 1-atmosphere pressure. By integration of $C_p dt$, the equation for enthalpy, H_p , at 1-atmosphere pressure in absolute joules per gram is obtained. Taking the value of $H_{\text{sat.}}$ as 0 at 0° C, the equation is

$$H_p = 0.102559 + 4.16928t + [5.8142(t + 100)^{6.26} \times 10^{-15} - 0.563485(10)^{-0.036t}] t_0,$$

where t is in degrees centigrade, and H_p in absolute joules per gram at 1-atmosphere pressure.

Values of both C_p and H_p are given in table 6. The values of H_p , in IT Cal, have been computed from the values in absolute joules per gram by use of the conversion factor 1 abs. j = 0.238846 IT Cal.

This gives values of H_p which are larger by 1 part in 100,000 than correspond to the present definition of the IT Cal but are in agreement with a redefinition of the IT Cal as 0.001163 abs. whr, which has been suggested for adoption when the change in electrical units takes place. This small discrepancy is less than the amount which is important in steam tables, and likewise less than the uncertainty of the present measurements.

The enthalpy of saturated liquid water is one of the important items in the compilation of steam tables. Values of this property were computed by use of the formula for $d\alpha/dt$ and values of β .

The formula for $d\alpha/dt$ in international joules per gram-degree centigrade is

$$d\alpha/dt = 4.1699 + 15.27 t \times 10^{-6} + 0.0467(10)^{-0.036t}.$$

By integration, the following equation for the increment of α is obtained:

$$\alpha'_0 = [4.1699t + 7.635t^2 \times 10^{-6} - 0.56376 \times 10^{-0.036t}]'_0.$$

Values of α'_0 computed by this equation, at every 5° point from 0° to 100° C, are given in table 7. Values of β , computed as previously described, are also given. Values of enthalpy are found by adding the increment of β to α'_0 , and are given in the table in international joules per gram and also converted to absolute joules per gram and to International Steam Table Calories per gram, using the conversion factors stated above.

TABLE 3.—Principal data from large-mass heat-capacity experiments

Date	Mass of water, M	Initial temperature	Final temperature	Heat leak	Pump energy	Energy for even temperature interval	$\Delta\alpha/\Delta t$	Deviation from formulation
	g	°C	°C	Int. j	Int. j	Int. j	Int. j/g-°C	Int. j/g-°C
12-7-37	1093.989	0.0104	0.9974	0.0	1.7	4,778.4	4.21286	-0.00187
12-9-37	603.781	.0565	.9522	.0	6.1	2,714.9	4.21563	.00090
12-10-37	603.781	.3232	1.0068	.1	15.6	2,713.9	4.21398	-.00075
12-14-37	603.781	.0324	.9938	.0	2.9	2,713.9	4.21398	-.00075
Average							4.21411	

Even temperature interval 0.0° to 1.0° C. $\Delta Z/\Delta t = 169.577$ int. j/°C. Formulated value of $\Delta\alpha/\Delta t = 4.21473$ int. j/g-°C

9-23-37	1091.161	0.1772	2.4587	0.6	2.7	11,918.6	4.21363	0.00153
10-6-37	1092.517	.4886	2.4624	-1	2.4	11,932.5	4.21349	.00139
10-8-37	1092.517	.2433	2.4981	-4	2.7	11,931.7	4.21320	.00110
10-14-37	1092.517	.1884	2.4990	-2	2.4	11,932.1	4.21334	.00124
10-21-37	1093.647	-.0385	2.5184	-1	2.4	11,939.6	4.21173	-.00037
10-26-37	1093.647	-.0376	2.4947	-1	2.4	11,941.4	4.21239	.00029
10-27-37	1093.647	.0120	2.4972	.2	2.4	11,941.1	4.21228	.00018
10-28-37	1093.647	.0070	2.4992	.1	2.4	11,941.1	4.21228	.00018
11-16-37	1096.489	-.0174	2.4588	.0	2.4	11,970.4	4.21205	-.00005
11-18-37	1096.489	-.0037	2.4867	-1	2.4	11,971.1	4.21231	.00021
12-2-37	1093.989	-.0586	2.5191	.4	2.9	11,945.7	4.21265	.00055
Average							4.21267	

Even temperature interval 0.0° to 2.5° C. $\Delta Z/\Delta t = 169.688$ int. j/°C. Formulated value of $\Delta\alpha/\Delta t = 4.21210$ int. j/g-°C

9-14-37	1091.161	0.1830	4.9763	1.3	5.6	23,809.2	4.20833	0.00016
9-21-37	1091.161	.1920	5.1873	.5	4.1	23,806.8	4.20789	-.00028
Average							4.20811	

Even temperature interval 0.0° to 5.0° C. $\Delta Z/\Delta t = 169.879$ int. j/°C. Formulated value of $\Delta\alpha/\Delta t = 4.20817$ int. j/g-°C

12-7-37	1093.989	1.0078	2.0054	-0.1	1.7	4,776.7	4.21118	0.00000
12-9-37	603.781	.9518	1.9649	.0	6.1	2,712.3	4.21109	-.00009
12-10-37	603.781	1.0041	2.0051	.0	15.6	2,712.2	4.21093	-.00025
12-14-37	603.781	.9964	1.9944	.0	2.9	2,711.8	4.21027	.00009
Average							4.21087	

Even temperature interval of 1.0° to 2.0° C. $\Delta Z/\Delta t = 169.725$ int. j/°C. Formulated value of $\Delta\alpha/\Delta t = 4.21118$ int. j/g-°C

TABLE 3.—Principal data from large-mass heat-capacity experiments—Continued

Date	Mass of water, <i>M</i>	Initial temperature	Final temperature	Heat leak	Pump energy	Energy for even temperature interval	$\Delta\alpha/\Delta t$	Deviation from formulation
	<i>g</i>	$^{\circ}\text{C}$	$^{\circ}\text{C}$	<i>Int. j</i>	<i>Int. j</i>	<i>Int. j</i>	<i>Int. j/g-°C</i>	<i>Int. j/g-°C</i>
12-7-37	1093.989	2.0054	3.0051	-.01	1.7	4,772.5	4.20719	-0.00072
12-9-37	603.781	1.9649	2.9776	-.1	2.5	2,710.7	4.20818	.00027
12-10-37	603.781	2.0051	2.9997	-.1	6.4	2,710.6	4.20802	.00011
12-14-37	603.781	1.9944	2.9979	.0	1.2	2,710.1	4.20719	-.00072
Average							4.20765	

Even temperature interval 2.0° to 3.0° C. $\Delta Z/\Delta t=169.876$ int. j°C . Formulated value of $\Delta\alpha/\Delta t=4.20791$ int. $\text{j/g-}^{\circ}\text{C}$

9-23-37	1091.161	2.4587	4.9962	0.0	2.4	11,890.7	4.20306	-0.00118
10-6-37	1092.517	2.4624	4.9935	-.3	2.4	11,905.5	4.20326	-.00098
10-8-37	1092.517	2.4981	4.9767	-.1	2.4	11,908.4	4.20432	.00008
10-14-37	1092.517	2.4990	4.9990	-.1	2.4	11,907.9	4.20414	-.00010
10-19-37	1093.647	2.5092	5.0043	-.2	2.4	11,918.8	4.20378	-.00046
10-21-37	1093.647	2.5184	5.0021	-.1	2.4	11,922.0	4.20495	.00071
10-26-37	1093.647	2.4947	5.0025	.0	2.4	11,919.6	4.20409	-.00015
10-27-37	1093.647	2.4963	5.0439	.4	2.4	11,918.4	4.20363	-.00061
10-28-37	1093.647	2.4983	4.9961	.4	2.4	11,919.6	4.20409	-.00015
11-16-37	1096.489	2.4585	5.0015	-.1	2.4	11,948.0	4.20354	-.00070
11-18-37	1096.489	2.4886	4.9970	.0	2.4	11,949.2	4.20397	-.00027
12-3-37	1093.989	2.4637	4.9717	.0	2.4	11,921.4	4.20342	-.00082
Average							4.20385	

Even temperature interval 2.5° to 5.0° C. $\Delta Z/\Delta t=170.071$ int. j°C . Formulated value of $\Delta\alpha/\Delta t=4.20424$ int. $\text{j/g-}^{\circ}\text{C}$

12-7-37	1093.989	3.0051	4.0045	0.0	1.7	4,770.4	4.20513	0.00023
12-9-37	603.781	2.9776	3.9911	-.1	2.5	2,708.8	4.20479	-.00011
12-10-37	603.781	2.9997	4.0005	-.1	6.4	2,709.1	4.20528	.00038
12-14-37	603.781	2.9979	3.9993	.0	1.2	2,709.6	4.20611	.00121
Average							4.20533	

Even temperature interval 3.0° to 4.0° C. $\Delta Z/\Delta t=170.030$ int. j°C . Formulated value of $\Delta\alpha/\Delta t=4.20490$ int. $\text{j/g-}^{\circ}\text{C}$

12-7-37	1093.989	4.0045	5.0036	0.0	1.7	4,766.4	4.20133	-0.00081
12-9-37	603.781	3.9911	5.0052	.0	2.5	2,707.6	4.20253	.00039
12-10-37	603.781	4.0005	5.0015	.0	6.4	2,707.8	4.20286	.00072
12-14-37	603.781	4.9993	4.9990	-.1	1.2	2,707.3	4.20204	-.00010
Average							4.20219	

Even temperature interval 4.0° to 5.0° C. $\Delta Z/\Delta t=170.188$ int. j°C . Formulated value of $\Delta\alpha/\Delta t=4.20214$ int. $\text{j/g-}^{\circ}\text{C}$

9-14-37	1091.161	4.9763	10.0026	1.3	4.4	23,741.4	4.19515	-0.00012
9-16-37	1091.161	5.0018	9.9480	.1	4.6	23,742.5	4.19536	.00009
9-21-37	1091.161	5.1873	9.9846	1.0	3.9	23,739.9	4.19488	-.00039
9-23-37	1091.161	4.9962	9.9910	-.4	3.7	23,743.6	4.19556	.00029
10-6-37	1092.517	4.9935	10.0029	-.6	3.7	23,771.7	4.19550	.00023
10-8-37	1092.517	4.9767	10.0084	-.2	3.7	23,772.9	4.19571	.00044
10-14-37	1092.517	4.9990	10.0050	-.1	3.7	23,772.5	4.19564	.00037
10-19-37	1093.647	5.0043	10.0104	-.2	3.7	23,795.6	4.19553	.00026
10-21-37	1093.647	5.0021	9.9988	.3	3.7	23,799.0	4.19615	.00088
10-26-37	1093.647	5.0025	10.0018	.0	3.7	23,797.3	4.19584	.00057
10-27-37	1093.647	5.0432	10.0077	.2	3.7	23,796.5	4.19570	.00043
10-28-37	1093.647	4.9954	9.9905	.3	3.7	23,795.9	4.19559	.00032
11-16-37	1096.489	5.0011	10.0036	-.2	3.7	23,853.3	4.19518	-.00009
11-18-37	1096.489	4.9965	10.0005	.0	3.7	23,853.9	4.19529	.00002
12-3-37	1093.989	4.9701	9.9808	.0	3.7	23,799.4	4.19491	-.00036
12-7-37	1093.989	5.0036	10.0067	-.3	3.7	23,798.3	4.19471	-.00056
12-9-37	603.781	5.0052	10.0755	.0	5.4	13,516.1	4.19445	-.00082
12-10-37	603.781	5.0015	10.0029	-.1	13.8	13,517.3	4.19485	-.00042
12-14-37	603.781	4.9990	9.9994	-.3	2.6	13,516.9	4.19472	-.00055
Average							4.19530	

Even temperature interval 5° to 10° C. $\Delta Z/\Delta t=170.687$ int. j°C . Formulated value of $\Delta\alpha/\Delta t=4.19527$ int. $\text{j/g-}^{\circ}\text{C}$

TABLE 3.—Principal data from large-mass heat-capacity experiments—Continued

Date	Mass of water, <i>M</i>	Initial temperature	Final temperature	Heat leak	Pump energy	Energy for even temperature interval	$\Delta\alpha/\Delta t$	Deviation from formulation
	<i>g</i>	$^{\circ}\text{C}$	$^{\circ}\text{C}$	<i>Int. j</i>	<i>Int. j</i>	<i>Int. j</i>	<i>Int. j/g-°C</i>	<i>Int. j/g-°C</i>
9-14-37	1091.161	10.0026	15.0032	0.9	3.9	23,697.0	4.18619	-0.00059
9-16-37	1091.161	9.9480	14.9471	-1	3.7	23,699.1	4.18658	-0.00020
9-21-37	1091.161	9.9846	15.0031	1.3	4.1	23,699.9	4.18672	-0.00006
9-23-37	1091.161	9.9910	14.9987	-5	3.7	23,701.9	4.18709	.00031
10-6-37	1092.517	10.0029	15.0069	-1	3.7	23,728.9	4.18684	.00006
10-8-37	1092.517	10.0084	15.0045	-3	3.7	23,730.5	4.18713	.00035
10-13-37	1092.517	10.0020	15.0123	-2	3.7	23,724.7	4.18607	-0.00071
10-14-37	1092.517	10.0050	15.0064	.0	3.7	23,729.6	4.18696	.00018
10-19-37	1093.647	10.0104	15.0098	-1	3.7	23,752.1	4.18675	-0.00003
10-21-37	1093.647	9.9988	14.9970	.3	3.7	23,753.9	4.18708	.00030
10-26-37	1093.647	10.0018	15.0000	.0	3.7	23,754.5	4.18719	.00041
10-27-37	1093.647	10.0077	15.0024	.0	3.7	23,755.2	4.18732	.00054
10-28-37	1093.647	9.9905	14.9997	.0	3.7	23,755.1	4.18730	.00052
11-16-37	1096.489	10.0036	14.9993	.0	3.7	23,808.8	4.18624	-0.00054
11-18-37	1096.489	9.9999	15.0004	.0	3.7	23,810.4	4.18654	-0.00024
12-3-37	1093.989	9.9808	14.9891	-1	3.7	23,757.9	4.18650	-0.00028
12-7-37	1093.989	10.0067	15.0097	.0	3.7	23,754.8	4.18594	-0.00084
12-9-37	603.781	10.0755	15.1357	-3	8.9	13,496.4	4.18644	-0.00034
12-10-37	603.781	10.0004	15.0065	-3	23.0	13,494.7	4.18587	-0.00091
12-14-37	603.781	9.9996	15.0019	-2	4.3	13,497.7	4.18687	.00009
Average							4.18668	

Even temperature interval 10° to 15° C. $\Delta Z/\Delta t=171.588$ int. j/°C. Formulated value of $\Delta\alpha/\Delta t=4.18678$ int. j/g-°C

9-16-37	1091.161	14.9471	19.8801	0.0	3.7	23,675.9	4.18140	0.00021
9-21-37	1091.161	15.0031	20.0047	-2	3.7	23,673.5	4.18096	-0.00023
9-23-37	1091.161	14.9987	19.9959	-4	3.7	23,675.9	4.18140	.00021
10-6-37	1092.517	15.0069	20.0025	.0	3.7	23,704.0	4.18135	.00016
10-8-37	1092.517	15.0045	20.0133	-2	3.7	23,705.6	4.18165	.00046
10-13-37	1092.517	15.0123	19.9903	.0	3.7	23,705.3	4.18159	.00040
10-14-37	1092.517	15.0064	20.0082	-1	3.7	23,704.5	4.18145	.00026
10-19-37	1093.647	15.0098	20.0137	.2	3.7	23,728.5	4.18151	.00032
10-21-37	1093.647	14.9970	19.9951	.0	3.7	23,729.6	4.18171	.00052
10-26-37	1093.647	15.0000	20.0426	.0	4.4	23,725.3	4.18093	-0.00026
10-27-37	1093.647	15.0024	19.9990	.1	3.7	23,730.5	4.18188	.00069
10-28-37	1093.647	14.9997	20.0012	.1	3.7	23,730.9	4.18195	.00076
11-16-37	1096.489	14.9993	20.0001	-1	3.7	23,784.3	4.18085	-0.00034
11-18-37	1096.489	15.0004	20.0018	.0	3.7	23,785.8	4.18113	-0.00006
12-3-37	1093.989	14.9891	19.9982	-2	3.7	23,732.0	4.18085	-0.00034
12-7-37	1093.989	15.0097	20.0096	.0	3.7	23,732.2	4.18088	-0.00031
12-9-37	603.781	15.1357	19.9751	-2	5.4	13,485.8	4.18125	.00006
12-10-37	603.781	15.0065	20.0009	.4	13.8	13,485.5	4.18115	-0.00004
12-14-37	603.781	15.0025	20.4957	.2	2.7	13,484.5	4.18082	-0.00037
Average							4.18130	

Even temperature interval 15° to 20° C. $\Delta Z/\Delta t=172.600$ int. j/°C. Formulated value of $\Delta\alpha/\Delta t=4.18119$ int. j/g-°C

9-16-37	1091.161	19.8801	24.9932	-0.2	3.7	23,657.6	4.17700	-0.00053
9-21-37	1091.161	20.0047	25.0045	-7	3.7	23,658.5	4.17716	-0.00037
9-23-37	1091.161	19.9959	24.9938	-3	3.7	23,659.5	4.17735	-0.00018
10-6-37	1092.517	20.0025	25.0089	.0	3.7	23,686.6	4.17712	-0.00041
10-8-37	1092.517	20.0133	25.0031	-1	3.7	23,689.1	4.17758	.00005
10-13-37	1092.517	19.9903	24.9999	.0	3.7	23,687.0	4.17734	-0.00033
10-14-37	1092.517	20.0082	25.0133	.0	3.7	23,687.8	4.17734	-0.00019
10-19-37	1093.647	20.0137	24.9982	.2	3.7	23,713.5	4.17720	-0.00020
10-21-37	1093.647	19.9951	24.9970	-1	3.7	23,710.6	4.17720	-0.00033
10-26-37	1093.647	20.0426	25.0031	.0	3.7	23,713.9	4.17780	.00027
10-27-37	1093.647	19.9990	25.0024	.1	3.7	23,713.6	4.17775	.00022
10-28-37	1093.647	20.0012	25.0023	.2	3.7	23,714.9	4.17798	.00045
11-16-37	1096.489	20.0001	25.0008	-1	3.7	23,768.8	4.17689	-0.00054
11-18-37	1096.489	20.0018	25.0001	.0	3.7	23,770.8	4.17735	-0.00018
12-3-37	1093.989	19.9982	25.0048	-1	3.7	23,716.6	4.17689	-0.00054
12-7-37	1093.989	20.0096	25.0079	.0	3.7	23,716.1	4.17690	-0.00063
12-9-37	603.781	19.9751	25.0376	-3	5.4	13,478.4	4.17691	-0.00062
12-10-37	603.781	20.0009	25.0050	.0	13.8	13,477.9	4.17675	-0.00078
Average							4.17728	

Even temperature interval 20° to 25° C. $\Delta Z/\Delta t=173.739$ int. j/°C. Formulated value of $\Delta\alpha/\Delta t=4.17753$ int. j/g-°C

TABLE 3.—Principal data from large-mass heat-capacity experiments—Continued

Date	Mass of water, M	Initial temperature	Final temperature	Heat leak	Pump energy	Energy for even temperature interval	$\Delta\alpha/\Delta t$	Deviation from formulation
	<i>g</i>	$^{\circ}\text{C}$	$^{\circ}\text{C}$	<i>Int. j</i>	<i>Int. j</i>	<i>Int. j</i>	<i>Int. j/g-°C</i>	<i>Int. j/g-°C</i>
9-16-37	1091.161	24.9932	29.9906	-0.1	3.7	23,655.1	4.17537	0.00024
9-21-37	1091.161	25.0045	29.9953	-9	3.7	23,655.3	4.17540	.00027
9-23-37	1091.161	24.9938	29.9913	-1	3.7	23,656.1	4.17554	.00041
10-6-37	1092.517	25.0089	29.9926	-1	3.7	23,683.9	4.17546	.00033
10-8-37	1092.517	25.0031	30.0106	-1	3.7	23,685.8	4.17581	.00068
10-13-37	1092.517	24.9999	30.0000	0	3.7	23,684.0	4.17548	.00035
10-14-37	1092.517	25.0133	30.0068	.1	3.7	23,683.4	4.17537	.00024
10-19-37	1093.647	24.9982	30.0054	0	3.7	23,706.9	4.17535	.00022
10-21-37	1093.647	24.9970	29.9945	.3	3.7	23,709.6	4.17584	.00071
10-26-37	1093.647	25.0031	29.9981	0	3.7	23,709.0	4.17573	.00060
10-27-37	1093.647	25.0024	30.0028	.2	3.7	23,710.0	4.17592	.00079
10-28-37	1093.647	25.0023	30.0017	-1	3.7	23,709.4	4.17581	.00068
11-16-37	1096.489	25.0008	30.0012	-1	3.7	23,764.4	4.17502	-.00011
11-18-37	1096.489	25.0001	30.0015	0	3.7	23,765.4	4.17519	.00006
11-19-37	1096.489	24.9997	30.0064	-1	3.1	23,764.6	4.17565	-.00008
12-3-37	1093.989	25.0048	30.0131	0	3.7	23,712.6	4.17509	-.00004
12-7-37	1093.989	25.0079	30.0051	-1	3.7	23,711.0	4.17480	-.00003
12-9-37	603.781	25.0376	29.9672	-1	5.4	13,479.1	4.17502	-.00011
12-10-37	603.781	25.0050	30.0028	.1	13.8	13,479.7	4.17522	-.00009
12-14-37	603.781	25.0430	30.0016	-.2	4.3	13,479.2	4.17506	-.00007
Average							4.17538	

Even temperature interval 25° to 30° C. $\Delta Z/\Delta t=175.025$ int. j/°C. Formulated value of $\Delta\alpha/\Delta t=4.17513$ int. j/g-°C

9-16-37	1091.161	29.9906	39.9768	-0.5	6.1	47,308.5	4.17313	0.00006
9-21-37	1091.161	29.9953	39.9841	-1.9	6.1	47,314.3	4.17366	.00059
9-23-37	1091.161	29.9913	39.9938	-0.2	6.1	47,309.7	4.17324	.00017
10-6-37	1092.517	29.9926	39.9994	0	6.1	47,365.0	4.17312	.00005
10-8-37	1092.517	30.0106	40.0110	-1	6.3	47,368.8	4.17347	.00040
10-13-37	1092.517	30.0000	39.9973	.1	6.1	47,366.4	4.17325	.00018
10-14-37	1092.517	30.0068	39.9938	.0	6.1	47,364.7	4.17310	.00003
10-19-37	1093.647	30.0054	40.0252	.4	6.1	47,413.2	4.17322	.00015
10-21-37	1093.647	29.9945	40.4984	.7	6.3	47,411.3	4.17305	-.00002
10-28-37	1093.647	30.0017	40.0038	.3	6.1	47,412.4	4.17315	.00008
11-16-37	1096.489	30.0012	40.0003	.0	6.1	47,525.0	4.17260	-.00047
11-18-37	1096.489	30.0015	40.0054	.1	6.1	47,529.0	4.17296	-.00011
11-19-37	1096.489	30.0059	40.0052	.5	6.1	47,526.2	4.17271	-.00036
12-3-37	1093.989	30.0131	40.0228	.0	6.1	47,422.7	4.17278	-.00029
12-7-37	1093.989	30.0051	40.0159	-.2	6.1	47,420.5	4.17258	-.00049
12-9-37	603.781	29.9672	40.0050	.1	8.9	26,967.2	4.17275	-.00032
12-10-37	603.781	30.0028	40.0067	.1	23.0	26,967.4	4.17279	-.00028
12-14-37	603.781	30.0016	40.0000	.0	4.3	26,967.6	4.17282	-.00025
Average							4.17302	

Even temperature interval 30° to 40° C. $\Delta Z/\Delta t=177.291$ int. j/°C. Formulated value of $\Delta\alpha/\Delta t=4.17307$ int. j/g-°C

9-16-37	1091.161	39.9768	49.9916	-0.3	6.1	47,330.3	4.17174	0.00000
9-21-37	1091.161	39.9841	49.9863	-2.4	6.1	47,325.2	4.17127	-.00047
9-23-37	1091.161	39.9938	49.9831	-0.4	6.3	47,331.9	4.17189	.00015
10-6-37	1092.517	39.9994	50.0157	-2	6.1	47,387.6	4.17181	.00007
10-8-37	1092.517	40.0110	50.0230	-1	6.1	47,390.1	4.17204	.00030
10-13-37	1092.517	39.9973	50.0000	.0	6.1	47,386.8	4.17173	-.00001
10-14-37	1092.517	39.9938	50.0149	-1	6.1	47,387.0	4.17175	.00001
10-19-37	1093.647	40.0252	49.9521	.3	6.1	47,433.4	4.17168	-.00006
10-21-37	1093.647	40.4984	49.9933	.5	5.9	47,435.8	4.17190	.00016
10-28-37	1093.647	40.0038	50.0085	.4	6.1	47,439.7	4.17226	.00002
11-16-37	1096.489	40.0003	50.0032	.0	6.1	47,548.0	4.17132	-.00042
11-18-37	1096.489	40.0054	49.9958	.0	6.1	47,551.4	4.17163	-.00011
11-19-37	1096.489	40.0052	50.0046	.3	6.1	47,549.8	4.17149	-.00025
11-20-37	1096.489	40.0003	50.0006	.4	6.1	47,549.7	4.17148	-.00026
12-3-37	1093.989	40.0228	50.0059	-.2	6.1	47,444.5	4.17139	-.00035
12-7-37	1093.989	40.0108	50.0111	-1	6.1	47,444.9	4.17143	-.00031
12-9-37	603.781	40.0050	49.9467	.1	8.9	26,997.3	4.17161	-.00013
12-10-37	603.781	40.0067	50.0083	-.1	23.0	26,996.2	4.17143	-.00031
12-14-37	603.781	40.0026	50.0011	-.2	7.0	26,997.2	4.17160	-.00014
Average							4.17165	

Even temperature interval 40° to 50° C. $\Delta Z/\Delta t=180.989$ int. j/°C. Formulated value of $\Delta\alpha/\Delta t=4.17174$ int. j/g-°C

TABLE 3.—Principal data from large-mass heat-capacity experiments—Continued

Date	Mass of water, <i>M</i>	Initial temperature	Final temperature	Heat leak	Pump energy	Energy for even temperature interval	$\Delta\alpha/\Delta t$	Deviation from formulation
	<i>q</i>	$^{\circ}\text{C}$	$^{\circ}\text{C}$	<i>Int. j</i>	<i>Int. j</i>	<i>Int. j</i>	<i>Int. j/q-°C</i>	<i>Int. j/q-°C</i>
9-16-37	1091.161	49.9916	59.9913	-0.1	6.1	47,375.0	4.17156	0.00032
9-21-37	1091.161	49.9863	59.9896	-1.9	6.1	47,374.8	4.17154	.00030
9-23-37	1091.161	49.9831	59.9923	-0.1	6.1	47,377.2	4.17176	.00052
10-6-37	1092.517	50.0157	60.0047	.0	6.1	47,432.1	4.17161	.00037
10-8-37	1092.517	50.0230	60.0065	-2.2	6.1	47,434.1	4.17179	.00055
10-14-37	1092.517	50.0149	59.9958	.0	6.1	47,430.2	4.17143	.00019
10-19-37	1093.647	49.9521	59.9329	.3	6.1	47,477.8	4.17147	.00023
10-21-37	1093.647	49.9933	59.9976	.7	6.1	47,477.7	4.17146	.00022
10-28-37	1093.647	50.0085	60.0019	.4	6.1	47,482.4	4.17189	.00065
11-16-37	1096.489	50.0032	60.0024	.0	6.1	47,590.1	4.17090	-.00034
11-18-37	1096.489	49.9958	60.0050	-1.1	6.1	47,594.8	4.17133	.00009
11-19-37	1096.489	50.0046	60.0081	.2	6.1	47,592.3	4.17110	-.00014
11-20-37	1096.489	50.0006	60.0114	.4	6.1	47,590.7	4.17096	-.00028
12-4-37	1093.989	50.0006	60.0322	.1	6.1	47,485.3	4.17086	-.00038
12-7-37	1093.989	50.0143	60.0080	-1.1	6.1	47,487.5	4.17106	-.00018
12-9-37	603.781	49.9513	59.9329	-2.2	8.9	27,040.3	4.17100	-.00024
12-10-37	603.781	50.0083	59.9993	.2	23.0	27,038.1	4.17063	-.00061
12-14-37	603.781	50.0009	59.9980	-5.5	5.0	27,042.4	4.17135	.00011
Average							4.17132	

Even temperature interval 50° to 60° C. $\Delta Z/\Delta t=185.663$ int. j/°C. Formulated value of $\Delta\alpha/\Delta t=4.17124$ int. j/g-°C

9-16-37	1091.161	59.9913	69.9814	0.2	6.1	47,429.1	4.17114	0.00003
9-21-37	1091.161	59.9896	70.9984	-2.1	6.8	47,431.6	4.17137	.00026
9-23-37	1091.161	59.9923	69.9831	0.1	6.1	47,432.4	4.17145	.00034
10-6-37	1092.517	60.0047	70.0140	-2.2	6.1	47,488.7	4.17142	.00031
10-8-37	1092.517	60.0065	70.0097	.0	6.1	47,491.3	4.17166	.00055
10-19-37	1093.647	59.9329	70.0336	.0	6.1	47,533.0	4.17116	.00005
10-21-37	1093.647	59.9976	69.9959	.3	6.1	47,535.5	4.17139	.00028
10-28-37	1093.647	60.0019	70.0089	-1.1	6.1	47,538.1	4.17163	.00052
11-16-37	1096.489	60.0024	70.0021	.0	6.1	47,648.1	4.17085	-.00026
11-18-37	1096.489	60.0050	70.0038	-2.2	6.1	47,654.0	4.17139	.00028
11-19-37	1096.489	60.0081	70.0056	.0	6.1	47,656.3	4.17160	.00049
11-20-37	1096.489	60.0114	70.0042	.4	6.1	47,649.5	4.17098	-.00013
12-3-37	1093.989	60.0104	70.0119	.0	6.1	47,547.4	4.17118	.00007
12-4-37	1093.989	60.0320	70.0076	.0	6.1	47,544.7	4.17093	-.00018
12-7-37	1093.989	60.0079	70.0183	.1	6.1	47,551.1	4.17151	.00040
12-9-37	603.781	59.9329	69.9511	-3.3	8.9	27,098.0	4.17085	-.00026
12-10-37	603.781	59.9993	69.9990	.3	23.0	27,095.9	4.17050	-.00061
Average							4.17124	

Even temperature interval 60° to 70° C. $\Delta Z/\Delta t=191.520$ int. j/°C. Formulated value of $\Delta\alpha/\Delta t=4.17111$ int. j/g-°C

9-16-37	1091.161	69.9814	79.9916	0.0	6.1	47,504.6	4.17140	0.00026
9-21-37	1091.161	71.0327	80.0364	-4.4	6.1	47,493.5	4.17038	-.00076
9-23-37	1091.161	69.9831	80.0028	.1	6.6	47,500.3	4.17101	-.00013
10-8-37	1092.517	70.0097	80.0089	.1	6.1	47,564.2	4.17168	.00054
10-19-37	1093.647	70.0336	80.0126	.2	6.1	47,607.4	4.17132	.00018
10-21-37	1093.647	69.9959	80.0016	.2	6.1	47,607.1	4.17129	.00015
11-16-37	1096.489	70.0021	80.0031	.0	6.1	47,721.0	4.17087	-.00027
11-18-37	1096.489	70.0038	80.0038	-1.1	6.1	47,726.5	4.17137	.00023
11-19-37	1096.489	70.0056	80.0038	.0	6.1	47,721.2	4.17086	-.00028
11-20-37	1096.489	70.0042	79.9993	.2	6.1	47,722.4	4.17099	-.00015
12-3-37	1093.989	70.0119	80.0090	-2.2	6.1	47,621.7	4.17132	.00018
12-4-37	1093.989	70.0076	80.0145	.0	6.1	47,615.5	4.17075	-.00039
12-7-37	1093.989	70.0183	80.0040	-1.1	6.1	47,616.1	4.17081	-.00033
12-9-37	603.781	69.9511	79.9741	-4.4	8.9	27,172.5	4.17114	.00000
12-10-37	603.781	69.9990	80.0085	.3	23.0	27,168.9	4.17054	-.00060
Average							4.17105	

Even temperature interval 70° to 80° C. $\Delta Z/\Delta t=198.795$ int. j/°C. Formulated value of $\Delta\alpha/\Delta t=4.17114$ int. j/g-°C

TABLE 3.—*Principal data from large-mass heat-capacity experiments—Continued*

Date	Mass of water, <i>M</i>	Initial temperature	Final temperature	Heat leak	Pump energy	Energy for even temperature interval	$\Delta\alpha/\Delta t$	Deviation from formulation
	<i>g</i>	°C	°C	<i>Int. j</i>	<i>Int. j</i>	<i>Int. j</i>	<i>Int. j/q</i> °C	<i>Int. j/q</i> °C
9-16-37	1091.161	79.9916	89.9950	0.0	6.1	47,597.1	4.17167	0.00043
9-21-37	1091.161	80.0364	89.9882	-.5	6.1	47,592.5	4.17125	-.00001
9-23-37	1091.161	80.0028	89.9957	-.4	6.3	47,592.2	4.17123	-.00001
10-19-37	1093.647	80.0126	90.0150	.2	6.1	47,696.4	4.17127	.00003
10-21-37	1093.647	80.0016	89.9994	.0	6.1	47,698.2	4.17144	.00020
10-28-37	1093.647	79.9989	89.9751	.4	6.1	47,703.6	4.17193	.00069
11-16-37	1096.489	80.0031	90.0029	.0	6.1	47,809.8	4.17080	-.00044
11-18-37	1096.489	80.0038	90.0003	-.3	6.1	47,815.6	4.17133	-.00009
11-19-37	1096.489	80.0041	90.0068	-.1	6.1	47,811.9	4.17099	-.00025
11-20-37	1096.489	79.9993	90.0060	.0	6.1	47,812.9	4.17109	-.00015
12-3-37	1093.989	80.0090	90.0074	.1	6.1	47,710.4	4.17125	-.00001
12-4-37	1093.989	80.0145	90.0123	.1	6.1	47,708.6	4.17108	-.00016
12-7-37	1093.989	80.0040	90.0032	-.1	6.1	47,711.2	4.17132	-.00008
12-9-37	603.781	79.9741	90.0319	-.4	8.9	27,263.1	4.17133	-.00009
12-10-37	603.781	80.0085	90.0092	-.1	23.0	27,263.7	4.17143	-.00019
Average							4.17129	

Even temperature interval 80° to 90° C. $\Delta Z/\Delta t=207.738$ int. j/°C. Formulated value of $\Delta\alpha/\Delta t=4.17124$ int. j/g°C

9-16-37	1091.161	89.9950	99.9843	-0.4	6.1	47,704.3	4.17152	0.00015
9-21-37	1091.161	89.9882	99.9992	.2	6.3	47,693.1	4.17049	-.00088
9-23-37	1091.161	89.9957	99.9887	-.4	6.1	47,696.9	4.17084	-.00053
10-19-37	1093.647	90.0150	100.0086	-.4	6.2	47,806.1	4.17135	-.00002
10-21-37	1093.647	89.9994	100.0027	.1	6.1	47,807.6	4.17148	-.00011
11-16-37	1096.489	90.0029	100.0024	-.2	6.1	47,920.8	4.17099	-.00038
11-18-37	1096.489	90.0003	100.0037	-.3	6.1	47,927.2	4.17158	-.00021
11-19-37	1096.489	90.0068	99.9942	.0	6.1	47,925.5	4.17142	-.00005
11-20-37	1096.489	90.0060	100.0045	-.3	6.1	47,921.9	4.17110	-.00027
12-3-37	1093.989	90.0074	100.0098	-.3	6.1	47,820.7	4.17138	-.00001
12-4-37	1093.989	90.0123	100.0076	-.2	6.1	47,828.1	4.17205	-.00068
12-9-37	603.781	90.0319	100.0076	-.3	8.9	27,371.6	4.17126	-.00011
12-10-37	603.781	90.0248	100.0075	.1	23.0	27,369.9	4.17098	-.00039
Average							4.17126	

Even temperature interval 90° to 100° C. $\Delta Z/\Delta t=218.626$ int. j/°C. Formulated value of $\Delta\alpha/\Delta t=4.17137$ int. j/g°C

TABLE 4.—*Principal data from small-mass heat-capacity experiments*

Date	Mass of water, <i>M</i>	Initial temperature	Final temperature	Heat leak	Pump energy	Energy for even temperature interval	$\Delta Z/\Delta t$
	<i>g</i>	°C	°C	<i>Int. j</i>	<i>Int. j</i>	<i>Int. j</i>	<i>Int. j/°C</i>
11-5-37	126.708	-0.0646	2.5102	-0.1	2.3	1,758.0	169.49
11-6-37	126.708	-.0401	2.5830	-.3	1.9	1,758.4	169.65
11-11-37	126.713	.0309	2.5359	-.1	1.9	1,758.5	169.67
11-12-37	126.713	.0045	2.5027	-.2	1.9	1,758.3	169.59
11-23-37	126.842	.0321	2.6038	-.5	3.7	1,760.5	169.93
11-24-37	126.842	-.0182	2.5545	.8	5.4	1,759.8	169.65
11-30-37	126.842	.0069	2.5444	.2	3.5	1,758.8	169.25
11-30-37	126.842	.0896	2.3173	.6	2.5	1,760.3	169.85
Average							169.64

Even temperature interval 0.0° to 2.5° C. $\Delta\alpha/\Delta t=4.21210$ int. j/g°C
Formulated value of $\Delta Z/\Delta t=169.69$ int. j/°C

11-5-37	126.708	2.5111	5.0085	0.0	1.9	1,756.2	169.77
11-6-37	126.708	2.5430	5.0009	-.2	1.9	1,757.3	170.21
11-11-37	126.713	2.5368	4.9962	-.2	1.9	1,757.1	170.11
11-12-37	126.713	2.5030	4.9980	-.2	1.9	1,756.8	169.99
11-23-37	126.842	2.6240	4.9988	.6	3.7	1,758.7	170.21
11-24-37	126.842	2.5754	5.0040	.5	2.5	1,757.4	169.69
11-30-37	126.842	2.3173	5.0053	-.2	2.5	1,758.3	170.05
Average							170.00

Even temperature interval 2.5° to 5.0° C. $\Delta\alpha/\Delta t=4.20424$ int. j/g°C
Formulated value of $\Delta Z/\Delta t=170.07$ int. j/°C

TABLE 4.—Principal data from small-mass heat-capacity experiments—Continued

Date	Mass of water, <i>M</i>	Initial temperature	Final temperature	Heat leak	Pump energy	Energy for even temperature interval	$\Delta Z/\Delta t$
	<i>g</i>	$^{\circ}\text{C}$	$^{\circ}\text{C}$	<i>Int. j</i>	<i>Int. j</i>	<i>Int. j</i>	<i>Int. j/°C</i>
9-27-37	127.140	5.0941	9.5974	-0.3	5.0	3,519.3	170.47
9-28-37	127.140	5.0468	10.0059	.1	4.2	3,520.3	170.67
9-29-37	127.140	5.0469	10.0019	-2	4.2	3,520.6	170.73
9-30-37	127.140	4.9889	10.0055	.0	4.2	3,520.0	170.61
10-1-37	127.140	5.0698	9.9952	-2	4.2	3,519.3	170.47
11-5-37	126.708	5.0086	10.0132	-2	2.9	3,510.6	170.55
11-6-37	126.708	5.0013	9.9995	-3	2.9	3,511.9	170.81
11-11-37	126.713	4.9966	10.0060	-5	2.9	3,511.4	170.68
11-12-37	126.713	4.9985	10.0012	-4	2.9	3,511.3	170.66
11-24-37	126.842	5.0065	10.0022	.4	3.8	3,513.0	170.46
11-30-37	126.842	5.0053	10.0091	-2	3.8	3,514.1	170.68
Average							170.61

Even temperature interval 5° to 10° C. $\Delta\alpha/\Delta t=4.19527$ int. j/g-°C
Formulated value of $\Delta Z/\Delta t=170.69$ int. j/°C

9-27-37	127.140	9.5974	15.0994	-0.3	4.5	3,520.3	171.75
9-28-37	127.140	10.0059	15.0066	-3	4.2	3,519.0	171.49
9-29-37	127.140	10.0019	15.0031	-1	4.2	3,519.1	171.51
9-30-37	127.140	10.0055	15.0155	-4	4.2	3,518.9	171.47
10-1-37	127.140	9.9952	15.1422	.1	4.2	3,518.4	171.57
11-5-37	126.708	10.0132	15.0025	-2	2.9	3,510.0	171.50
11-6-37	126.708	9.9995	15.0001	-3	2.9	3,511.1	171.72
11-11-37	126.713	10.0131	14.9993	-4	2.9	3,510.9	171.66
11-12-37	126.713	10.0012	15.0015	-2	2.9	3,510.5	171.58
11-24-37	126.842	10.0022	15.0063	-3	3.9	3,512.1	171.56
11-30-37	126.842	10.0091	15.0004	-2	3.8	3,513.1	171.56
Average							171.54

Even temperature interval 10° to 15° C. $\Delta\alpha/\Delta t=4.18678$ int. j/g-°C
Formulated value of $\Delta Z/\Delta t=171.59$ int. j/°C

9-27-37	127.140	15.0994	20.0230	-0.4	4.3	3,521.2	172.64
9-28-37	127.140	15.0066	19.9974	-3	4.3	3,520.6	172.52
9-29-37	127.140	15.0031	20.0028	-2	4.3	3,521.0	172.60
9-30-37	127.140	15.0155	19.9961	-3	4.3	3,520.7	172.54
10-1-37	127.140	15.1422	20.0015	-1	4.2	3,519.3	172.26
11-5-37	126.708	15.0025	20.0054	-3	3.0	3,512.0	172.61
11-6-37	126.708	15.0001	20.0011	-3	3.0	3,512.7	172.75
11-11-37	126.713	14.9993	20.0015	-4	3.0	3,512.7	172.73
11-12-37	126.713	15.0015	20.0013	-2	3.0	3,512.4	172.67
11-24-37	126.842	15.0063	20.0075	-1	3.8	3,514.1	172.47
11-30-37	126.842	15.0004	19.9991	-3	3.8	3,514.4	172.53
Average							172.57

Even temperature interval 15° to 20° C. $\Delta\alpha/\Delta t=4.18119$ int. j/g-°C
Formulated value of $\Delta Z/\Delta t=172.60$ int. j/°C

9-27-37	127.140	20.0230	24.9939	-0.2	4.6	3,524.2	173.71
9-28-37	127.140	19.9974	24.9946	-3	4.3	3,523.7	173.61
9-29-37	127.140	20.0028	24.9979	-4	4.3	3,524.3	173.73
9-30-37	127.140	19.9961	24.9962	-2	4.3	3,524.0	173.67
10-1-37	127.140	20.0015	25.0055	-4	4.3	3,522.8	173.43
11-5-37	126.708	20.0054	25.0067	-3	3.0	3,514.9	173.65
11-6-37	126.708	20.0011	24.9988	-3	3.0	3,515.6	173.79
11-11-37	126.713	20.0015	24.9971	-3	3.0	3,515.8	173.81
11-12-37	126.713	20.0013	24.9966	-2	3.0	3,515.4	173.73
11-24-37	126.842	20.0075	25.0031	-2	3.9	3,517.2	173.55
11-30-37	126.842	19.9991	24.9978	-4	3.9	3,517.4	173.59
Average							173.66

Even temperature interval 20° to 25° C. $\Delta\alpha/\Delta t=4.17753$ int. j/g-°C
Formulated value of $\Delta Z/\Delta t=173.74$ int. j/°C

TABLE 4.—Principal data from small-mass heat-capacity experiments—Continued

Date	Mass of water, <i>M</i>	Initial temperature	Final temperature	Heat leak	Pump energy	Energy for even temperature interval	$\Delta Z/\Delta t$
	<i>g</i>	$^{\circ}\text{C}$	$^{\circ}\text{C}$	<i>Int. j</i>	<i>Int. j</i>	<i>Int. j</i>	<i>Int. j/°C</i>
9-27-37	127.140	24.9939	29.9932	-0.2	4.3	3,530.2	175.21
9-28-37	127.140	24.9946	29.9991	-1	4.3	3,529.3	175.03
9-29-37	127.140	24.9979	29.9949	-3	4.3	3,529.2	175.01
9-30-37	127.140	24.9962	29.9948	-2	4.3	3,529.8	175.13
10-1-37	127.140	25.0058	30.0080	-4	4.3	3,528.9	174.95
11-5-37	126.708	25.0067	30.0113	-2	3.0	3,520.1	175.00
11-6-37	126.708	24.9988	29.9981	-2	3.0	3,520.5	175.08
11-11-37	126.713	24.9971	29.9968	-2	3.0	3,521.0	175.16
11-12-37	126.713	24.9966	29.9974	-2	3.0	3,520.4	175.04
11-24-37	126.842	25.0031	30.0057	-2	3.9	3,522.4	174.90
11-29-37	126.842	25.0033	29.9767	-3	4.2	3,523.0	175.02
Average							175.05
Even temperature interval 25° to 30° C. $\Delta\alpha/\Delta t=4.17513$ int. j/g·°C Formulated value of $\Delta Z/\Delta t=175.02$ int. j/°C							
9-27-37	127.140	29.9932	39.9929	-0.5	7.3	7,078.8	177.32
9-28-37	127.140	29.9991	39.9917	-1	7.3	7,078.1	177.25
9-29-37	127.140	29.9949	39.9848	-4	7.3	7,079.1	177.35
9-30-37	127.140	29.9948	39.9923	-6	7.3	7,078.4	177.27
10-1-37	127.140	30.0080	39.9991	-9	7.3	7,078.1	177.25
11-5-37	126.708	30.0117	40.0274	-2	5.2	7,059.9	177.23
11-8-37	126.708	29.9930	39.9952	-1	5.2	7,059.2	177.16
11-11-37	126.713	29.9968	39.9884	-5	5.2	7,061.5	177.37
11-12-37	126.713	29.9974	39.9950	-3	5.2	7,059.7	177.19
11-24-37	126.842	30.0057	40.0131	-3	6.6	7,064.5	177.13
11-29-37	126.842	29.9797	40.0490	-7	6.6	7,065.1	177.19
Average							177.25
Even temperature interval 30° to 40° C. $\Delta\alpha/\Delta t=4.17307$ int. j/g·°C Formulated value of $\Delta Z/\Delta t=177.29$ int. j/°C							
9-27-37	127.140	39.9929	49.9881	-0.6	7.5	7,115.4	181.14
9-28-37	127.140	39.9917	50.0028	-5	7.5	7,113.2	180.92
9-29-37	127.140	39.9848	50.0068	-5	7.5	7,114.9	181.09
9-30-37	127.140	39.9923	50.0015	-6	7.5	7,113.3	180.93
10-1-37	127.140	39.9991	50.0037	-7	7.5	7,114.2	181.02
11-5-37	126.708	40.0274	50.0222	-3	5.3	7,095.7	180.98
11-8-37	126.708	39.9952	49.9983	-2	5.3	7,095.1	180.92
11-11-37	126.713	39.9967	49.9975	-3	5.3	7,095.5	180.94
11-12-37	126.713	40.0046	50.0032	-4	5.3	7,094.4	180.83
11-24-37	126.842	40.0231	50.0078	-3	6.7	7,099.9	180.84
11-29-37	126.842	40.0490	50.0050	-4	6.7	7,100.5	180.90
Average							180.96
Even temperature interval 40° to 50° C. $\Delta\alpha/\Delta t=4.17174$ int. j/g·°C Formulated value of $\Delta Z/\Delta t=180.99$ int. j/°C							
9-27-37	127.140	49.9881	59.9833	-0.7	7.6	7,160.4	185.71
9-28-37	127.140	50.0028	59.9990	-8	7.6	7,159.4	185.61
9-29-37	127.140	50.0068	59.9980	-3	7.6	7,159.9	185.66
9-30-37	127.140	50.0015	60.0036	-1	7.6	7,159.9	185.66
10-1-37	127.140	50.0037	60.0053	-7	7.6	7,160.1	185.68
11-5-37	126.708	50.0222	60.0165	-2	5.4	7,142.6	185.73
11-8-37	126.708	49.9983	59.9981	-5	5.4	7,141.6	185.63
11-11-37	126.713	49.9975	59.9969	-6	5.4	7,142.2	185.67
11-12-37	126.713	50.0032	59.9945	-1	5.4	7,141.1	185.56
11-24-37	126.842	50.0225	60.0085	-2	6.9	7,145.8	185.49
11-29-37	126.842	50.0050	60.0022	-3	6.8	7,146.1	185.52
Average							185.63
Even temperature interval 50° to 60° C. $\Delta\alpha/\Delta t=4.17124$ int. j/g·°C Formulated value of $\Delta Z/\Delta t=185.66$ int. j/°C							

TABLE 4.—Principal data for small-mass heat-capacity experiments—Continued

Date	Mass of water, <i>M</i>	Initial temperature	Final temperature	Heat leak	Pump energy	Energy for even temperature interval	$\Delta Z/\Delta t$
	<i>g</i>	$^{\circ}C$	$^{\circ}C$	<i>Int. j</i>	<i>Int. j</i>	<i>Int. j</i>	<i>Int. j/°C</i>
9-27-37	127.140	59.9833	69.9959	-1.1	7.7	7,219.3	191.61
9-28-37	127.140	59.9990	69.9834	-1.0	7.7	7,218.1	191.49
9-29-37	127.140	59.9980	69.9870	-0.2	7.7	7,217.9	191.47
9-30-37	127.140	60.0036	70.0132	-0.2	8.0	7,217.0	191.88
10-1-37	127.140	60.0053	69.9886	-1.1	7.7	7,218.7	191.55
11-5-37	126.708	60.0165	70.0135	-0.3	5.6	7,200.8	191.57
11-8-37	126.708	59.9973	70.0845	-3	5.6	7,199.2	191.41
11-12-37	126.713	59.9945	69.9967	-4	5.6	7,200.0	191.47
11-24-37	126.842	60.0085	69.9908	-4	7.0	7,204.5	191.88
11-29-37	126.842	60.0022	69.9523	-4	7.0	7,204.8	191.41
Average							191.47
Even temperature interval 60° to 70° C. $\Delta\alpha/\Delta t=4.17111$ int. j/g-°C Formulated value at $\Delta Z/\Delta t=191.52$ int. j/°C							
9-27-37	127.140	69.9959	79.9973	-1.2	7.8	7,292.0	198.88
9-28-37	127.140	69.9834	80.0011	-5	7.8	7,291.1	198.79
9-29-37	127.140	69.9870	80.0073	-3	7.8	7,290.8	198.76
9-30-37	127.140	70.0132	80.0058	-2	8.8	7,289.9	198.67
10-1-37	127.140	69.9886	80.0043	-6	7.8	7,291.5	198.83
11-5-37	126.708	70.0135	80.0056	-1	5.7	7,273.6	198.84
11-8-37	126.708	70.0845	79.9952	-4	5.7	7,272.8	198.76
11-29-37	126.842	69.9523	79.9922	-3	7.1	7,277.7	198.69
Average							198.78
Even temperature interval 70° to 80° C. $\Delta\alpha/\Delta t=4.17114$ int. j/g-°C Formulated value of $\Delta Z/\Delta t=198.79$ int. j/°C							
9-27-37	127.140	79.9973	89.9929	-0.5	8.0	7,381.9	207.86
9-28-37	127.140	80.0011	90.0146	-2	8.6	7,379.7	207.64
9-29-37	127.140	80.0073	90.0104	-5	8.0	7,381.1	207.78
9-30-37	127.140	80.0058	90.0117	-8	8.3	7,379.7	207.64
10-1-37	127.140	80.0043	89.9998	-6	8.0	7,381.5	207.82
11-5-37	126.708	80.0056	89.9972	-3	5.8	7,363.4	207.81
11-8-37	126.708	79.9952	90.0004	-7	5.8	7,363.2	207.79
11-29-37	126.842	79.9922	90.0033	-3	7.2	7,367.7	207.68
Average							207.75
Even temperature interval 80° to 90° C. $\Delta\alpha/\Delta t=4.17124$ int. j/g-°C Formulated value of $\Delta Z/\Delta t=207.74$ int. j/°C							
9-27-37	127.140	89.9929	99.9985	-0.7	8.1	7,489.8	218.63
9-28-37	127.140	90.0146	100.0007	-2	8.7	7,488.9	218.54
9-29-37	127.140	90.0104	99.9982	-1	8.7	7,489.5	218.60
9-30-37	127.140	90.0117	99.9985	-4	8.4	7,488.2	218.47
10-1-37	127.140	89.9998	99.9970	-6	8.1	7,489.9	218.64
11-5-37	126.708	89.9972	99.9959	-6	5.9	7,471.8	218.63
11-8-37	126.708	90.0004	100.0010	-9	6.7	7,472.6	218.71
11-29-37	126.842	90.0170	100.0005	-4	7.3	7,476.0	218.50
Average							218.59
Even temperature interval 90° to 100° C. $\Delta\alpha/\Delta t=4.17137$ int. j/g-°C Formulated value of $\Delta Z/\Delta t=218.61$ int. j/°C							

TABLE 5.—Calculation of specific heat at 1-atmosphere pressure

Temperature interval	$\Delta\alpha/\Delta t$, measured	Reductions to give C_p at 1 atmosphere			C_p , experimental	C_p , formulated	Deviation exp.—form.	Mid-temperature of interval
		$\frac{\Delta H}{\Delta t} - \frac{\Delta\alpha}{\Delta t}$	$\left(\frac{\Delta H}{\Delta t}\right)_{p=1} - \left(\frac{\Delta H}{\Delta t}\right)_{sat}$	$C_{p=1} - \left(\frac{\Delta H}{\Delta t}\right)_{p=1}$				
1	2	3	4	5	6	7	8	9
°C	Int. j/g-°C	Int. j/g-°C	Int. j/g-°C	Int. j/g-°C	Int. j/g-°C	Int. j/g-°C	Int. j/g-°C	°C
0 to 1	4.21411	0.00085	-0.00054	-0.00001	4.21441	4.21508	-0.00067	0.5
0 to 2.5	4.21267	.00089	-0.00052	-0.00008	4.21296	4.21242	.00054	1.25
1 to 2	4.21087	.00090	-0.00051	-0.00001	4.21125	4.21158	-.00033	1.5
0 to 5	4.20811	.00096	-0.00051	-0.00027	4.20829	4.20837	-0.00008	2.5
2 to 3	4.20764	.00096	-0.00051	-0.00001	4.20808	4.20837	-0.00029	2.5
3 to 4	4.20533	.00101	-0.00050	-0.00001	4.20583	4.20542	.00041	3.5
2.5 to 5.0	4.20385	.00103	-0.00050	-0.00006	4.20432	4.20472	-0.00040	3.75
4 to 5	4.20219	.00107	-0.00050	-0.00001	4.20275	4.20272	.00003	4.5
5 to 10	4.19530	.00127	-0.00047	-0.00018	4.19592	4.19588	.00004	7.5
10 to 15	4.18668	.00167	-0.00045	-0.00012	4.18778	4.18784	-0.00006	12.5
15 to 20	4.18130	.00217	-0.00045	-0.00008	4.18294	4.18280	.00014	17.5
20 to 25	4.17728	.00279	-0.00045	-0.00006	4.17956	4.17977	-0.00021	22.5
25 to 30	4.17538	.00354	-0.00047	-0.00004	4.17840	4.17814	.00026	27.5
30 to 40	4.17302	.00500	-0.00053	-0.00010	4.17739	4.17744	-0.00005	35
40 to 50	4.17165	.00761	-0.00065	-0.00007	4.17854	4.17866	-0.00012	45
50 to 60	4.17132	.01122	-0.00084	-0.00006	4.18164	4.18161	.00003	55
60 to 70	4.17124	.01606	-0.00110	-0.00006	4.18614	4.18604	.00010	65
70 to 80	4.17105	.02239	-0.00144	-0.00007	4.19193	4.19200	-0.00007	75
80 to 90	4.17129	.03049	-0.00188	-0.00008	4.19982	4.19972	.00010	85
90 to 100	4.17126	.04063	-0.00241	-0.00010	4.20939	4.20947	-0.00008	95

TABLE 6.—Heat capacity of air-free water at 1 atmosphere pressure

Temperature °C	C_p		Enthalpy, H_p		Temperature °C	C_p		Enthalpy, H_p	
	Abs. $J/g\text{-}^\circ C$		Abs. J/g	IT Cal/g		Abs. $J/g\text{-}^\circ C$		Abs. J/g	IT Cal/g
0	4.2177		0.1026	0.0245	50	4.1807	209.3729	50.0079	
1	4.2141		4.3184	1.0314	51	4.1810	213.5538	51.0065	
2	4.2107		8.5308	2.0376	52	4.1814	217.7350	52.0051	
3	4.2077		12.7400	3.0429	53	4.1817	221.9166	53.0039	
4	4.2048		16.9462	4.0475	54	4.1820	226.0984	54.0027	
5	4.2022		21.1498	5.0515	55	4.1824	230.2806	55.0016	
6	4.1999		25.3508	6.0549	56	4.1828	234.4632	56.0006	
7	4.1977		29.5496	7.0578	57	4.1832	238.6462	56.9997	
8	4.1957		33.7463	8.0602	58	4.1836	242.8296	57.9989	
9	4.1939		37.9410	9.0621	59	4.1840	247.0134	58.9982	
10	4.1922		42.1341	10.0636	60	4.1844	251.1976	59.9975	
11	4.1907		46.3255	11.0647	61	4.1849	255.3822	60.9970	
12	4.1893		50.5155	12.0654	62	4.1853	259.5673	61.9966	
13	4.1880		54.7041	13.0659	63	4.1858	263.7529	62.9963	
14	4.1869		58.8916	14.0660	64	4.1863	267.9390	63.9962	
15	4.1858		63.0779	15.0659	65	4.1868	272.1256	64.9961	
16	4.1849		67.2632	16.0655	66	4.1874	276.3127	65.9962	
17	4.1840		71.4476	17.0650	67	4.1879	280.5003	66.9964	
18	4.1832		75.6312	18.0642	68	4.1885	284.6885	67.9967	
19	4.1825		79.8141	19.0633	69	4.1890	288.8772	68.9972	
20	4.1819		83.9963	20.0622	70	4.1896	293.0665	69.9977	
21	4.1813		88.1778	21.0609	71	4.1902	297.2564	70.9985	
22	4.1808		92.3589	22.0596	72	4.1908	301.4469	71.9994	
23	4.1804		96.5395	23.0581	73	4.1915	305.6381	73.0004	
24	4.1800		100.7196	24.0565	74	4.1921	309.8299	74.0016	
25	4.1796		104.8994	25.0548	75	4.1928	314.0224	75.0030	
26	4.1793		109.0788	26.0530	76	4.1935	318.2155	76.0045	
27	4.1790		113.2580	27.0512	77	4.1942	322.4094	77.0062	
28	4.1788		117.4369	28.0493	78	4.1949	326.6039	78.0080	
29	4.1786		121.6157	29.0474	79	4.1957	330.7992	79.0101	
30	4.1785		125.7943	30.0455	80	4.1964	334.9952	80.0123	
31	4.1784		129.9727	31.0435	81	4.1972	339.1920	81.0147	
32	4.1783		134.1510	32.0414	82	4.1980	343.3897	82.0172	
33	4.1783		138.3293	33.0394	83	4.1988	347.5881	83.0200	
34	4.1782		142.5076	34.0374	84	4.1997	351.7873	84.0230	
35	4.1782		146.6858	35.0353	85	4.2005	355.9874	85.0262	
36	4.1783		150.8641	36.0333	86	4.2014	360.1883	86.0295	
37	4.1783		155.0423	37.0312	87	4.2023	364.3902	87.0331	
38	4.1784		159.2207	38.0292	88	4.2032	368.5929	88.0369	
39	4.1785		163.3991	39.0272	89	4.2042	372.7966	89.0410	
40	4.1786		167.5777	40.0253	90	4.2051	377.0012	90.0452	
41	4.1787		171.7563	41.0233	91	4.2061	381.2068	91.0497	
42	4.1789		175.9351	42.0214	92	4.2071	385.4135	92.0545	
43	4.1791		180.1141	43.0195	93	4.2081	389.6211	93.0594	
44	4.1792		184.2933	44.0177	94	4.2092	393.8297	94.0647	
45	4.1795		188.4726	45.0159	95	4.2103	398.0395	95.0701	
46	4.1797		192.6522	46.0142	96	4.2114	402.2503	96.0759	
47	4.1799		196.8320	47.0125	97	4.2125	406.4622	97.0819	
48	4.1802		201.0120	48.0109	98	4.2136	410.6753	98.0882	
49	4.1804		205.1923	49.0094	99	4.2148	414.8895	99.0947	
					100	4.2160	419.1049	100.1015	

TABLE 7.—*Enthalpy of saturated liquid water*

Temperature °C	α 's		β			Enthalpy	
	<i>Int. j/g</i>	<i>Int. j/g</i>	<i>Int. j/g</i>	<i>Abs. j/g</i>	<i>IT Cal/g</i>		
0	0. 0000	0. 0121	0. 0000	0. 0000	0. 0000	0. 0000	0. 0000
5	21. 0408	. 0169	21. 0456	21. 0496	21. 0496	5. 0276	5. 0276
10	42. 0172	. 0233	42. 0283	42. 0363	42. 0363	10. 0402	10. 0402
15	62. 9511	. 0316	62. 9706	62. 9826	62. 9826	15. 0431	15. 0431
20	83. 8571	. 0425	83. 8875	83. 9034	83. 9034	20. 0400	20. 0400
25	104. 7447	. 0564	104. 7890	104. 8089	104. 8089	25. 0332	25. 0332
30	125. 6204	. 0741	125. 6824	125. 7063	125. 7063	30. 0244	30. 0244
35	146. 4883	. 0963	146. 5725	146. 6003	146. 6003	35. 0149	35. 0149
40	167. 3511	. 1241	167. 4631	167. 4949	167. 4949	40. 0055	40. 0055
45	188. 2108	. 1583	188. 3570	188. 3928	188. 3928	44. 9968	44. 9968
50	209. 0685	. 2002	209. 2566	209. 2964	209. 2964	49. 9896	49. 9896
55	229. 9251	. 2510	230. 1640	230. 2077	230. 2077	54. 9842	54. 9842
60	250. 7810	. 3123	251. 0812	251. 1289	251. 1289	59. 9811	59. 9811
65	271. 6366	. 3858	272. 0102	272. 0619	272. 0619	64. 9808	64. 9808
70	292. 4921	. 4730	292. 9530	293. 0087	293. 0087	69. 9839	69. 9839
75	313. 3477	. 5760	313. 9116	313. 9712	313. 9712	74. 9907	74. 9907
80	334. 2035	. 6970	334. 8883	334. 9519	334. 9519	80. 0019	80. 0019
85	355. 0596	. 8381	355. 8856	355. 9532	355. 9532	85. 0180	85. 0180
90	375. 9159	1. 0019	376. 9057	376. 9773	376. 9773	90. 0395	90. 0395
95	396. 7726	1. 1909	397. 9514	398. 0270	398. 0270	95. 0671	95. 0671
100	417. 6296	1. 4082	419. 0257	419. 1053	419. 1053	100. 1016	100. 1016

V. REVIEW OF EARLIER WORK AND COMPARISONS

It is of interest to present a résumé of comparisons between the present results and the earlier results, but unfortunately, it seems impossible to make all such comparisons on the basis of definite evaluation. As mentioned above, so many uncertain factors regarding units, standards, and experimental technique have been involved in some of the earlier work that the results of much of the pioneer research is difficult to interpret and appraise in terms of present standards. In spite of the care with which these various determinations were made, the diversity of results indicates that in some of the work, the uncertainties were greater than supposed.

Since the present determinations have been made by use of the present standards of electromotive force and electric resistance, they yield values for the heat capacity of water in international electric-energy units. They are comparable, in kind, to two types of previous measurements, those in which the variation of specific heat with temperature has been observed, and those in which the heat capacity of water has been measured, either in mechanical or electrical units of energy.

Comparisons of the determinations of the variation of specific heat may be made, independently of the absolute value of the energy units. These comparisons may easily be made by arbitrarily choosing a temperature at which the observed specific heat is taken as unity. Differences in temperature scales used and such calorimetric errors as heat leaks, however, would affect the accord.

For the evaluation of the heat capacity or specific heat of water in the fundamental or absolute units of energy, the choice of values for

the relations between units and standards of different periods is involved, particularly for measurements made by the method of electric heating. The data available for this purpose are not adequate to yield satisfactory appraisals of all the experimental data. The opinions of some who have studied this matter are interesting.

For example, in the discussion of T. H. Laby's [13] critical review paper on the mechanical equivalent of heat, several physicists have given their views. F. E. Smith said that he "had little faith in the values of physical constants obtained by applying corrections long after the date of the observations." G. M. Clark said "I doubt whether much is gained by discussing the results of other observers by making known corrections that arise through the light of later knowledge * * * the halo of nebulosity surrounding any physical determination is probably greater than the original experimenter cared to acknowledge to himself. I am also of the opinion that the only person who can revise any old determination is the person who made it." Ezer Griffiths said "I view with misgivings attempts to correct old work unless made by the investigators themselves, as they alone are acquainted with all the facts concerning the apparatus." E. H. Griffiths said "I confess that it appears to me that it is the final and not the earlier conclusions of an author which should be quoted." In this very frank discussion, several authors gave reappraisals of their earlier numerical values, which are most helpful to reviewers.

In comparing various appraisals made in the past, much can be found to support these views. It seems, however, that part of the discord which has baffled reviewers may be removed by use of more complete correction data, without too ruthless rejection of early experimental work.

In accord with the above warnings of caution, the present authors propose to accept at their face values the experimenters' own reappraisals, where available. In view of the impossibility of precise interpretation and reduction to present standards of much of the earlier work, and since this service has been already so thoroughly performed by previous reviewers, a complete review will not be undertaken here. Instead, only a few of the determinations which have been cited in the past as important or authoritative have been selected for examination and correlation to indicate the extent of corroboration. In order to coordinate them for intercomparison, some reductions have been made by using equivalents or ratios which are based on more complete experimental evidence than those used in former reviews. These data will be examined in two respects, the first by considering the experimental data yielding values for the mechanical equivalent of heat, each in terms of some definite heat unit, and second, by considering data on the change of specific heat with temperature.

James Prescott Joule

Joule [14] appears to have been the first to undertake systematic measurements of the mechanical equivalent. In 1850, from experiments by a number of methods, he chose a value of 772 foot-pounds per heat unit. Later, in 1878, by water friction in a calorimeter, he obtained the value 772.6 foot-pounds per 62° F heat unit. Because these experiments belong to an early period in the development of standards of physical measurements, it is impossible to evaluate the results in terms of present standards, but their pioneer nature and

classical refinement set them apart as exempt from any purely numerical appraisal of their relative accuracy. Tribute to Joule's work is perpetuated by the use of his name to designate the unit of work.

Henry A. Rowland

Rowland [15] followed Joule by making a series of elaborate experiments similar in principle to Joule's, but with greater care and refinements in some respects. Although the thermometry of that time was less precise than later, Rowland's measurements were made and recorded so carefully that they could be revised later when the thermometers that he used had been compared with better-known standards. William S. Day [16], with Rowland's permission and advice, compared Rowland's thermometers with the Paris Standard (international hydrogen scale) and made a revision of the results 20 years after the original work.

At the conclusion of his paper, Rowland says "Between the limits of 15° and 25° C, I feel almost certain that no subsequent experiments will change my values of the equivalent so much as 2 parts in 1,000, and even outside those limits, say between 10° and 30°, I doubt whether the figures will ever be changed much more than that amount." This concluding estimate seems to have been conservative.

Table 8 gives the values reported by Rowland and the values corrected by Day at five temperatures from 10° to 30° C. It also gives the NBS values reduced to the same temperature intervals and rounded to the same number of figures. The last two columns give the deviations of Rowland's original and Day's revision from the NBS. Rowland's smoothed results differ most from the NBS at the ends of the range from 10° to 30° C, and there, by less than his estimated 2 parts in 1,000.

TABLE 8.—Comparison of specific heat values of Rowland with NBS values

Temperature	Rowland, 1879	Day's revision, 1898	NBS 1939	Rowland minus NBS	Day's revision minus NBS
°C	<i>j/g°C</i>	<i>j/g°C</i>	<i>j/g°C</i>	<i>j/g°C</i>	<i>j/g°C</i>
10	4.200	4.196	4.192	0.008	0.004
15	4.189	4.188	4.186	.003	.002
20	4.179	4.181	4.182	-.003	-.001
25	4.173	4.176	4.180	-.007	-.004
30	4.171	4.174	4.179	-.008	-.005
Average				-0.0016	-0.0010

Rowland's values are greater than the NBS values in the lower part of this range and less in the upper part. It seems probable that these departures can be explained by the correction he applied for heat leak, or "radiation," as he called it. This correction amounted to over 2 percent of the energy input when the temperature of the calorimeter differed from that of the jacket by 10° C. He determined the "coefficients of radiation" by measurement, but in discussing them he says "the circumstances in the experiments are not the same as when the radiation was obtained." These circumstances, he states, "tend to give *too small* [italics Rowland's] coefficients of radiation, and this is confirmed by looking over the final tables." He, however, did not feel at liberty to make corrections on this

basis. Had these coefficients been greater by nearly 4 percent, it would have accounted for the difference in slope of Rowland's curve from that of the NBS, as will be seen by referring to table 8. At 20° C, which is the midtemperature of the range in which Rowland estimated his greatest precision, Rowland's revised value is less than the NBS value by about 1 part in 4,000. At 15° C, which was about the average jacket temperature, and where the heat leak would have been zero, Rowland's revised value is greater than the NBS value by 1 part in 2,000.

It is possible that his remarkable accord with recent determinations is accidental, but it appears more likely to be due to the thoroughness with which he is known to have worked.

Reynolds and Moorby

These workers [17] determined the mechanical equivalent of heat by means of a hydraulic brake driven by a steam engine. The measurements were carried out on an engineering scale, the power input being in some experiments as large as 65 hp. This feature has sometimes been considered an advantage as compared with lesser proportions. The heat developed was used to raise the temperature of water over a range of nearly 100° C. These distinctions give these measurements an importance for purposes of comparison.

It must be recognized that in some other respects, the apparatus and technique were less refined than in the case of some of the other determinations. Although the work is described at great length, it is difficult to ascertain all details which would aid in correlating the numerical result with others. This is the case with the record of the initial and final temperatures and pressures of the water which absorbed the energy input as sensible heat. It seems that for the final value of 4.1832 abs. j/g-°C, the approximate range of state was from a temperature of 1.3° C and a pressure of 1.53 atmospheres, to a final temperature of 100° C and a pressure of 1.43 atmospheres. The change in enthalpy for this change of state may be computed from the NBS data as follows:

Enthalpy at 1.3° C, pressure 1 atm.....	5. 583 abs. j/g.
Change for 0.53 atm.....	0. 054 abs. j/g.
Enthalpy at 1.3° C, pressure 1.53 atm.....	5. 637 abs. j/g.
Enthalpy at 100° C, pressure 1 atm.....	419. 105 abs. j/g.
Correction for 0.43 atm.....	0. 033 abs. j/g.
Enthalpy at 100° C, pressure 1.43 atm.....	419. 138 abs. j/g.
Change in enthalpy 1.3° C, 1.53 atm, to 100° C and 1.43 atm.....	413. 501 abs. j/g.
Change per degree by NBS value.....	4. 1895 abs. j/g-°C.
Reynolds and Moorby's value.....	4. 1832 abs. j/g-°C.
R. and M.-NBS.....	0. 0063 abs. j/g-°C (or 1 part in 660)

The accord of this result with the NBS result is inferior to the accord of Rowland's result after Day's revision for temperature scale. Inasmuch as the means of protection from heat leak in Reynolds and Moorby's work were less complete and the range of temperature considerably greater, it is very probable that this may account in part for the greater discrepancy. Although this extensive research suffers by comparison with modern technique, the approximate confirmation of smaller scale laboratory measurements has served for many years as a classical contribution to engineering data.

Laby and Hercus

They [18] determined the mechanical equivalent of heat by direct mechanical measurements using an induction dynamometer and the method of continuous-flow calorimetry. The ingenuity of design and refinements of technique justify their aim at "the highest precision attainable with the present developments of physical technique."

There have been two serious criticisms of Laby and Hercus' work. Birge [19] has proposed a reevaluation of their result by disregarding the experiments near 20° C on account of their large residual. In a later paper, Laby and Hercus [20] have noted this criticism and have accepted the proposal. Jessel [21] has reported finding differences in the specific heat of air-free water and air-saturated water and has questioned Laby and Hercus' result on the score that air-free water was not used. In replying to this criticism, Laby and Hercus [20] deny the validity of Jessel's conclusions in their own case and show by computation that the effect is negligible. As a reappraisal in 1935 of the final result of their measurements, Laby and Hercus give for the mechanical equivalent for both deaerated and aerated water, the value of 4.1852×10^7 ergs/15° cal, which may be taken as their appraisal of their results for purposes of comparison. The present NBS measurements give the value of 4.1858 j (abs.)/g-°C for C_p at 15° C and 1 atmosphere, which agrees within 1 part in 7,000 with Laby and Hercus' value.

Callendar and Barnes

Their work [22] on the measurement of the heat capacity of water between 5° and 95° C by the continuous electric-calorimetric method is without doubt more pretentious and comprehensive than any of the other researches on this property of water. The results which were obtained from measurements made by Barnes in 1899 and 1900 in terms of the electrical standards of that period have since been the subject of numerous reviews [13, 22, 23, 24, 25], mostly with the object of deriving better appraisals of the value of the mechanical equivalent of heat by applying corrections to bring them into accord with known standards. The diversity of these reappraisals emphasizes the difficulty and uncertainty involved. Even Callendar, who cooperated in the design and preparation of the apparatus, and Barnes, who carried out the experimental part of the program, differed in their opinions of the validity of the accounting for heat leak. It seems that for the purpose of comparisons, the best course is to take the authors' own latest estimates. These along with others are given in table 9.

In 1909 Barnes [22] revised his original figures of 1902 by applying corrections for the value of the standard cells. Callendar [26] reviewed previous experiments on the variation of specific heat of water, described experiments by a new method, and derived a formula for specific heat. It is somewhat difficult to differentiate Callendar's interpretations of these several elements, and, for purposes of comparison, it seems best to take his tabulated figures, referred to the value at 20° C as unity. Callendar later, in 1925 [13], in a discussion of T. H. Laby's paper on the Mechanical Equivalent of Heat, has given a reappraisal of the value at 20° C from the Callendar and Barnes' experiments as 4.178 abs. j/g-°C. This value is practically the same as the value 4.1785 given by Barnes in 1909. Laby's

appraisal of Callendar and Barnes' value made at the same time is 4.1795 at 20° C. The NBS value for 20° C at present is 4.1819, which is about 1 part in 1,200 greater than Barnes' figure. Barnes' estimated values of the specific heats at other temperatures deviate from the NBS values by as much as 1 in 500, while Callendar's estimate is for the most part within 1 part in 1,000 of the NBS value. Barnes' mean value between 5° and 95° C of 4.1835 is about 1 part in 1,000 less than the corresponding mean value of 4.1877 from the NBS measurements.

TABLE 9.—*Comparison of specific heat value of Callendar and Barnes with NBS value*

Temperature	Barnes original 1902	Barnes revised 1909	Callendar revised 1925	Laby's revision of Callendar and Barnes 1925	Callendar 1912	Barnes 1909	NBS 1939
°C	<i>Abs. j/g-°C</i>	<i>Abs. j/g-°C</i>	<i>Abs. j/g-°C</i>	<i>Abs. j/g-°C</i>	<i>cal₂₀/g-°C</i>	<i>cal₂₀/g-°C</i>	<i>cal₂₀/g-°C</i>
0							1.00857
5	4.2105	4.2052			1.00596	1.00639	1.00487
10	4.1979	4.1926			1.00310	1.00337	1.00247
15	4.1895	4.1842			1.00122	1.00136	1.00094
20	4.1838	4.1785	4.178	4.1795	1.00000	1.00000	1.00000
25	4.1801	4.1748			0.99922	0.99911	0.99946
30	4.1780	4.1727			.99877	.99861	.99919
35	4.1773	4.1720			.99856	.99844	.99913
40	4.1773	4.1720			.99856	.99844	.99921
45	4.1782	4.1729			.99871	.99866	.99942
50	4.1798	4.1745			.99901	.99904	.99973
55	4.1819	4.1766			.99942	.99955	1.00013
60	4.1845	4.1792			.99994	1.00017	1.00061
65	4.1870	4.1817			1.00055	1.00077	1.00119
70	4.1898	4.1845			1.00125	1.00144	1.00185
75	4.1925	4.1872			1.00201	1.00208	1.00261
80	4.1954	4.1901			1.00288	1.00278	1.00348
85	4.1982	4.1929			1.00380	1.00348	1.00446
90	4.2010	4.1957			1.00479	1.00412	1.00556
95	4.2038	4.1985			1.00583	1.00479	1.00679
Mean		4.1835					
100							1.00817

Although it is difficult to explain this degree of discord, it seems possible that inaccurate accounting for heat leak may have been responsible for much of the difference. It is difficult to believe that Barnes' estimate in 1909 that the error of the measurements in any part of the range did not exceed 1 part in 10,000, or Callendar's estimate of 1 part in 4,000 for the absolute value of the mechanical equivalent, took into account all the possibilities for deviations from the true values.

Jaeger and von Steinwehr

Their measurements [27] were made at the Physikalisch-Technische Reichsanstalt in 1921, by the electric-heating method, and extending over the range from 5° to 50° C, are free from some of the uncertainties of units and standards which affect much of the earlier work. There is very little doubt that the temperature scale and the electrical standards used were substantially the same as those now in use as international standards. The numerical values as given originally may therefore be taken to represent the experimental data between 5° and 50° C smoothed by an empirical formula of the second degree.

These values are given in table 10 with corresponding NBS values for comparison.

Henning and Jaeger [28] quote the value of 4.1842 int. j/g °C for the heat capacity of water at 15° C., estimating the accuracy as about 2 parts in 10,000. The PTR formula accords with the NBS value at this temperature to this estimated accuracy but, elsewhere, the deviations are larger.

It is of interest to examine the individual experimental results to see to what extent this peculiarity may be the result of the type of formula used. It is a well-known fact that formulas of the power series type often show a pronounced tendency to deviate near the ends of an experimental range, even though fitted to the data by least-squares adjustment.

In figure 6 the deviation of the PTR formula from the NBS formula is shown by the smooth curved line. The deviations of the PTR (observed-minus-calculated) values as given by Jaeger and von Steinwehr in their table 11 are shown by

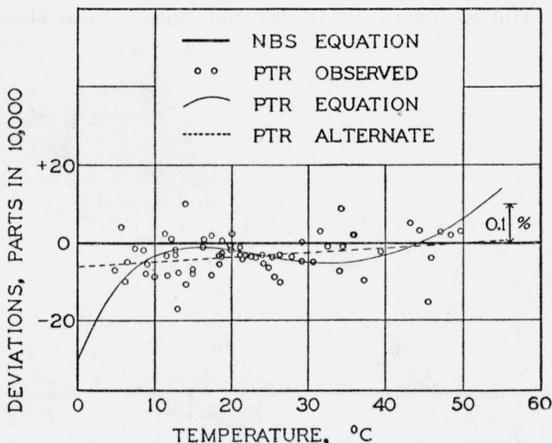


FIGURE 6.—Deviations of PTR from NBS values of C_p .

The points designated as "PTR obs." The dotted line designated as "PTR Alternate" represents a re-formulation of the PTR data in the light of the present work. This was found by fitting a linear equation to the deviations of the PTR data from the NBS equation, and therefore this alternate interpretation of the PTR results differs from the NBS formulation of C_p only by addition of a correction equal to $[-0.00256 + 0.0000486t]$. This alternate formulation accords with the observed values slightly better than the PTR equation does, and is of a type which is consistent with experimental data outside their range of temperature. The greater spread of the PTR data is to be expected from the smaller temperature intervals used which were only about 1.4° C, and the general accord may be considered as satisfactory.

TABLE 10.—Comparison of specific heat values of Jaeger and von Steinwehr with NBS value

Temperature	Jaeger and von Steinwehr	Jaeger and von Steinwehr alternate	NBS 1939	Temperature	Jaeger and von Steinwehr	Jaeger and von Steinwehr alternate	NBS 1939
°C	Int. j/g·°C	Int. j/g·°C	Int. j/g·°C	°C	Int. j/g·°C	Int. j/g·°C	Int. j/g·°C
5.....	4.1966	4.1991	4.2014	30.....	4.1755	4.1766	4.1777
10.....	4.1897	4.1893	4.1914	35.....	4.1753	4.1765	4.1774
15.....	4.1842	4.1832	4.1850	40.....	4.1764	4.1772	4.1778
20.....	4.1800	4.1795	4.1811	45.....	4.1788	4.1783	4.1787
25.....	4.1771	4.1775	4.1788	50.....	4.1825	4.1798	4.1799

National Bureau of Standards

The earlier measurements of the enthalpy of saturated water made in this laboratory and published in 1930 [2] furnish data from which values of specific heat of water at 1 atmosphere in the range 0° to 100° C may be derived. These measurements were not intended primarily for determining the specific heat, having been made to furnish data for enthalpy of water and steam for compiling steam tables, and values of the specific heat were not published. Beside other limitations on the accuracy of the NBS 1930 data, the larger temperature intervals then used gave less convincing evidence of the trend of specific heat in the lower range of temperature where the change is most rapid.

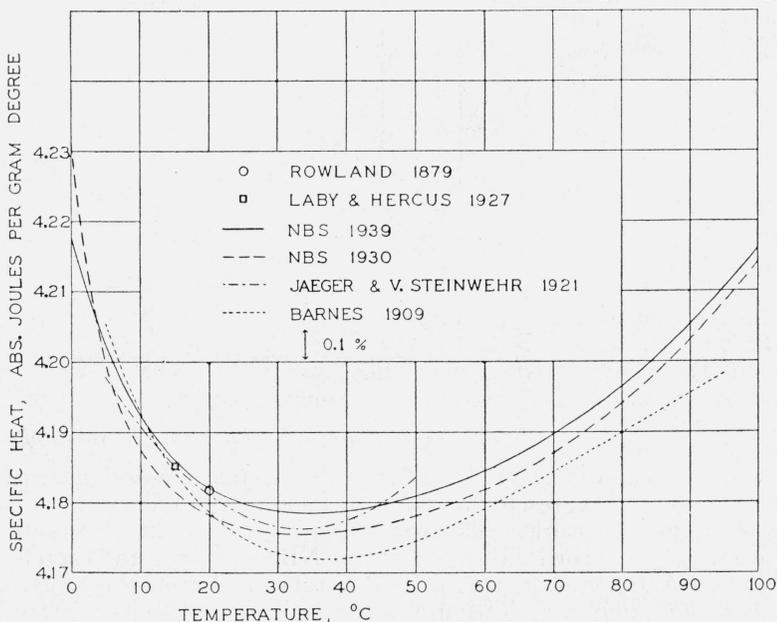


FIGURE 7.—Comparison of values of C_p .

Nevertheless, these results have been taken as a basis for values of heat capacity of water used in measurements of enthalpy of superheated steam by several of the laboratories cooperating in the international steam research project. It is therefore of interest to note the difference between the old and the new results, expressed as specific heat. For the purpose of intercomparison, the values of C_p at 1-atmosphere pressure have now been computed from the formulated results of the 1930 report as represented by the following formula given for alpha in the range 0° to 170° C:

$$\alpha = 1.240777 \log_{10} \left(\frac{t+7}{7} \right) + 415.2412 \left(\frac{t}{100} \right) + 0.6912 \left(\frac{t}{100} \right)^2 - 0.044874 \left(\frac{t}{100} \right)^4$$

This computation of C_p was made in a manner similar to those for the present new results as previously described in this report, using the same value for β and $[H_t]^{1 \text{ atm}}_{\text{sat}}$. The values of C_p thus derived are given in table 11 and are designated as $C_{p \text{ (NBS 1930)}}$, together with the 1939 NBS values.

Comparative values of specific heat in absolute joules from the determinations just reviewed are shown graphically in figure 7.

TABLE 11.—Comparison of specific-heat values of NBS 1930 with NBS 1939 values

Temperature	C_p NBS 1930	C_p NBS 1939	Temperature	C_p NBS 1930	C_p NBS 1939
°C	Int. j/g·°C	Int. j/g·°C	°C	Int. j/g·°C	Int. j/g·°C
0	4.2297	4.2169	50	4.1771	4.1799
5	4.1986	4.2014	55	4.1787	4.1816
10	4.1865	4.1914	60	4.1808	4.1836
15	4.1804	4.1850	65	4.1833	4.1860
20	4.1771	4.1811	70	4.1861	4.1888
25	4.1753	4.1788	75	4.1894	4.1920
30	4.1746	4.1777	80	4.1932	4.1956
35	4.1745	4.1774	85	4.1974	4.1997
40	4.1749	4.1778	90	4.2022	4.2043
45	4.1758	4.1787	95	4.2075	4.2095
			100	4.2134	4.2152

As a summary of the review and comparisons just made, it is found that the results of Rowland, Laby and Hercus, and Jaeger and von Steinwehr for the mechanical or electrical equivalent of the heat capacity of water in the range 15° to 20° C, are corroborated by the results of the present investigation, and are in accord with a value of 1.00019 for the ratio of the international volt-ampere to the absolute, or mechanical watt. It is further found that the results of Jaeger and von Steinwehr throughout their experimental range, 5° to 50° C, are in satisfactory accord with the present NBS results. It has not been found possible to reconcile the discord between the results of Callendar and Barnes and the present NBS results. The likelihood that uncertainty in heat-leak accounting may have been the cause of unsuspected error is suggested. The close control of this factor in the present work may be considered in a choice of definitive values without detracting from esteem of the earlier work.

The values of specific heat derived from the earlier (1930) determinations of the NBS are less trustworthy than the new results and are not considered by the authors as entitled to inclusion in any new appraisal of values of specific heat in the range 0° to 100° C.

Part 3. Heat of Vaporization of Water in the Range 0° to 100° C

I. INTRODUCTION

The heat of vaporization of water is not only a large part of the enthalpy, or heat content, of steam, but it is also one of the terms in the Clapeyron equation by which saturation specific volumes are correlated with saturation vapor pressure. Hence, independent values of this property are important data in the compilation of tables of the properties of steam.

The existing data from direct measurements in the range 0° to 100° C by different experimenters lacked the accord desired in standard steam tables. In the range 0° to 50° C, the deviations of these values from the international skeleton table were as much as 0.2 percent. Since the skeleton table was based on appraisal of the whole ensemble of available data, which in this region were relatively scanty, it was desired to obtain a more positive verification by a systematic redetermination of the heat of vaporization.

This was undertaken in connection with the redetermination of the heat capacity of liquid water from 0° to 100° C, and in the construc-

tion of the calorimeter, as described in part 1, provision was made for measurements of heat of vaporization. Without sacrifice of the aim of high precision in the heat-capacity measurements, it was possible to include features adapting the apparatus to accurate vaporization measurements over the range 0° to 100° C.

II. METHOD AND APPARATUS

Since the method and apparatus have been described in part 1, only a brief resumé is given here of the general scheme of measurement before describing the experimental procedure in detail.

The calorimeter, consisting of a metal shell, protected from unmeasured heat leak by a controlled insulating envelope, contained a sample of air-free water, both liquid and vapor. The liquid was vigorously circulated through an electric heater by an immersed pump.

In the vaporization experiments the measured heat was supplied electrically to evaporate liquid, while vapor was withdrawn at a rate which was controlled manually to keep a constant temperature of evaporation. The energy added per unit mass removed as vapor, designated as gamma, γ , exceeds the latent heat of vaporization, L , by the quantity beta, β . That is, according to the theory [1]

$$\gamma = L + \beta$$

where

$$\beta = T u \frac{dP}{dT}$$

The values of β used in deriving values of L from the observed values of γ were calculated from known values of the vapor-pressure derivative, dP/dT , and of u , the specific volume of the liquid. This reduction term is very small at low pressures, and at 100° C amounts to only 1/1600 of γ .

III. EXPERIMENTAL PROCEDURE

1. ACCOUNTING FOR MASS, ENERGY, AND CHANGE IN STATE OF THE WATER SAMPLE

The accounting for the mass, energy, and change in state of the water sample in the vaporization experiments was for the most part the same as in the heat-capacity experiments. The few differences will be pointed out briefly here.

The amount of water evaporated and collected by condensation in an average experiment was about 20 g. To make the weighings with suitable precision, the glass containers holding the condensed water samples were subjected to a standard conditioning treatment before weighing them. The glass container, after a sample of water had been collected as ice by condensation in liquid air, was warmed carefully to melt the ice and bring it slightly above the temperature of the room. The container was then wiped dry and placed in the balance case. Air in the balance case was circulated by a fan for at least 5 min to bring the container to the balance case temperature as well as to insure a standard surface condition. Weighings were then made by substitution, estimating to one-tenth of a milligram. A substitute or tare glass container, which displaced the same amount

of air as the weighing container, was kept in the case and was weighed either just before or after the collecting container. This eliminated errors of weighing due to variation in length of the balance arm or change of weight of the counterpoise.

In the vaporization process, larger temperature gradients were induced in the calorimeter than in the heat-capacity experiments. In order to diminish these gradients, the pump speed was increased to 106 rpm at the expense of a larger pump power. Since the pump power was also less constant than before, determinations of it were made oftener. Several pump-power determinations were made on each day, the experiments being arranged so that pump-power determinations were made usually just before and just after one or two evaporation experiments. By interpolating between pump-power determinations, account was taken of changes in pump power, including that due to changes in liquid level. In all, 131 determinations of pump power were made during the 152 evaporation experiments.

Owing to the greater disturbance of temperature by the evaporation process, the heat-leak accounting was slightly less exact than in the heat-capacity measurements. A small supercorrection, depending on the location of the liquid level, was applied, sometimes amounting to as much as 1 part in 50,000.

During the withdrawal of steam from the calorimeter, the upper tube was tempered by the outgoing steam, so for this period there was no correction for heat leak in the upper tube.

The initial and final temperatures of the water in the calorimeter were observed in the same manner as in the heat-capacity experiments. The temperature of the steam leaving the calorimeter was indicated by the group of four thermoelements, *JT*, representing the average temperature of the upper part of the calorimeter, and the single thermoelements, *J7*, *J6*, and *J5*, representing the temperatures along the upper tube.

A study of the thermoelement indications and their correlation with the observed values of heat of vaporization indicated that the temperature of the upper part of the calorimeter (measured by *JT*) is the best representation of the temperature of the steam withdrawn from the calorimeter and likewise of the temperature of evaporation.

Special details of the experimental procedure will next be described.

2. DESCRIPTION OF VAPORIZATION EXPERIMENTS

In preparation for an experiment, the calorimeter was charged with about 800 g of air-free water in the manner described in part 2. Trials with different charges showed that amounts between about 800 and 500 g gave the most satisfactory operating conditions. The calorimeter temperature was adjusted to the chosen temperature of the experiment by either electric heating, or cooling by the process of withdrawing vapor. During this adjustment of the calorimeter temperature, the throttle valve was heated by its electric heater to maintain it warmer than the calorimeter. The envelope temperature also was maintained above the calorimeter temperature. These precautions opposed condensation of water in the upper tube, which later, by removal, might give erroneous accounting for mass and energy. Consistency of the results with varying rates of withdrawal showed that this danger had been removed.

The temperatures of the envelope and reference block were next brought very slightly above the calorimeter temperature. During this period of adjustment, the circulating pump was started and the space between the calorimeter and envelope was evacuated for the purpose of insulation. A weighed evacuated glass container, *SR*, was connected to the vapor line, as shown in figure 3 in part 1. After evacuation of the line, the glass container was opened to the vapor throttle valve. The apparatus was then ready for the beginning of an experiment.

The equilibrium temperature of the calorimeter and contents was observed. At the start of the heating period, the current from the storage battery was shifted from the substitute resistor to the calorimeter heater by the automatic switch actuated by the time signals. Using the indications of the four thermoelements, *JT*, as guides, the throttle valve was opened and steadily adjusted so as to keep the value of *JT* practically zero. The reference block was kept at a constant temperature, as shown by the resistance thermometer indications. In this way, the temperature of the upper part of the calorimeter, which closely followed the evaporation temperature, was maintained constant at the initial reference block temperature by withdrawing enough steam to balance the energy put into the calorimeter. During this time, the bottom part of the calorimeter, which was in contact with the circulating liquid, became warmer than the top part by the amount of superheating necessary to conduct the heat to the surface for evaporation.

In order to evaluate heat-leak factors and the temperature of the withdrawn steam, the thermoelements on the upper tube, lower tube, calorimeter, and envelope were observed at 1-min. intervals. The readings of the resistance thermometer were recorded every minute so that the thermoelement observations could be referred to the International Temperature Scale. Occasional surveys of all thermoelements were made to guide proper control of the experiments. The current and potential drop in the calorimeter heater were observed on alternate minutes starting $\frac{1}{2}$ minute after the power was switched on. At the end of the chosen number of minutes, the calorimeter heating was stopped and enough more vapor withdrawn before closing the valve to bring the calorimeter and contents to final equilibrium temperature near the initial temperature. The final temperature was then observed.

In all, 152 satisfactory vaporization experiments were made between 0° and 100° C. For most of these experiments, the time of evaporation was about 20 min., and the total time of the experiment about 30 min. Of these, 64 experiments were made at an evaporation rate of about 1 g/min. In tests to detect any significant change of the result with the rate of withdrawal, a number of the other experiments were made at various rates ranging from 0.25 to 2.22 g/min. The purpose of these tests was to ascertain whether there was any appreciable amount of liquid in the steam withdrawn. Examination of the results revealed no definite evidence of such an effect.

IV. RESULTS OF VAPORIZATION EXPERIMENTS

The data and computations for the vaporization experiments were so similar to those described in part 2 for the heat-capacity experiments that sample sheets need not be given. The principal data from the

vaporization experiments, as reduced to give values of gamma, γ , are given in table 12. In addition to the data taken in the heat-capacity experiments, both thermometer readings and the thermoelement, $J\dot{T}$, readings were observed every minute during the evaporation period. The combination of the readings permitted the calculation throughout the experiment of the temperature of the top part of the calorimeter, which was found to represent closely the temperature of evaporation.

The computations of temperature and electric energy were made in the same manner as in the heat-capacity computations. In computing the total energy, the corrections were made as shown previously, except that in the case of the upper tube the heat leak was considered as zero during the outflow of steam. A correction was always necessary to account for the energy involved in the difference of the final temperature of the calorimeter and contents from the initial temperature. This correction was usually for temperature changes of less than 0.01°C, and was calculated, using the data from the heat-capacity experiments. Values are given in table 12 as "corrections for change of temperature."

Dividing the total energy thus obtained by the mass of water withdrawn gives a value of gamma, γ , at the effective evaporation temperature. This temperature was usually within 0.03° C of the even temperature, making the correction applied to the energy for the difference usually less than 1 part in 30,000.

The mean values of γ at the even temperatures were then found, weighting the separate determinations in proportion to the rates of evaporation. These weighted means and the deviations of the measured values from them are given in table 12. Study of the deviations justifies this mode of weighting for the rates used. The results were then ready for final formulation for use in computing heat of vaporization.

TABLE 12.—Principal data from vaporization experiments

Date	Evaporation temperature	Approximate rate	Mass of vapor removed	Heat leak	Pump energy	Correction for change in temperature	Entire energy added	γ at even temperature	Deviation from weighted mean
	°C	g/min	g	Int. j	Int. j	Int. j	Int. j	Int. j/g	Int. j/g
5-5-38.....	0.13	0.63	12.6135	-1.9	33.3	-12.7	31,539.0	2500.73	0.01
5-5-38.....	.15	.63	12.6135	-2.3	31.8	-7.0	31,542.1	2501.01	.29
5-5-38.....	.15	.63	12.6076	-1.9	32.4	-33.0	31,522.9	2500.67	-.06
5-5-38.....	.16	.63	12.6365	-3.9	32.9	44.5	31,592.6	2500.49	-.23
5-5-38.....	.14	.63	12.6160	-2.0	33.5	-5.2	31,544.6	2500.69	-.03

Even temperature 0.0° C. Weighted mean value of $\gamma_{0.0}$ =2500.72 int. j/g.

3-14-38.....	1.12	0.28	5.5299	-1.9	20.6	19.7	13,810.9	2497.78	-0.14
3-14-38.....	1.12	.65	12.9825	-3.6	21.3	1.4	32,419.9	2497.48	-.44
3-15-38.....	1.09	.70	14.0974	-2.3	32.2	-2.4	35,212.4	2498.00	.08
3-15-38.....	1.11	.70	14.0984	-3.5	23.6	4.7	35,209.4	2497.66	-.26
3-30-38.....	1.03	.70	14.0606	-2.0	27.0	17.9	35,118.8	2497.74	-.18
3-30-38.....	1.02	.70	14.0586	-2.2	26.1	22.6	35,115.0	2497.81	-.11
3-30-38.....	1.03	.25	4.9895	-.2	25.5	-18.5	12,464.2	2498.15	.23
3-30-38.....	1.03	.25	5.0009	-.2	24.4	-2.5	12,488.1	2497.24	-.68
3-30-38.....	1.02	.25	5.0032	-.2	25.3	7.2	12,495.7	2497.59	-.33
3-30-38.....	1.03	.25	4.9988	-.5	25.7	-2.7	12,484.0	2497.47	-.45
5-4-38.....	0.99	.70	14.0962	-1.4	25.5	9.2	35,215.8	2498.23	.31
5-4-38.....	1.00	.71	14.1013	-1.5	26.1	9.9	35,228.3	2498.23	.31
5-4-38.....	1.00	.70	14.0920	-1.4	28.3	-12.8	35,205.0	2498.23	.31
5-4-38.....	1.00	.71	14.1014	-1.4	27.1	1.2	35,227.7	2498.18	.26
5-4-38.....	1.00	.71	14.1054	-1.3	27.6	6.8	35,236.7	2498.10	.18

Even temperature 1.0° C. Weighted mean value of $\gamma_{1.0}$ =2497.92 int. j/g.

TABLE 12.—Principal data from vaporization experiments—Continued

Date	Evaporation temperature	Approximate rate	Mass of vapor removed	Heat leak	Pump energy	Correction for change in temperature	Entire energy added	γ at even temperature	Deviation from weighted mean
	$^{\circ}\text{C}$	<i>g/min</i>	<i>g</i>	<i>Int. j</i>	<i>Int. j</i>	<i>Int. j</i>	<i>Int. j</i>	<i>Int. j/g</i>	<i>Int. j/g</i>
3-31-38	5.00	0.91	18.1421	-2.6	28.7	26.7	45,142.0	2488.24	-0.10
3-31-38	5.00	.91	18.1191	-3.9	29.2	-11.8	45,089.1	2488.48	.14
3-31-38	5.01	.25	5.0913	-8	29.6	-3.4	12,669.4	2488.46	.12
3-31-38	5.02	.25	5.0952	-9	29.5	-13.3	12,677.7	2488.22	-.12
3-31-38	5.02	.25	5.0972	-1.1	29.3	-5.8	12,683.7	2488.32	-.02
5-3-38	5.00	.92	18.3058	-8.7	24.4	-12.4	45,553.6	2488.48	.14
5-3-38	5.00	.92	18.3167	-5.5	23.0	-15.1	45,579.2	2488.39	.05
5-3-38	5.00	.92	18.3298	-4.5	23.1	3.2	45,609.4	2488.27	-.07
5-3-38	5.00	.92	18.3372	-4.0	23.1	4.7	45,627.5	2488.25	-.09
5-3-38	5.01	.92	18.3425	-2.7	23.2	-1.9	45,639.9	2488.22	-.12
5-3-38	5.01	.92	18.3463	-2.2	23.3	2.3	45,651.5	2488.35	.01

Even temperature 5° C. Weighted mean value of $\gamma_5=2488.34$ int. j/g.

3-22-38	10.04	0.56	11.2389	-5.6	27.3	-7.0	27,836.6	2476.90	0.17
3-22-38	10.05	.26	5.1646	-2.4	28.4	-8.8	12,788.6	2476.32	-.41
3-22-38	10.07	1.05	20.9428	-9.8	30.4	-12.1	51,862.3	2476.54	-.29
4-1-38	9.97	1.03	10.3408	-2.9	19.4	-9.9	25,609.1	2476.44	-.20
4-1-38	9.99	0.26	5.1040	-0.9	30.0	-0.6	12,640.0	2476.47	-.26
4-1-38	9.99	.26	5.1106	-8	31.0	-2.7	12,659.3	2477.05	.32
4-1-38	10.01	.26	5.1326	-9	31.5	7.4	12,711.9	2476.74	.01
4-1-38	10.01	.26	5.1070	-8	31.5	-13.8	12,647.6	2476.54	-.19
4-1-38	10.01	.26	5.1057	-9	31.5	-16.6	12,643.2	2476.31	-.42
4-25-38	10.00	1.03	20.5761	-6.7	24.5	27.5	50,971.4	2477.21	.48
4-25-38	10.01	1.03	20.5738	-6.3	21.9	-25.6	50,953.8	2476.65	-.08
4-25-38	10.02	0.57	11.3193	-2.4	26.0	-1.0	28,019.9	2477.14	.41
4-25-38	10.02	.57	11.3326	-2.1	27.3	8.4	28,037.4	2477.00	-.27
4-25-38	10.03	.57	18.5282	-4.0	28.2	8.4	28,065.2	2476.55	-.18

Even temperature 10° C. Weighted mean value of $\gamma_{10}=2476.73$ int. j/g.

3-28-38	15.04	1.04	20.8145	-13.2	27.4	5.6	51,306.7	2465.04	0.23
3-28-38	15.04	1.04	20.7958	-10.4	27.3	-7.4	51,255.2	2464.78	-.03
3-28-38	15.06	0.26	5.1292	-2.3	27.9	-3.9	12,642.1	2464.87	.06
3-28-38	15.06	.26	5.1420	-2.5	30.4	5.9	12,674.7	2465.08	.27
3-28-38	15.06	.26	5.1417	-2.6	28.9	-0.2	12,671.8	2464.66	-.15
3-28-38	15.06	.26	5.1421	-2.6	29.3	-3.7	12,669.3	2463.98	-.83

Even temperature 15° C. Weighted mean value of $\gamma_{15}=2464.81$ int. j/g.

3-21-38	20.05	0.57	11.3473	-6.9	28.7	-12.4	27,841.8	2453.73	0.37
3-21-38	20.06	.57	11.3539	-6.4	28.3	2.3	27,860.8	2453.99	.63
3-21-38	20.08	.26	5.2151	-2.6	27.7	-10.8	12,797.3	2454.08	.72
3-21-38	20.10	1.06	16.9431	-9.8	23.0	1.9	41,561.4	2453.24	-.14
4-26-38	19.98	1.03	20.6986	-6.5	25.2	-20.2	50,779.4	2453.22	-.14
4-26-38	19.99	1.03	20.6905	-6.8	27.5	-20.1	50,758.2	2453.19	-.17
4-26-38	20.01	0.57	11.3518	-3.0	26.1	-4.8	27,849.1	2453.30	-.06
4-26-38	20.02	.57	11.3453	-3.1	26.3	-22.2	27,835.7	2453.55	-.19
4-26-38	20.02	.57	11.3570	-3.2	26.5	1.4	27,856.5	2452.85	-.51
4-26-38	20.03	.57	11.3506	-3.3	27.7	2.0	27,845.5	2453.15	-.21

Even temperature 20° C. Weighted mean value of $\gamma_{20}=2453.36$ int. j/g.

3-25-38	25.01	1.06	21.1489	-8.8	26.3	1.3	51,627.7	2441.17	-0.14
3-25-38	25.01	1.06	21.1399	-7.8	26.2	-5	51,610.4	2441.39	.08
3-25-38	25.01	.26	5.2053	-1.6	26.1	-11.9	12,706.7	2441.13	-.18
3-25-38	25.03	.26	5.2216	-2.0	26.8	5.2	12,744.0	2440.70	-.61
3-25-38	25.03	.26	5.2151	-1.9	25.5	-11.4	12,726.1	2440.31	-1.00
4-4-38	24.99	.29	5.7987	-1.3	23.7	-44.6	14,160.0	2441.91	.60
4-4-38	24.99	.57	11.4234	-3.9	24.7	-18.9	27,893.9	2441.80	.49
4-4-38	25.00	1.05	21.1590	-5.2	28.0	-19.9	51,652.3	2441.21	-.10
4-4-38	25.01	1.05	20.9658	-4.6	15.6	28.6	51,188.2	2441.53	.22
4-8-38	24.98	1.05	21.2868	-13.6	24.5	23.2	51,952.5	2440.55	-.76
4-8-38	24.98	2.08	41.5416	-21.0	26.6	-40.3	101,426.3	2441.51	.20
4-8-38	25.01	.29	5.7624	-2.3	25.7	-12.0	14,071.6	2441.99	.68
4-8-38	25.01	.57	11.3594	-6.3	23.5	.3	27,735.8	2441.68	.37

Even temperature 25° C. Weighted mean value of $\gamma_{25}=2441.31$ int. j/g.

TABLE 12.—Principal data from vaporization experiments—Continued

Date	Evaporation temperature	Approximate rate	Mass of vapor removed	Heat leak	Pump energy	Correction for change in temperature		Entire energy added	γ at even temperature	Deviation from weighted mean
	°C	g/min	g	Int. j	Int. j	Int. j	Int. j	Int. j/g	Int. j/g	
3-19-38	30.02	0.57	11.4735	-6.4	25.1	-17.8	27,880.5	2430.04	0.61	
3-19-38	30.03	.57	11.4791	-6.6	25.8	-7.4	27,893.3	2429.99	.56	
4-12-38	30.03	2.15	42.9434	-11.9	25.9	-11.5	104,302.5	2428.91	-.52	
4-12-38	30.04	2.15	42.9255	-12.0	23.9	-31.3	104,266.4	2429.12	-.31	
4-13-38	30.00	.29	5.8389	-2.4	26.9	-5.0	14,185.1	2429.41	-.02	
4-13-38	30.01	.29	5.8419	-2.5	26.9	5.2	14,194.9	2429.86	.43	
4-13-38	30.01	.58	11.5218	-5.7	26.9	1.1	27,990.2	2429.34	-.09	
4-13-38	30.01	.58	11.5076	-5.1	27.0	-11.2	27,959.8	2429.70	.27	
4-13-38	30.01	1.07	21.4137	-10.7	27.7	-1.3	52,032.2	2429.88	.45	
4-13-38	30.01	1.07	21.4173	-10.4	29.3	.2	52,037.6	2429.72	.29	
4-13-38	30.01	1.07	21.4198	-10.1	30.7	3.6	52,041.0	2429.57	.14	
Even temperature 30° C. Weighted mean value of γ_{30} =2429.43 int. j/g.										
3-18-38	40.03	0.58	11.6219	-6.2	24.3	9.3	27,962.7	2406.10	0.23	
3-18-38	40.04	.58	11.6027	-5.9	25.5	-5.7	27,918.9	2406.34	.47	
3-18-38	40.05	1.08	21.6436	-13.9	26.1	25.7	52,067.5	2405.82	-.05	
3-18-38	40.05	.27	10.6672	-5.9	44.1	-2.5	25,664.4	2406.04	.17	
4-18-38	40.02	.29	5.8071	-3.6	24.7	-3.7	13,971.8	2406.04	.17	
4-18-38	40.02	.29	5.8067	-3.4	29.1	-9.8	13,968.9	2405.70	-.17	
4-18-38	40.02	.58	11.5896	-7.6	25.1	8.5	27,883.7	2405.97	.10	
4-18-38	40.02	1.10	22.0565	-14.6	25.5	1.3	53,065.9	2405.96	.09	
4-18-38	40.03	2.10	42.0339	-26.8	26.8	5.8	101,117.2	2405.68	-.19	
4-18-38	40.03	2.10	42.0039	-24.3	29.1	-9.2	101,049.1	2405.78	-.09	
Even temperature 40° C. Weighted mean value of γ_{40} =2405.87 int. j/g.										
3-17-38	50.03	0.58	11.7417	-9.1	21.2	-4.2	27,971.7	2382.32	0.48	
3-17-38	50.04	.58	11.7431	-8.7	23.4	0.3	27,975.5	2382.39	.55	
3-17-38	50.05	.30	5.9655	-2.9	25.0	-26.5	14,211.8	2382.45	.61	
4-15-38	50.03	2.13	42.6496	-16.8	18.9	-25.6	101,565.8	2381.47	-.37	
4-15-38	50.04	0.30	6.0205	-2.0	18.6	8.6	14,336.3	2381.35	-.49	
4-15-38	50.04	.30	6.0117	-2.3	20.0	-16.8	14,318.2	2381.82	-.02	
4-15-38	50.04	.58	11.7121	-4.8	20.9	-1.9	27,894.8	2381.81	-.03	
4-15-38	50.04	.58	11.7095	-4.8	21.4	-7.5	27,885.6	2381.55	-.29	
4-15-38	50.05	1.09	21.8394	-7.4	22.8	-31.8	52,017.0	2381.92	.08	
5-25-38	49.99	1.08	21.5345	-4.4	27.3	17.8	51,292.4	2381.85	.01	
5-25-38	49.99	1.08	21.5660	-5.4	28.8	17.4	51,372.4	2382.08	.24	
Even temperature 50° C. Weighted mean value of γ_{50} =2381.84 int. j/g.										
5-13-38	59.99	1.12	22.4288	-22.0	25.5	-10.7	52,891.7	2358.18	0.53	
5-13-38	59.99	1.12	22.4230	-19.5	24.7	-21.0	52,870.3	2357.84	.19	
5-13-38	60.01	2.20	44.0762	-29.6	29.9	-9.7	103,905.8	2357.43	-.22	
5-13-38	60.00	2.20	44.0688	-24.2	27.3	14.0	103,889.5	2357.44	-.21	
5-13-38	60.01	1.12	22.4740	-10.7	32.4	-7.7	52,983.3	2357.56	-.09	
5-13-38	60.02	1.12	17.9796	-8.4	25.7	-2.1	42,392.7	2357.87	.22	
5-25-38	60.01	1.09	21.7726	-8.9	26.5	-10.6	51,333.5	2357.73	.08	
5-25-38	60.01	1.09	21.7708	-8.4	26.7	75.7	51,325.9	2357.58	-.07	
Even temperature 60° C. Weighted mean value of γ_{60} =2357.65 int. j/g.										
5-9-38	70.01	2.18	21.7659	-14.3	16.7	-46.9	50,787.9	2333.39	0.14	
5-9-38	70.02	1.12	22.4433	-19.1	25.7	34.5	52,366.3	2333.32	.07	
5-9-38	70.02	1.12	22.4376	-18.0	22.5	-8.5	52,352.2	2333.29	.04	
5-9-38	70.01	1.12	22.4550	-17.7	22.5	21.7	52,386.9	2332.99	-.26	
5-9-38	70.02	1.12	22.4530	-14.7	23.3	1.9	52,381.7	2333.00	-.25	
5-9-38	70.02	1.12	22.4598	-13.3	25.2	23.7	52,406.1	2333.38	.13	
Even temperature 70° C. Weighted mean value of γ_{70} =2333.25 int. j/g.										
5-24-38	80.06	1.10	11.0280	-4.3	19.8	-28.7	25,456.1	2308.47	-0.04	
5-24-38	80.08	1.10	22.0315	-15.3	25.5	-17.6	50,856.3	2308.54	-.03	
5-24-38	80.08	1.11	22.2351	-15.6	29.9	-0.1	51,329.2	2308.68	.17	
5-24-38	80.09	1.11	22.2461	-12.3	28.8	9.9	51,349.2	2308.45	-.06	
5-24-38	80.08	1.11	23.4033	-11.2	28.9	69.8	54,019.6	2308.40	-.11	
5-26-38	80.00	1.10	22.0608	-12.3	38.3	-4.0	50,932.6	2308.74	.23	
5-26-38	80.00	1.10	22.0742	-12.2	39.1	20.6	50,959.5	2308.55	.04	
5-26-38	80.01	0.63	12.5791	-5.8	39.1	8.2	29,040.1	2308.62	.11	
5-26-38	80.01	.63	12.5686	-6.2	38.7	-10.1	29,014.5	2308.51	.00	
5-26-38	80.03	.63	12.5666	-6.5	38.2	2.4	29,007.1	2308.34	-.17	
5-26-38	80.03	.63	12.5659	-6.5	38.0	5.0	29,002.5	2308.10	-.41	
Even temperature 80° C. Weighted mean value of γ_{80} =2308.51 int. j/g.										

TABLE 12.—Principal data from vaporization experiments—Continued

Date	Evaporation temperature	Approximate rate	Mass of vapor removed	Heat leak	Pump energy	Correction for change in temperature	Entire energy added	γ at γ temperature	Deviation from weighted mean
	$^{\circ}\text{C}$	g/min	g	Int. j	Int. j	Int. j	Int. j	Int. j/g	Int. j/g
5-10-38.....	90.01	2.22	22.1958	-9.4	18.4	-2.8	50,683.1	2283.48	0.07
5-10-38.....	90.01	2.22	44.3722	-22.9	31.8	8.7	101,321.2	2283.47	.06
5-10-38.....	90.01	1.16	23.2875	-13.9	36.1	-8.9	53,171.6	2283.30	-1.11
5-10-38.....	90.01	1.17	23.3241	-12.0	38.9	3.9	53,285.2	2283.30	-1.11

Even temperature 90°C . Weighted mean value of $\gamma_{90}=2283.41$ int. j/g.

5-11-38.....	99.99	1.18	23.5914	-13.7	33.9	4.3	53,261.8	2257.65	0.33
5-11-38.....	100.00	1.18	23.5977	-13.7	31.8	3.4	53,272.1	2257.51	.19
5-11-38.....	100.01	0.63	12.5763	-7.8	31.8	-7.0	28,392.8	2257.66	.34
5-11-38.....	100.01	.63	12.5796	-8.0	30.9	-4.2	28,396.0	2257.33	.01
5-11-38.....	100.01	.63	12.5795	-8.1	31.1	-6.7	28,393.3	2257.13	-19
6-1-38.....	99.99	1.13	22.5785	-25.6	24.9	53.0	50,964.4	2257.18	-14
6-1-38.....	99.99	1.13	22.5522	-24.8	21.5	-6.5	50,900.1	2256.96	-56
6-1-38.....	99.99	1.13	22.5650	-18.4	21.4	17.4	50,932.4	2257.11	-21
6-1-38.....	99.99	1.13	22.5745	-14.3	18.9	19.3	50,946.0	2256.76	-56
6-2-38.....	100.00	1.12	22.4874	-14.3	28.0	-12.2	50,766.3	2257.54	.22
6-2-38.....	100.01	1.12	22.4909	-13.8	24.6	3.2	50,778.9	2257.78	.46
6-2-38.....	100.01	1.12	22.4899	-12.6	24.1	-2.6	50,764.6	2257.25	-07
6-2-38.....	100.01	1.12	22.4959	-11.7	23.6	3.3	50,776.8	2257.19	-13
6-3-38.....	100.01	1.13	22.5822	-11.2	29.2	29.0	50,977.9	2257.47	.15
6-3-38.....	100.01	1.13	22.5659	-10.9	29.9	1.2	50,939.2	2257.38	.06
6-3-38.....	100.02	1.13	22.5644	-10.2	30.2	3.1	50,931.4	2257.21	-11
6-3-38.....	100.02	1.13	22.5616	-10.8	30.3	9.4	50,927.8	2257.33	.01

Even temperature 100°C . Weighted mean value of $\gamma_{100}=2257.32$ int. j/g.

In addition to the measurements described here, there was a series of results of similar measurements made in this laboratory (1930-32) [2, 29] with an earlier stirred calorimeter and extending from 50° to 270°C ; also another series (1937) [3] extending from 100° to 374°C , made with a later unstirred calorimeter.

Although these older measurements lacked some of the refinements of the present series, the fact that they were obtained with two calorimeters of different design from the present calorimeter and covered a much greater range of temperature, entitles them to inclusion in the scheme of formulation. In the range where they overlap or duplicate present measurements, the degree of accord furnishes a measure of the corroboration, while the greater range of the older data contributes greater directive control to a formulation than would result from the more accurate present results. A formulation was sought which comprised a smoothed appraisal of the experimental evidence over considerable range, and an empirical equation for γ was derived which satisfactorily does this over the range 0° to 200°C . After appraising the reliability of the various measurements, it was decided to weight them according to the number of observations and to give the observations of 1930-32 and those of 1937, respectively, one-fourth and one-half the weight of the observations of the present series.

The empirical equation for γ , as finally adjusted to these weighted data by the least-squares method, is written

$$\gamma = 2500.5 - 2.3233t - 10^x,$$

where $x + 5.1463 - 1,540/T$, t is in degrees centigrade, T is in degrees Kelvin ($t + 273.16$), and γ is in international joules per gram. This equation represents not only the present values of γ between 0° and

100° C but also the earlier values between 50° and 200° C from previous reports. The degree of accord between the observed and calculated values is shown graphically in figure 8.

Between 170° and 200° C the equation gives values which are practically identical with the formulation of 1937, and therefore these values merge smoothly in this region. From 0° to 200° the new formulation supersedes the previous one, and together they complete the determination of γ over the entire range from the ice point to the critical region.

Values of the latent heat of vaporization, L , are calculated from γ by applying the corresponding values of β , which are computed as described in part 2 of this report. Table 13 includes the experimental mean values of γ which were used in the formulation, corresponding values of β , and calculated values of γ and L .

Values of the specific volume of the saturated vapor, u' , were calculated from γ by the relation

$$\gamma = u' T dP/dT.$$

The values of the Clapeyron factor, TdP/dT , were calculated from vapor-pressure derivatives, as described in part 2.

TABLE 13.—Formulation of data on heat of vaporization

Temperature °C	γ , Observed				γ_i calculated	β	Heat of vaporization, L	Clapeyron factor $T \frac{dP}{dT}$	Specific volume of vapor u'
	1930. 1932.	1937	1939	Weighted mean					
0	Int. j/g	Int. j/g	Int. j/g 2500. 72	Int. j/g 2500. 72	Int. j/g 2500. 18	Int. j/g 0. 012	Int. j/g 2500. 17	Int. j/dm ³ 12. 1198	cm ³ /g 206288
1			2497. 92	2497. 92	2497. 84				
5			2488. 34	2488. 34	2488. 48	. 017	2488. 46	16. 9112	147150
10			2476. 73	2476. 73	2476. 76	. 023	2476. 74	23. 2730	106422
15			2464. 81	2464. 81	2465. 02	. 032	2464. 99	31. 6138	77973
20			2453. 36	2453. 36	2453. 25	. 042	2453. 21	42. 4173	57836
25			2441. 31	2441. 31	2441. 46	. 056	2441. 40	56. 2535	43401
30			2429. 43	2429. 43	2429. 64	. 074	2429. 57	73. 7846	32929
35					2417. 78	. 096	2417. 68	95. 7734	25245
40			2405. 87	2405. 87	2405. 88	. 124	2405. 76	123. 089	19546
45					2393. 93	. 158	2393. 77	156. 714	15275
50	2382. 0		2381. 84	2381. 85	2381. 93	. 200	2381. 73	197. 752	12045
55					2369. 88	. 251	2369. 63	247. 430	9578. 0
60			2357. 65	2357. 65	2357. 76	. 312	2357. 45	307. 097	7677. 6
65					2345. 58	. 386	2345. 19	378. 234	6201. 4
70	2333. 9		2333. 25	2333. 40	2333. 31	. 473	2332. 84	462. 470	5045. 3
75					2320. 97	. 576	2320. 39	561. 544	4133. 2
80			2308. 51	2308. 51	2308. 53	. 697	2307. 83	677. 319	3408. 3
85					2296. 00	. 838	2295. 16	811. 815	2828. 2
90	2283. 7		2283. 41	2283. 45	2283. 35	1. 001	2282. 35	967. 152	2360. 9
95					2270. 60	1. 191	2269. 41	1145. 57	1982. 1
100	2258. 71	2257. 79	2257. 32	2257. 73	2257. 71	1. 408	2256. 30	1349. 52	1673. 0
130	2177. 15			2177. 15	2177. 26				
150	2119. 64	2119. 50		2119. 57	2119. 87				
170	2058. 78			2058. 78	2058. 63				
200	1957. 96	1957. 11		1957. 44	1957. 93				

V. COMPARISONS WITH EARLIER WORK

A review of determinations of heats of vaporization of water previous to 1930 has already been made by Fiock [24]. No further attempt will be made here to review critically those determinations. However, since some of the results of earlier experiments are expressed in terms of the heat capacity of water, it is necessary to use heat-capacity data to convert those results to electric-energy units. In the review by Fiock these conversion data were obtained from the 1930 measurements at the NBS. The measurements given in part 2 of this report supply more accurate conversion data which will be used, where necessary, to interpret early results. The determinations of heats of vaporization will be briefly mentioned.

Dieterici

Dieterici [30] used a Bunsen ice calorimeter to measure the heat of vaporization at 0° C. In interpreting his results, uncertainty in units is avoided by using his own calibration of his ice calorimeter in terms of the mean calorie. By using the NBS value of the mean calorie along the saturated path (4.1903 int. j/g-°C) Dieterici's value of the heat of vaporization at 0° C becomes 2492.2 int. j/g.

Griffiths

Griffiths [31] measured the heats of vaporization at 30° and 40° C. The greatest uncertainty in the reduction of his data is in the evaluation of his electrical units. On the assumption that the electromotive force of his Clark cell was 1.4328 int. v instead of the 1.4342 that he used, his values are

$$L_{30^\circ} = 2425.2 \text{ int. j/g}$$

$$L_{40^\circ} = 2400.0 \text{ int. j/g}$$

Henning

Henning [32] made measurements in 1906 on the heat of vaporization between 30° and 100° C. His summary in 1919 gives values of his formulated results below 100° C, as follows:

$$\begin{aligned} L_{30^\circ} &= 2426.0 \text{ int. j/g.} \\ L_{40^\circ} &= 2403.8 \text{ int. j/g.} \\ L_{50^\circ} &= 2380.8 \text{ int. j/g.} \\ L_{60^\circ} &= 2357.4 \text{ int. j/g.} \end{aligned}$$

$$\begin{aligned} L_{70^\circ} &= 2333.1 \text{ int. j/g.} \\ L_{80^\circ} &= 2308.0 \text{ int. j/g.} \\ L_{90^\circ} &= 2282.5 \text{ int. j/g.} \\ L_{100^\circ} &= 2255.7 \text{ int. j/g.} \end{aligned}$$

A. W. Smith

Smith [33] made determinations between 14° and 100° C by evaporating water into a stream of air. Correction is made to the 1907 data for the revised Clark cell voltage. The values from Smith's experiments are as follows:

$$\begin{aligned} L_{14^\circ} &= 2463.5 \text{ int. j/g.} \\ L_{21^\circ} &= 2447.6 \text{ int. j/g.} \\ L_{28^\circ} &= 2431.1 \text{ int. j/g.} \end{aligned}$$

$$\begin{aligned} L_{40^\circ} &= 2401.4 \text{ int. j/g.} \\ L_{100^\circ} &= 2261.6 \text{ int. j/g.} \end{aligned}$$

Richards and Mathews

Richards and Mathews, and Mathews [34] measured the heat of vaporization at 100° C by a condensation method. After correction of the 1911 series, as later suggested by Mathews, the 1911 and 1917

series yield essentially the same result. Using the 1939 NBS heat-capacity data, their average value for the heat of vaporization at 100° C is 2257.3 int. j/g.

Carlton-Sutton

Carlton-Sutton [35] used a modification of Joly's classical apparatus to measure the heat of condensation of water directly in terms of the mean calorie without any reference to electrical standards. His final value of 538.88 mean cal, when interpreted by the NBS-39 value for

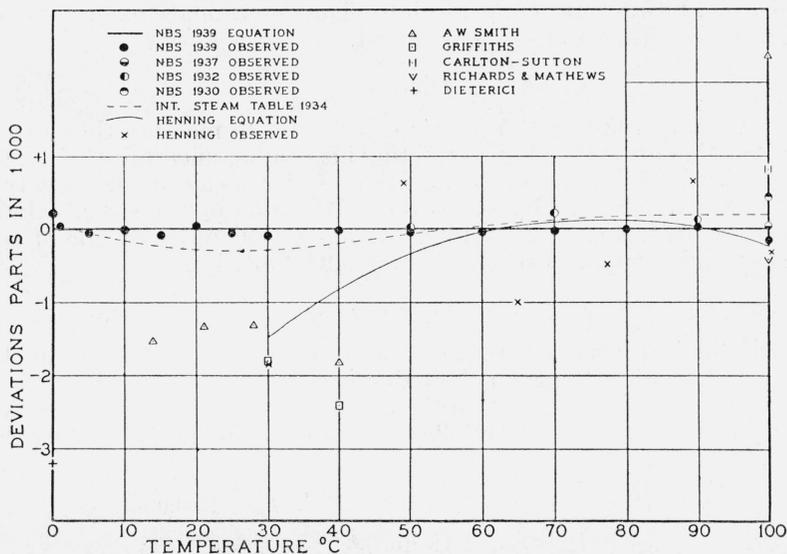


FIGURE 8.—Comparison of values of heat of vaporization.

the mean calorie along the saturated path, yields the value 2258.0 int. j/g for the heat of vaporization at 100° C.

National Bureau of Standards

Measurements at the National Bureau of Standards in 1930 [2] and 1932 [29] were made with an earlier calorimeter of different design from that of the present calorimeter. The observed values of heat of vaporization, L , in the range 50° to 100° C were:

$$\begin{aligned} L_{50}^{\circ} &= 2381.8 \text{ int. j/g.} & L_{90}^{\circ} &= 2282.7 \text{ int. j/g.} \\ L_{70}^{\circ} &= 2333.6 \text{ int. j/g.} & L_{100}^{\circ} &= 2257.3 \text{ int. j/g.} \end{aligned}$$

Measurements above 100° C were made at the National Bureau of Standards in 1937 [3] with another calorimeter. The value observed in 1937 of heat of vaporization, L , at 100° C, was 2256.38 int. j/g.

It is believed that the measurements made with these two earlier calorimeters are inferior in precision to the present results using an improved calorimeter, but since these earlier results were obtained in calorimeters of different design from that of the present, they were included in the formulation in the present report.

In figure 8, a comparison is given of the various measurements of the heats of vaporization between 0° and 100° C. The base line in this figure is taken from the NBS-39 formulation.

The formulations of heat capacity and heat of vaporization, which have been given in this report, are considered more reliable than those given in previous reports from this laboratory in the range 0° to 100° C. Inasmuch as the values of some of the properties of saturated water and steam above 100° C depend partly on the values below 100° C a reappraisal has been made of all the measurements made at the National Bureau of Standards and the results compiled into a single table of smoothed values in the entire range 0° to 374.15° C. This compilation appears elsewhere in this journal [36].

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