SPECIFIC HEAT OF SOME CALCIUM CHLORIDE SOLUTIONS BETWEEN −35° C AND +20° C.

By H. C. Dickinson, E. F. Mueller, and E. B. George.

CONTENTS.

I. THE CONTINUOUS-FLOW CALORIMETER.

(H. C. Dickinson and E. F. Mueller.)

The circulating medium now most generally used in refrigerating plants is calcium chloride brine. The specific heat of this solution seems never before to have been determined with any considerable degree of accuracy for temperatures below 0° C, so that the values found are not applicable to the ordinary conditions of use. The present investigation was undertaken with a view to determining, with an accuracy of 0.1 or 0.2 per cent, the values of the specific heat at temperatures generally employed in practice.

The determination of the specific heat of a liquid which can not be mixed with water, at temperatures 60° below that of the surrounding atmosphere, presented some difficulties, particularly as in this case it was desirable to make determinations over temperature ranges of only 5° or 10°, e. g., −35° to −25° C. The con-

tinuous-flow calorimeter seemed to be adapted to the requirements of this problem.

Calorimeter.—To fulfill these special requirements, a calorimeter was constructed on the following general principle. A constant stream of cooled brine is made to flow through a coil immersed in a calorimeter, while the temperature of the calorimeter is maintained constant, and the same as that of its surroundings by heating electrically. The temperature of the brine at the inlet and outlet of the coil in the calorimeter is measured, and the amount of brine flowing in a given time is determined by weighing.

The details of this calorimeter are shown somewhat diagrammatically in figure 1. The calorimeter proper (*C*) is made of nickel-plated brass about 2 millimeters thick, in such a way that the cup can be withdrawn and the cover left in place supporting the brine coil (*S*), the heating coil (*M*), and the stirrer (*P*). The brine coil consists of about 2 meters of 6-millimeter copper tubing, which was first wound with cotton-covered constantan wire, then bent into a spiral and covered with a thick layer of shellac, to reduce the heat conductivity between the brine and the liquid (kerosene) in the calorimeter. The second heating coil (*M*) is also made of constantan, wound on an open frame and immersed directly in the kerosene. Each of the heating coils has a resistance of about 22 ohms. The three leads required for the two resistance coils are led out through fiber bushings in the cover. The interchangeable inlet and outlet for the brine coil are enlarged glass tubes, which contain thin copper thermometer sheaths (T), fitted with copper vanes.

The inner vessel or calorimeter proper is supported from the cover of the larger outer vessel, but has no metallic connection with it, fiber blocks being used for all supports to avoid conduction of heat from one vessel to the other. Particular care is taken to avoid transfer of heat between the incoming brine and the cover of the outer vessel. All the openings through the outer cover, except that for the stirrer shaft, are sealed, so that the whole outer vessel may be immersed in ice and water or in a stirred water bath, to keep its temperature constant. The air space within is kept dry by anhydrous $CaCl_2$ to avoid any possible heat transfer by precipitation of moisture.
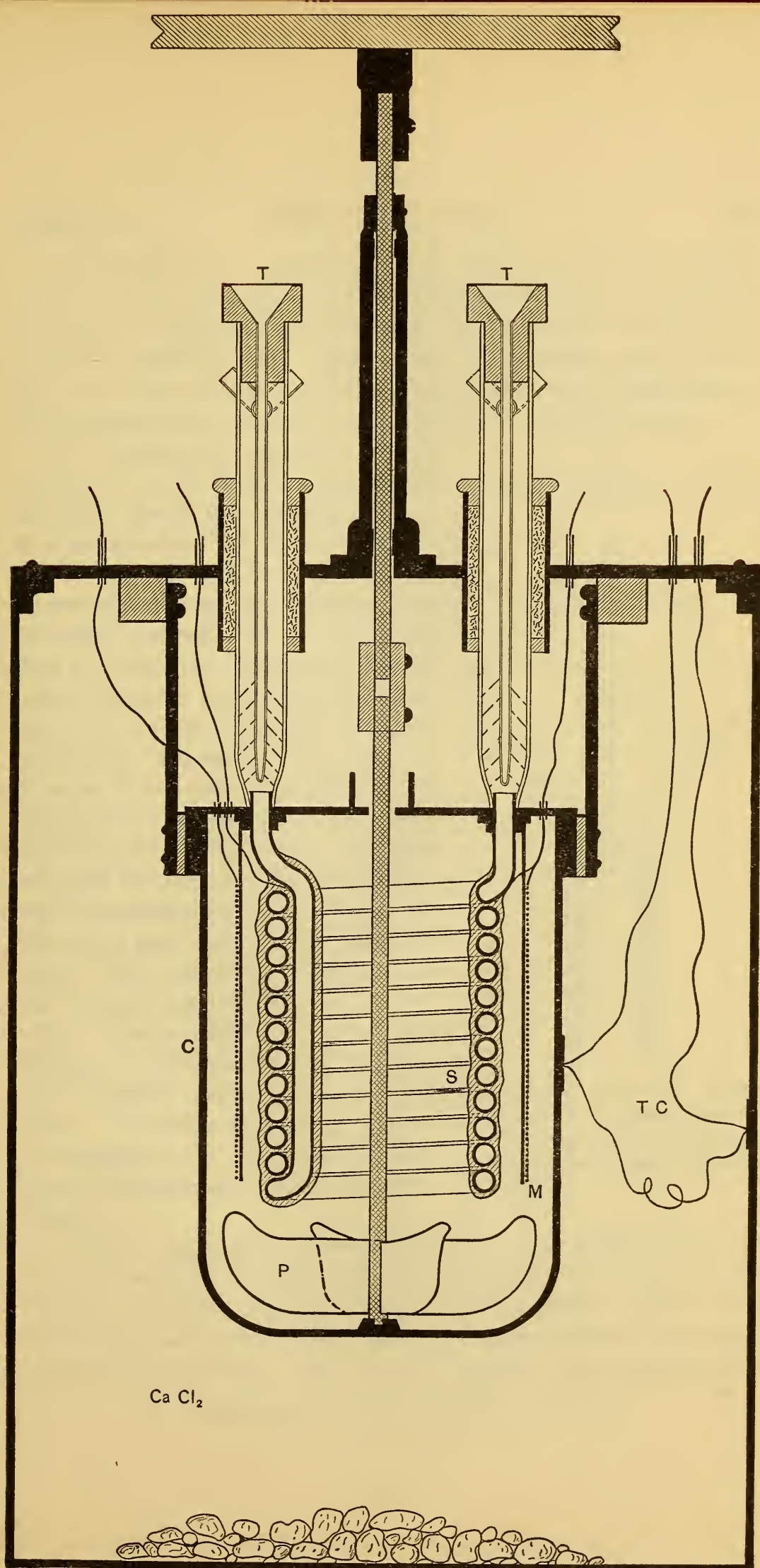
Fig. 1.—*Continuous-flow calorimeter for determining the specific heat of brine.* C, *calorimeter proper;* S, *brine coil;* M, *heating coil;* P, *stirrer;* TC, *thermo-couple;* T, T, *thermometer cases.*

In operation, the calorimeter (C) is kept at the same temperature as the surrounding vessel, equality being shown by means of the copper-constantan thermocouple (TC) connected directly to a sensitive galvanometer. Differences of temperature not exceeding one or two tenths of a degree may occur, and a calibration of the thermocouple enabled a correction to be made for them.

The centrifugal propeller (P) is driven by a belt from a small motor and the speed kept constant by a friction governor on the motor.

The use of two heating coils, as mentioned above, one of which is in intimate contact with the brine coil but not with the calorimeter liquid, while the other is immersed directly in the calorimeter liquid, makes it possible to choose both the rate of flow of brine and the difference of temperature between inlet and outlet within rather wide limits, by simply varying the ratio of the amounts of energy supplied by the two coils. In this way, also, observations could be made with the same solution over the same temperature range, but with either a small or a very large difference between the temperature of the outer bath and that of the brine. This was done in a number of instances as a check on the accuracy of the method, with satisfactory results.

Fig. 2.—*Wheatstone bridge and thermometer circuit, showing the method of connecting platinum-resistance thermometers for obtaining temperature differences.*

Auxiliary apparatus.—Measurement of the temperature difference between the inlet and outlet is made by means of two sensitive platinum resistance thermometers, which, together with the bridge used in making the resistance measurements, have been previously described.[1] The two thermometers are inserted in the
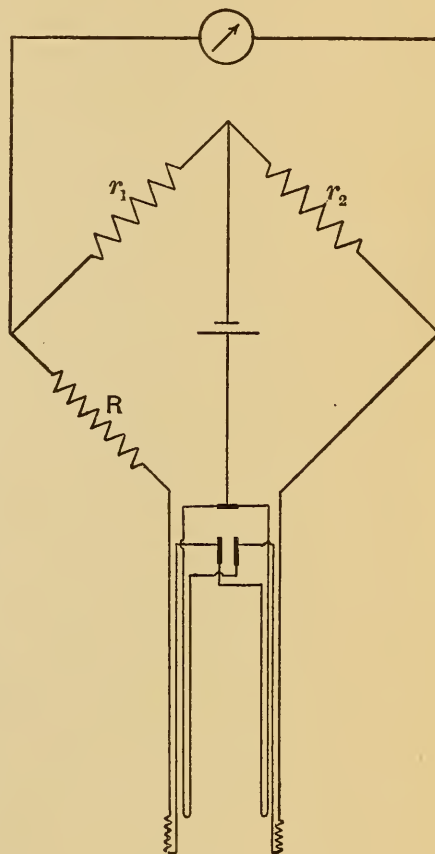
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[1] This Bulletin, **3**, p. 641; 1907 (Reprint No. 68).

sheaths previously mentioned and the leads connected so that the difference in the resistances is measured on the bridge. The arrangement of the thermometers in the bridge circuit is shown in figure 2. The resistances are set to the nearest 0.01 or 0.005 ohm on the bridge, corresponding to 0°.1 or 0°.05 in temperature and the additional figures to .0°.001 are determined from galvanometer deflections. The galvanometer used gave a deflection of about 7 millimeters per 0°.1. The measurement of this difference offers considerable difficulty on account of the imperfect mixing of the emergent stream of brine in passing the thermometer and because the difference is not quite constant, sometimes varying by as much as 1 per cent. Equalization of temperature throughout the stream was secured by adding the vanes to the thermometer sheaths, while the mean temperature difference was computed from readings taken at ten-second intervals. The temperature of the brine as it enters the calorimeter is measured occasionally by means of the thermometer in the inlet side. This temperature need not be known closer than a few tenths of a degree.

In addition to the temperature measurement, the determination of specific heat with this calorimeter required measurements of time, mass, and electrical energy. The time (usually a ten-minute interval) was taken by means of a carefully rated watch, read with a telescope, and this measurement is reliable to about 0.05 per cent. An outlet tube is provided, which can be quickly turned at the beginning and end of a run to let the stream flow either into the weighing bottles or the waste bottle. The weight of brine which flowed through the calorimeter in ten minutes ranged from 3 to 5 kilograms and was weighed to tenths of a gram in the large glass bottle which received it.

The electrical energy supplied (at the rate of 100 to 300 watts) during the time the brine runs into the weighing bottle is computed from the time, the current flowing, and the difference of potential across the terminals of the heating coils. These measurements are made with a potentiometer in connection with a 0.1 ohm standard resistance and a volt box. The measuring system is protected against leakage from the high potential used on the heating coils by an equipotential shield.[2] When the two heating

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[2] W. P. White, Potentiometer Installation, Phys. Rev. **25**, p. 340; 1907.

coils are used in parallel, each with its separate rheostat, the volt
box is switched from the one to the other while the standard
resistance is used to measure the total current. If the resistances
of the two coils under working conditions are known the total
energy can be computed. The electrical instruments have been
frequently calibrated and measurements are all corrected to 0.01
per cent.

The supply of brine for these experiments is contained in an
iron tank of about 100 liters capacity, immersed in a larger tank
of brine containing an ammonia expansion coil for cooling to the
desired temperature. The whole is so well packed with ground
cork that the temperature of the inner tank changes only $0°.2$
or $0°.3$ per hour at $-35°$. The brine tank is arranged to give a
constant head.

Observations.—Two observers are required and the observations
are carried out in the following manner. After the supply of brine
has been brought to the desired temperature, the brine is allowed
to flow through the calorimeter, and the rate of flow adjusted to
give about 400 grams per minute, and at the same time the switches
are closed to send current through the heating coils. The current
in the inner coil is then adjusted to give the desired rise of tem-
perature (usually $10°$), and finally the current in the outer coil is
adjusted to maintain the calorimeter temperature the same as that
of the outer vessel as shown by the thermocouple. When all con-
ditions are steady the flow of brine is switched into the weighing
bottle and allowed to run for exactly ten minutes, while one
observer takes temperature readings every ten seconds and the
other reads current and voltage and observes the temperature
difference between the inner and outer vessels, and the time.
Finally, the brine is weighed and its density determined.

Computation.—If the change of specific heat between tempera-
tures T_1 and T_2 is proportional to change in temperature, then the
specific heat σ at the temperature $\dfrac{T_1 + T_2}{2}$ may be computed from
the following formula:

$$\sigma = \frac{(E_1 I_1 + E_2 I_2)t + m}{JW(T_2 - T_1)}$$

Where E_1 and E_2 are the potential differences at the terminals of the inner and outer coils, respectively; I_1 and I_2 the currents in these coils; t the time; and m a correction term (seldom amounting to 1 per cent of the total energy) to account for the energy due to stirring and change in the temperature of the calorimeter; W is the mass of brine; T_1 and T_2 the inlet and outlet temperatures; and J the number of joules per calorie, on the basis of the electrical units used. In these computations J has been taken as 4.196. The electrical units are the international ohm, and volt equal to $\dfrac{1000}{1434}$ of the emf. of the Clark cell at 15° C.

The following Table I is a sheet taken from the observations to serve as an illustration:

Date 2–24–08. Ten-minute run. Brine density 1.203. Two heating coils in parallel. Inlet temperature −20°0 C. Calorimeter temperature 0°00 (ice bath outside). All figures given have been corrected for instrumental errors and are the means of several readings.

	Inner coil.	Outer coil.	
Potential difference	60. 459 volts	29. 067 volts	
Resistance (under working conditions)	22. 757 ohms	22. 475 ohms	
Observed sum of currents			3. 9501 amp.
Computed currents	2. 6568 amp.	1. 2933 amp.	
Computed sum of currents			3. 9501 amp.
Power	160. 63 watts	37. 59 watts	
Energy $(E_1 I_1 + E_2 I_2)\,t$			118930 joules
Energy supplied by stirrer (261 R. P. M.)		+409	
Energy for change in temp. of calorimeter (−0°08)		+209	
Total correction to energy, $(m) = +409 + 209$			+618
Energy supplied to brine			119550 joules
Weight of brine			3999. 6 grams
$T_2 - T_1$ (from 50 readings)			10°155

$$\text{Specific heat at } +14°9 \text{ C.} = \frac{119550}{3999.\,6 \times 10.\,155 \times 4.\,196} = .7021$$

Results.—Results have been obtained for solutions of one of the purest commercial calcium chlorides at densities 1.259, 1.203, 1.140, 1.071, and for pure water. The latter was used as a check on the apparatus and method. The analysis of this sample of calcium chloride is given under No. 4, in Table VI.

The following Table contains the results of all the observations on a solution of density 1.203:

TABLE II.

Density 1.203

No. of Obs.	$\dfrac{T_1+T_2}{2}$	T_2-T_1 approximate	σ	Obs.—comp.
	° C.	° C.		
4	+ 3.8	9.7	.715	+.002
4	+ 4.9	10.0	.716	+.001
4	+13.7	10.3	.720	.000
1	+11.3	5.4	.717	—.001
3	—14.9	10.0	.703	+.001
2	— 7.2	5.0	.706	.000
2	— 4.8	9.1	.708	+.001
4	—16.5	10.2	.699	—.002
4	— 2.5	10.3	.708	—.001
4	+14.6	10.1	.720	—.001

The results of all the observations on this sample are summarized in the following formulas:

$$\text{Density } 1.260 \quad \sigma = 0.666 + .00064\, t \quad (\text{from } -35° \text{ to } +15° \text{ C})$$
$$\text{``} \quad\quad 1.200 \quad \sigma = .708 + .00064\, t \quad (\quad\text{``}\quad -20° \text{ ``} +15° \text{ C})$$
$$\text{``} \quad\quad 1.140 \quad \sigma = .772 + .00064\, t \quad (\quad\text{``}\quad -10° \text{ ``} +15° \text{ C})$$
$$\text{``} \quad\quad 1.070 \quad \sigma = .869 + .00057\, t \quad (\quad\text{``}\quad 0° \text{ ``} +15° \text{ C})$$

where σ is the specific heat and t is the temperature. All densities are referred to a temperature of 20° C in terms of water at 4°. It will be noted that the relation between specific heat and temperature is linear within the limits of observational error. The following table is computed from these formulas:

TABLE III.

Temp.	Density 1.26	Density 1.20	Density 1.14	Density 1.07	Water .998
° C.					
—35	.644				
—30	.647				
—20	.653	.695			
—10	.660	.702	.766		
0	.666	.708	.772	.869	
+10	.672	.714	.778	.875	
+15	.676	.718	.782	.878	.9995

II. THE VACUUM-JACKETED CALORIMETER.

(H. C. Dickinson and E. B. George.)

Since an important part of this investigation is the comparison of the specific heats of different samples of commercial calcium chloride, a method was sought which would be more convenient than the flow calorimeter had proved to be, which would require a smaller amount of each sample of brine, and at the same time would serve as a check on the accuracy of the previous results. The somewhat familiar device of using a Dewar flask to reduce the heat transfer between the calorimeter and its surroundings seemed, with some modifications, to offer a basis for the construction of a calorimeter which could be filled with a weighed amount of cold liquid, as much as 50° below room temperature, and used in the ordinary manner, by measuring the heat supplied and the rise of temperature. After some preliminary experiments, a spherical Dewar bulb of about 6 liters capacity and with an excellent vacuum was selected as a basis of construction.

The method requires that the bulb be filled to a given level with the sample of solution at the lowest temperature to be observed and that the temperature be raised in steps (usually 5 degrees) by supplying energy electrically, alternating with accurate measurements of temperature by means of a platinum resistance thermometer, and finally that the amount of solution used be determined by weighing in the calorimeter. The calorimeter and auxiliary apparatus as finally used are described in the following pages.

Calorimeter.—The calorimeter proper, as shown by the accompanying figure 3, is a 6-liter, silvered, spherical Dewar flask D fitted with a brass top B, firmly fastened in place by means of plaster of Paris. A hard rubber cover C is fitted to this top and held in place by two thumb nuts. This removable cover supports rigidly the following: First, a heating coil H built up of two layers of "Advance" resistance ribbon, wound over mica on a thin brass tube and closed in by covering it with a sheet of very thin copper. The coil is thus hermetically sealed, and the brass and copper covering is protected from the action of the salt solution by a coating of elastic varnish. Current and potential leads from
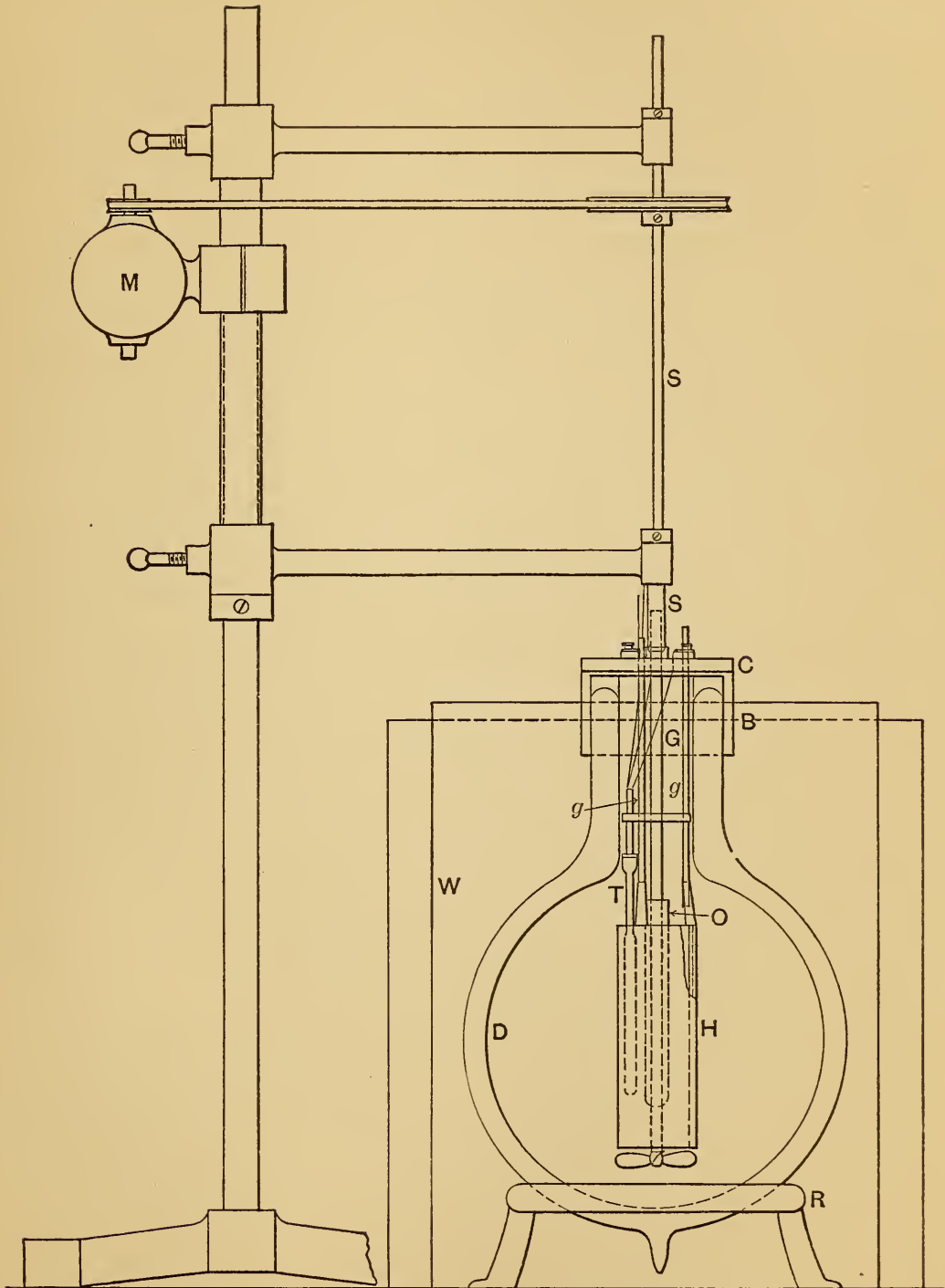
Fig. 3.—*Dewar flask calorimeter and accessories.*

this coil are led out through two of the three glass tubes g which support the coil from the cover. The third of these glass tubes has a small opening at the level of the top of the liquid in the calorimeter, and serves to indicate when the calorimeter is filled to the proper height and to draw off any excess of liquid. While filling, this tube is kept connected to the vacuum system, and the sound indicates when the liquid reaches the small inlet hole. Second, a very sensitive resistance thermometer T inclosed in a thin copper sheath and constructed in a manner similar to the two thermometers used in the first part of this investigation, except that three leads are used instead of four and the sensibility is somewhat greater. Third, an overflow tube O, which is continuously immersed in the liquid and serves to take up the amount which expands on heating. This device keeps the level of the liquid constant during an experiment, thus avoiding change in the amount of glass surface submerged and consequent change in the water equivalent of the calorimeter. The stirring device is also loosely supported from the cover in such a way that during operation there is no contact between the two. This stirrer consists of a glass tube G fitted at one end with a screw propeller and at the other end with a tapered brass sleeve fitting rigidly within the stirrer shaft S, which runs in bearings above the calorimeter and supports the glass tube and propeller free from contact with the calorimeter cover. The glass tube serves for filling or emptying the calorimeter, so that either operation can be carried out with the calorimeter fixed in position. The propeller is placed just below the hollow cylindrical heating coil so that a positive circulation is produced.

When in use the calorimeter rests on a rubber-covered ring R within a double-walled galvanized-iron tank w, and is immersed in a mixture of ice and water, or, for higher temperatures, in water only, at constant temperature.

Auxiliary apparatus.—The auxiliary apparatus used may be considered under three heads, mechanical, electrical, and apparatus for measurement of time. The mechanical arrangements for cooling the brine and filling the calorimeter are shown in figure 4. The solution to be used is prepared and cooled by immersing earthen jugs of the same in the brine reservoir of the
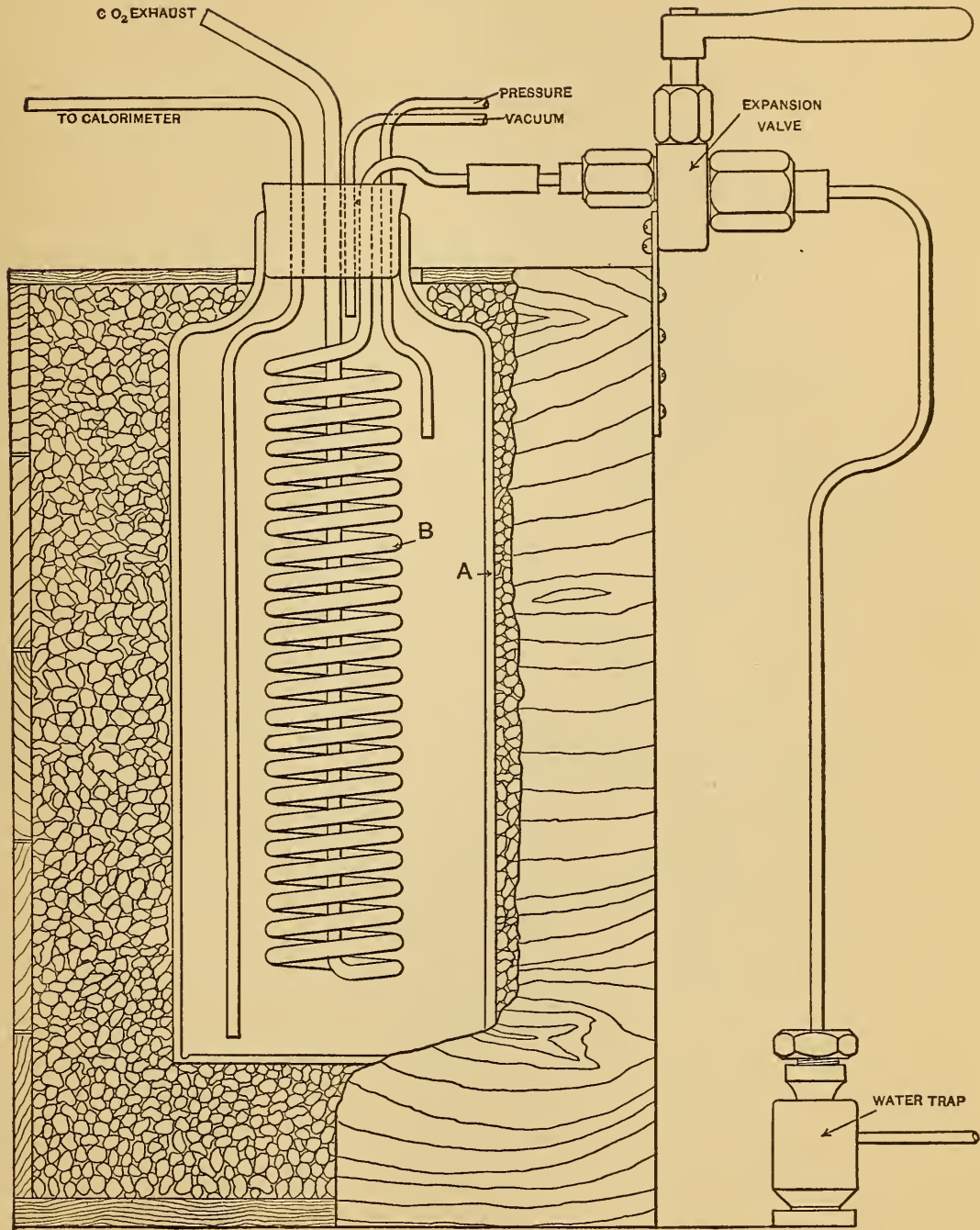
Fig. 4.—*Apparatus for cooling brine and filling calorimeter.*

bureau refrigerating system. When cooled the solution is drawn from the jugs into the refrigerating bottle A and there cooled by expansion of carbon dioxide in the coil B until crystals of ice begin to show. Enough of the solution is then forced from the bottle A into the calorimeter by means of compressed air to bring the surface of the solution in the calorimeter to the outlet previously described. At the end of a set of observations when the temperature within the calorimeter has been raised to 15° or 20°, the calorimeter is removed from the containing tank, carefully dried, and weighed by suspending it directly from the arm of a balance. From this weighing and the known weight of the calorimeter the weight of solution is found.

The electrical measurements consist of a determination of temperature by means of an accurate resistance thermometer used in connection with the special resistance bridge referred to in the previous part of this paper, and a determination of current and voltage during the time when the heating current is flowing through
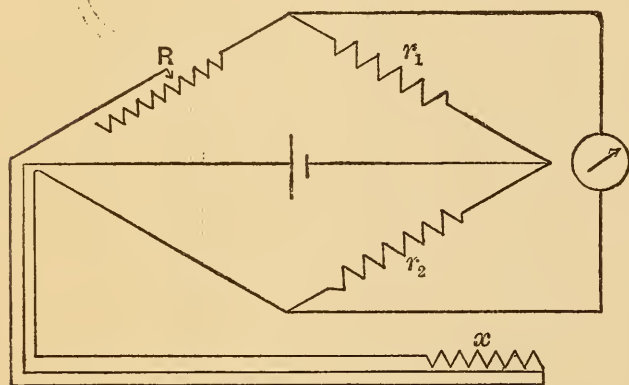

Fig. 5.—*Wheatstone bridge and thermometer circuit.*

the calorimeter heating coil. The arrangement of the thermometer and bridge circuits is shown in figure 5. Since measurements must be taken with a changing temperature the method used is to set the bridge resistance to a given value and note the time when the galvanometer deflection becomes zero. Several such observations are taken at temperature intervals corresponding to from 0°.01 to 0°.001, according to the rate of temperature change. The arrangement of circuits for measurement of current and voltage and for recording the time is shown in figure 6. The adjustable resistance R is made equal to the resistance of the heating coil in the calorimeter, so that on throwing the quick-break switch S, no change is made in the current taken from the storage battery, and by using a battery which is partly discharged it is possible to keep the current constant to

well within 0.01 per cent for the time (usually five minutes) during which it is flowing through the heating coil. Measurements of current and voltage are taken alternately by throwing the switch *K*, which connects the potentiometer with either the standard 0.1 ohm or the volt box. All the resistances in the bridge, potentiometer, and volt box, and the standard 0.1 ohm were often checked, as in the first part of the work.

For the measurement of time a tape chronograph is used in connection with the Riefler clock kept by the Division of Weights and Measures. By the arrangement of switches shown in figure
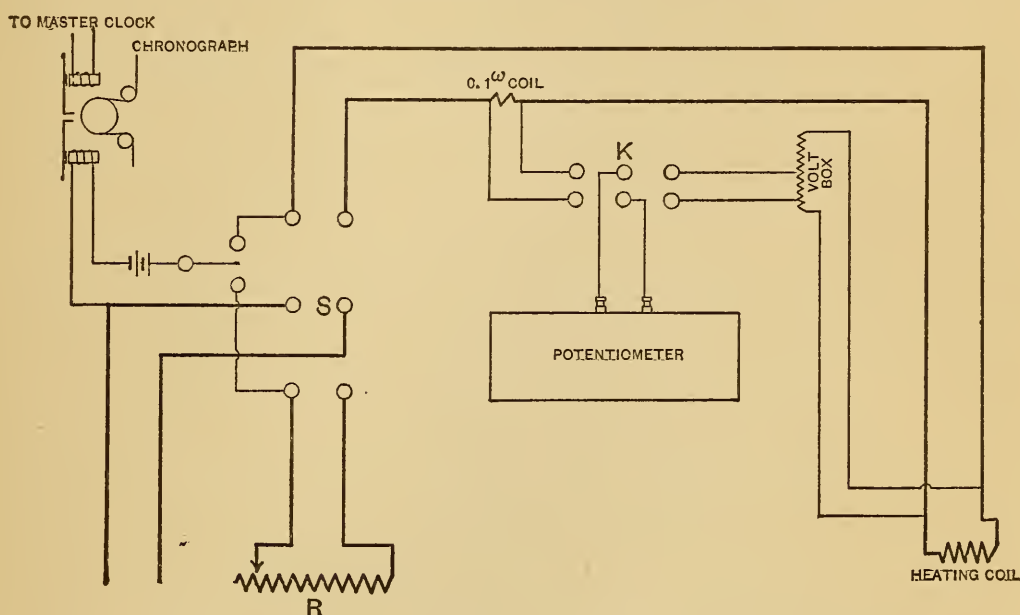
Fig. 6.—*Diagram of circuits used for measuring energy and operating chronograph.*

6 the operation of throwing the switch *S* automatically closes the chronograph circuit. The chronograph tape runs about 1 centimeter per second, so that times can be read easily to 0.02 or 0.03 second. The quick-break switch *S*, which operates the main current circuit and the chronograph circuit, is so made that there is not more than 1 or 2 millimeters of motion between the opening of the circuit on one side and the closing of the circuit on the other side. The time required to move this distance evidently enters as an error in the chronograph time interval, but since this error could not exceed a few thousandths of a second or a part in 100,000 it is neglected.

Calibration of the calorimeter.—The first step in the calibration of a calorimeter is usually the determination of its water equivalent. In the present case the water equivalent of the glass forming the inner wall of the Dewar bulb, up to the level of the surface of the liquid used, amounts to only about 1 per cent of the water equivalent of the solution, and the water equivalent of the heating coil, thermometer, stirrer, and overflow tube amounts to about 1 per cent more. Though the total water equivalent is thus only 2 per cent, its determination offers considerable difficulty. To determine this constant, observations were made with the calorimeter filled with pure water up to the designated level, measuring the energy supplied and the rise of temperature in the usual manner. Then three light rubber balloons having a volume of about 700 cubic centimeters were fastened down within the calorimeter and observations were taken with the water level the same as before but with the total mass of water some 700 grams less. By a comparison of these two sets of observations it is evident that the water equivalent may be computed independently of the value of the calorie in electrical units, but the accuracy of the water equivalent obtainable by this method is so far below the accuracy of the observations themselves that the method was considered impracticable.[3] The only way to improve the relative

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[3] Assuming two observations made under similar conditions, except that the amount of water in the calorimeter is changed and the corresponding energy supply is so regulated that the same temperature rise is measured in the two cases, the equations

$$(W_1+x)\theta J=E_1 \qquad (W_2+x)\theta J=E_2$$

represent the two observations.

W_1 and W_2 are the amounts of water used

E_1 and E_2 are the total energy supplied

x is the water equivalent to be found

θ and J are respectively temperature rise and the mechanical equivalent.

Combining the two above equations to eliminate J, and differentiating with respect to E and x

$$(W_1+x)dE_2+E_2dx=(W_2+x)dE_1+E_1dx$$

Let K be the ratio $\dfrac{W_2+x}{W_1+x}$ then $W_2+x=K(W_1+x)$ and $E_2=KE_1$.

Substituting to eliminate E_2 and W_2 and making $dE_2=-dE_1=dE$ and writing $W_1=W$ and $E_1=E$.

$$(W+x)dE+KEdx=-K(W+x)dE+Edx$$

accuracy would have been to increase the amount of water displaced by the rubber balloons and a further enlargement of them would have changed the conditions of the experiment without greatly increasing the accuracy. Since the object aimed at was a determination of the specific heat of calcium chloride solutions in terms of water, and since the volume specific heat is not very different for these solutions and for water, it is evident that a computation of the water equivalent based upon an assumed value of the specific heat of water in terms of the electrical units, may be used throughout the series of experiments without introducing in them more than a small fraction of any error in the assumed specific heat of water.[4] The calorie is taken as 4.196

$$dE(W+x)(1+K)=Edx(1-K)$$

$$\frac{dx}{W+x}=\frac{dE}{E}\frac{1+K}{1-K}$$

Or the percentage error introduced by using a value of x found in this way is equal to $\frac{1+K}{1-K}$ times the percentage error in the energy measurement used to determine x. The same would be true if θ were varied instead of E. In the present work $K=.8$, so that $\frac{1+K}{1-K}=9$, i. e., an error of 0.1 per cent in energy measurements or temperature differences used for determining the water equivalent might introduce an enormous error in the value found for the water equivalent and a systematic error of 0.9 per cent in the final value of the specific heats.

[4] Suppose that the water equivalent x is determined by assuming the value of J and that the same values of x and J are used in a subsequent specific heat observation, the two equations

(1)	(2)

$$(W+x)\theta J=E_1 \qquad (M\sigma+x)\theta J=E_2$$

(using the notation of the previous note with $M\sigma$ the product of mass of brine and its specific heat) represent the observations.

Substituting $x=\frac{E_1}{\theta J}-W$ from (1) in (2)

$$\left(M\sigma+\frac{E_1}{\theta J}-W\right)\theta J=E_2$$

differentiating with respect to J and σ and dividing by θJ

$$M\sigma dJ+MJd\sigma-WdJ=0$$

$$\frac{d\sigma}{\sigma}=-\frac{dJ}{J}+\frac{W}{M\sigma}\frac{dJ}{J}=\frac{dJ}{J}\left(\frac{W}{M\sigma}-1\right)$$

joules throughout this investigation. The method of observing and of computing the results for determination of the water equivalent is the same as for determinations of specific heat, described later, except that for observations with water the space outside the calorimeter was filled with water kept at a constant temperature and stirred during the observations.

Radiation rate.[5]—The radiation rate for the calorimeter was found to be, as might be expected, proportional to the temperature difference between the inner and outer walls, to within the limits of observational error. This being the case, it seemed probable that the most reliable results would be obtained by the use of a radiation constant deduced from a series of observations rather than the rate obtained from each observation. For the determination of this constant, careful observations were made of the rate of temperature rise of the calorimeter with the stirrer running at constant speed, when the temperature within the calorimeter ranged all the way between $-35°$ and $+20°$, with the outside temperature at $0°$ C. The stirrer is so mounted that there is no possibility of any friction within the calorimeter except fluid friction, and the rate of stirring was regulated by means of a friction governor so that the energy supplied by the stirrer, only a few tenths of a watt, could be taken as constant. The temperature at which the calorimeter, with the stirrer running, was in equilibrium with its surroundings was determined from radiation rates taken near this equilibrium temperature, and the loss (or gain) of heat by the calorimeter was determined in joules per second per degree difference between this equilibrium temperature and the observed temperature of the calorimeter.

(Note continued from page 393.)

Therefore a percentage error in the assumed value of J produces in the final result, a percentage error only $\left(\dfrac{W}{M\sigma}-1\right)$ times the error in J. In the present case

$$0 \mathrel{\overline{7}} \left(\frac{W}{M\sigma}-1\right) \mathrel{\overline{7}} -0.2$$

i. e., an error of 1 per cent in the assumed value of J would introduce an error of from 0.0 per cent to 0.2 per cent in the results.

Evidently if $W=M\sigma$ (that is if the total water equivalent of the liquid in the two cases is the same) J is entirely eliminated.

[5] "Radiation rate" here refers to the change of temperature due to all outside causes.

Observations of the radiation constant for different temperàtures between $-35°$ and $20°$ C indicate that it changes by a small amount, perhaps 5 per cent, but this change can not be readily determined and the use of different values is inconvenient. For this reason a method of computation was adopted which allows the use of the mean radiation constant over the whole range without introducing any error greater than that in the determination of the mean constant itself. The method is as follows:

The total correction in joules for an observation is $j = cT(\theta - \theta_0)$ where c is the radiation constant, T is a time interval, θ and θ_0 are respectively the mean temperature of the calorimeter and the equilibrium temperature.[6] If the radiation rate is observed at two temperatures, say $20°$ below and $20°$ above θ_0 and if the values of c as computed from these two rates and the observed θ_0, differ slightly, a small change in θ_0 will serve to make the two values of c equal, leaving the total observed corrections the same, so that no error is introduced at $+20°$ and $-20°$ by using these new values of c and θ_0. At other temperatures nearer θ_0 a small error is introduced which is greatest near θ_0 where $\theta - \theta_0$ is small.

In practice the value of c taken from a series of observations is $.197 \pm .002$; T is about 300 seconds, θ_0 *assumed*, never differs by more than $1°$ from the mean *observed* value, the total supply of energy in any one determination is about 100,000 joules, therefore the maximum error is 60 joules in 100,000, or .06 per cent.

The following table gives the series of values found for this constant and the mean which was used in all the computations.

TABLE IV.

$\theta - \theta_0$	c	$\theta - \theta_0$	c
$+20°$	0.190	$-25°$	0.205
$-19°$	0.191	$-23°$	0.188
$+20°$	0.198	$-22°$	0.195
$+21°$	0.204	$+20°$	0.201
$+20°$	0.193	$-19°$	0.206

Mean $c = 0.197$.

[6] That is, the temperature at which the "radiation rate" becomes o.

The total correction to be applied for radiation seldom exceeds 2 per cent and that only at the lowest temperatures in the case of the more dense solutions.

Method of observation.—A series of observations on a single filling of the calorimeter generally consists of from five to eight independent parts, each of which gives a mean value of specific heat for a temperature range of 5 degrees. These observations range from the lowest temperature at which the solution can be used up to room temperature, and are carried out in the following manner. After the calorimeter is filled with cold brine, as previously described, the stirrer is connected up and started. As soon as temperature equilibrium is established within the liquid, a series of observations of temperature is begun. At the lowest temperatures there are sometimes differences of temperature in the mass of the liquid amounting to as much as a hundredth of a degree, as shown by irregular indications of the resistance thermometer, so that in order to get a satisfactory measurement of the temperature of the whole mass some ten observations are made, as follows. The bridge is set for a resistance a little higher than that of the thermometer and the time is recorded when the galvanometer shows that a balance is reached, then the bridge is again set for a higher resistance, and so on by steps of .001 to .0005 ohm, corresponding to 0°.01 to 0°.005 C.

The mean of these resistances is taken as the true resistance at the mean time observed, and the true temperature is thus determined.[7] When a satisfactory temperature measurement has been made the heating current is switched on to the calorimeter coil at a given time, the exact time is automatically registered on the chronograph tape, which is only allowed to run for a few seconds to include the even minute on the clock and the time of throwing the switch. The observer's watch is relied upon for starting the chronograph and throwing the switch. As soon as the switch is thrown an observer begins to take alternate readings, on the potentiometer, of current and voltage as described in connection with the electrical apparatus. At the end of five minutes (usually) the

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[7] Sometimes two such sets of observations were made, separated by an interval of several minutes, in order to compute or check the value of the radiation constant *c*.

current is thrown off, the time being again noted automatically, and as soon as the temperature distribution in the calorimeter becomes uniform a second series of temperature measurements is begun, as previously described. When the temperature in the calorimeter approaches that of the outside the change due to radiation becomes less and observations are taken at smaller temperature intervals down to $0°001$. In this way alternate observations are taken on the temperature and the energy supplied. The energy supply at each step is sufficient to raise the temperature about 5 degrees. A sample sheet (Table V), taken directly from the series of observations, shows the method of observing and computing results.

The formula used in the above computation is as follows:

$$\sigma = \frac{1}{W\theta}\left\{\frac{EIT+j}{4.196} - \theta x\right\}$$

in which

σ = Specific heat.

E = emf. at terminals of heating coil (volts).

I = Current in amperes.

T = Time during which the current passes.

j = Radiation correction in joules.

θ = Difference of temperature produced by the energy supplied electrically and by radiation.

x = Water equivalent of the calorimeter and accessories.

W = Weight of brine.

The temperature differences θ are the differences of resistance $R_2 - R_1$, $R_3 - R_2$, etc., each multiplied by a factor which depends upon the constants of the particular platinum thermometer, and upon the mean resistances $\frac{R_2 + R_1}{2}$, $\frac{R_3 + R_2}{2}$, etc.

The radiation correction j, which amounts to less than 2 per cent of the energy supply, is computed in terms of energy and difference in resistance of the resistance thermometer from its resistance at the equilibrium temperature of the calorimeter. The constant c (p. 395) is in practice modified to correspond with differences of resistance instead of differences of temperature.

TABLE V.

[Sample observation sheet.]

Department of Commerce and Labor
BUREAU OF STANDARDS
Washington

Made by ....
Date *11.-10.-08*

Book No. ....
Page No. ....*1*...........

Density of brine at 20° C = 1.2033
Sp. Ht. correction to brine of density 1.200 = +.0027

7 9 2 6.7	wt. of flask + brine
1 4 6 1.3	" "
6 4 6 5.4	" "
6.5	bouyancy correction
6 4 7 1 9	corrected wt of brine = w

				Setting	Diff	Time	Coils.
				.05050	18	2- 47- 5	20.00551
				.05100	20	47-23	10.00267
				.05150	21	47-43	.2,0095
				.05200	21	48- 4	2,0054
				.05250		48-25	.00011
$\Delta R = 2.12$ w	$R = 31.48570$ w						1.00070
$K_1 = 3.18$	$T_1 = 3- 4- 5$			.07200	49	3- 2-32	31.40998
$T = 275.$	$d_r = .61810$ w			.07300	45	3-21	.00172
$J = 875$	$\theta = 4.6304$			.07400	46	4- 6	31.41170
	$w\theta = 2.9966$			.07500	42	4-52	.07400
	$\theta x = 454$			.07600		5-34	31.48570 w
	Mean Temp.= 13.35			.07400	mean	3- 4- 5	

Time.	Volts	Amperes	E I T	
3- 6- 0	54.304	54.144	88050	89728 = Joules Corrected.
Chr. 3.64	54.304	54.142	+ 875	21361 = Calories (C)
	54.304	54.142	+ 803	454 = θx
11- 0	54.305	54.141	89728	20907 = $C - \theta x$
Chr. 3.50	54.303	54.192		.6980 = $c - \theta x / w\theta$
299.86	54.304	- 6		.0027 = Density Cor.
	- 65	54.137		.7007 = σ (Sp. Ht.)
	54.239			

				.00150	29	3-13-38	20.00551
$\Delta R = 1.40$ w				.00200	42	14- 7	10.00267
$k_2 = 2.10$				.00250	31	14-49	1.00036
$T_2 = 382$				.00300	34	15-20	.05011
$J = 803$				.00350	32	15-54	.02000
	$R_2 = 32.10380$			.00400		16-26	.02000
	$T_2 = 3- 15- 2$						1.00066
	$d_r = .60967$			.00275		3-15-2	32.09931
	$\theta = 4.5733$						.00174
	$w\theta = 2.9597$						32.10105
$T_2 = 278$	$\theta x = .447$						
$J = 584$	$M T = 8.65$						

3- 17- 0	54.299	54.135	88100	89118			
3.33	54.300	54.135	+584	21217			
	54.300	54.132	+434	447			
22- 0	54.298	54.130	89118	20770			
3.54	54.298	54.133		.7017			
300.21	54.299	- 5		.0027			
	- 65	54.128		.7044			
	54.234						

$\Delta R = .89$				.00100	28	3-23-48	20.00551
$k_3 = 1.34$				.00120	26	24-13	10.00267
$T_3' = 324$				.00140	21	24-39	1.00036
$J = 434$				.00160	25	25- 0	.50029
				.00180	35	25-25	.2,0054
	$R_3 = 32.71347$			.00200	22	26- 0	1.00070
	$T_3 = 3- 25- 4$			.00220		26-22	32.71009
							.00178
Process continued to			.00160		3- 25-4	32.71187
+20.0 C							

A study of the temperature rise of the calorimeter during the time when energy is being supplied to raise its temperature about $1°$ per minute indicates that the effective radiating temperature of the outer surface of the calorimeter lags about ten seconds behind the temperature as computed from the energy supplied, except at the beginning and end of the rapid temperature rise. But the variations at the beginning and end were found to almost exactly balance each other, so that for the purpose of computation it is assumed that the radiation rate K_1 holds from T_1 to a time ten seconds later than the middle point of the time while energy is being supplied, and that the radiation rate K_2 holds from this point to the time T_2.

Sources of error.—The errors in this determination of specific heats may be conveniently discussed under the heads of systematic errors and fortuitous errors. The chief sources of systematic errors are evidently in the determination of water equivalent, radiation constant, and calibration of the resistance thermometer and resistances. A constant error in the timing device might be considered, but in this case any error here has been shown to be too small to consider in comparison with the others. The water equivalent was determined with an apparent probable error of less than 2 per cent and the radiation constant with an error of less than 4 per cent. Since the water equivalent itself is only 2 per cent the probable error due to this determination is under 0.04 per cent. Since the radiation correction is less than 1 per cent for all but the lowest temperatures the probable error due to radiation is of about the same magnitude. Errors in the electrical measurements were always kept smaller than 0.02 per cent. The results at $0°$ as compared with those obtained by means of the continuous-flow method described in the earlier part of this paper show no difference as great as 0.05 per cent, except for brine of a density 1.26 which was so viscous that the results by the continuous-flow method were always somewhat in doubt.

Since the calibration of the calorimeter was carried out with the surrounding bath at a temperature of about $20°$ C while the observations on brine were made with this bath at $0°$, it is evident that an error in the method of correcting for radiation, as described above, would enter systematically into the results. With this fact

in view, a series of observations were taken on the same sample of brine of density 1.07, first with the outer bath at 0°, then at 25°. The mean results of these two series were identical, showing that whatever error exists is too small to be observed.

Errors which are purely accidental may occur in so many parts of the observations that a full discussion of them can not be undertaken here. The weighing of the mass of brine used in the calorimeter and determination of density were subject to the most serious error and an error in either of these measurements affects a series of from five to eight specific heats. Weighings were made to 0.01 per cent, but because of an unexplained steady change in the weight of the empty calorimeter amounting to nearly 0.1 per cent of the weight of brine, the weighings, taken at frequent intervals, are reduced to correspond to individual weighings of the filled calorimeter, and on this account the final weights may be in error by 0.02 or 0.03 per cent. The density determinations have about the same order of accuracy as the weighings of brine. Densities were determined by weighing samples of the brine used in each series of determinations in a calibrated liter flask. Uncertainties in the true mean temperature of the whole mass of brine in the calorimeter, because of imperfect stirring, seem to have affected the results for the less dense solutions.[8] The final collection of data shows that the accidental errors are much larger in the case of lower densities, and since all other causes of error are the same or less for these solutions and the different sets of observations are interspersed so that not all the observations on the denser brine came together, it seems to be shown conclusively that the lack of uniformity in temperature is almost entirely responsible for the larger range of observational errors for the less dense solutions. This defect could have been readily eliminated if it had been suspected, but the apparent regularity of the temperature changes at all temperatures except the lowest, indicated that equilibrium was established to within 0°.001 or 0°.002.

Considering all the sources of error, the accuracy of the final results should exceed 0.1 per cent at all points. In the case of

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[8] At first thought it appeared that the mixing of the less dense solutions must be better than that of the more dense, but it is evident upon further thought that the apparent constancy of the thermometer in the less dense solutions may indicate merely uniformity of the stream lines, while an unstirred layer remains next the walls. With greater viscosity this layer is set in motion.

the more dense solutions, the variation of observed values from a
smooth curve does not exceed this amount at any point. From
the nature of the case an accuracy greater than this is not of suffi-
cient importance to warrant further observations. The appa-
ratus in its present condition, however, can be relied upon to give
an accuracy of better than 0.1 per cent for any single observa-
tion provided sufficient care is taken in making the individual
measurements and provided the rate of stirring is increased for
solutions of low density.

Samples of calcium chloride tested.—The present investigation
comprises observations on solutions of C. P. calcium chloride at
densities of 1.07, 1.14, 1.20, and 1.26, on solutions of calcium
chloride from the same lot as that used in the flow calorimeter
and on samples from three other sources. The samples differ
largely in composition, as is shown by the following chemical
analysis (Table VI) made by the Chemical Division of the Bureau
of Standards on samples of the solution after the specific heat
determinations.

TABLE VI.

Chemical Analyses of Commercial Samples.

	No. 1	No. 2	No. 3	No. 4
$CaCl_2$	17.72	19.09	16.33	24.75
$MgCl_2$	6.53	3.92	5.98	0.00
NaCl	.62	0.67	0.55	0.63
Total solids.....	24.87	23.68	22.86	25.38
Water................	75.13	76.32	77.14	74.62

Recalculated to per cent Total Solids.

	No. 1	No. 2	No. 3	No. 4
$CaCl_2$	71.25	80.62	71.44	97.52
$MgCl_2$	26.26	16.55	26.16	0.00
NaCl	2.49	2.83	2.41	2.48
	100.00	100.00	100.00	100.00

Note.—NaCl determined by weighing as Na_2SO_4.

TABLE VII.

Observed Specific Heats of Chemically Pure Calcium Chloride Solutions.

Temperatures		Densities			
		1.07	1.14	1.20	1.26
−25° C	−13° F				0.648
−20°	− 4°			0.695	.651
−15°	5°		0.764	.700	.654
−10°	14°		.768	.705	.657
− 5°	23°	0.873	.772	.709	.660
0°	32°	.877	.775	.712	.663
5°	41°	.880	.778	.715	.667
10°	50°	.882	.781	.719	.670
15°	59°	.884	.784	.722	.673
20°	68°	.887	.787	.725	.676

NOTE.—The following empirical formula gives a relation between density and specific heat at 0° C., satisfying the above observations to within 0.1 per cent.

$$D = 2.8821 - 3.6272\sigma + 1.7794\sigma^2.$$

D = Density.

σ = Specific heat.

The results of experiment on solutions of C. P. chloride are summarized in Table VII, and the results of individual observations are shown on the curves of figure 7.

From the curves given in figure 8 it may be seen that the specific heats of the various commercial samples differ from that of chemically pure brine by less than 0.5 per cent and are in some cases higher and in others lower.

Table VIII is made out for conveniently determining the heat capacity of brines of different densities. This table is computed by means of the formula given in Table VII.

To use the table it is only necessary to look up the specific heats for the desired density of brine at the upper and lower limits of the temperature range to be covered. Since the specific heat varies almost linearly, the mean of these two values will be the mean specific heat over the range of temperature to be used. For ex-
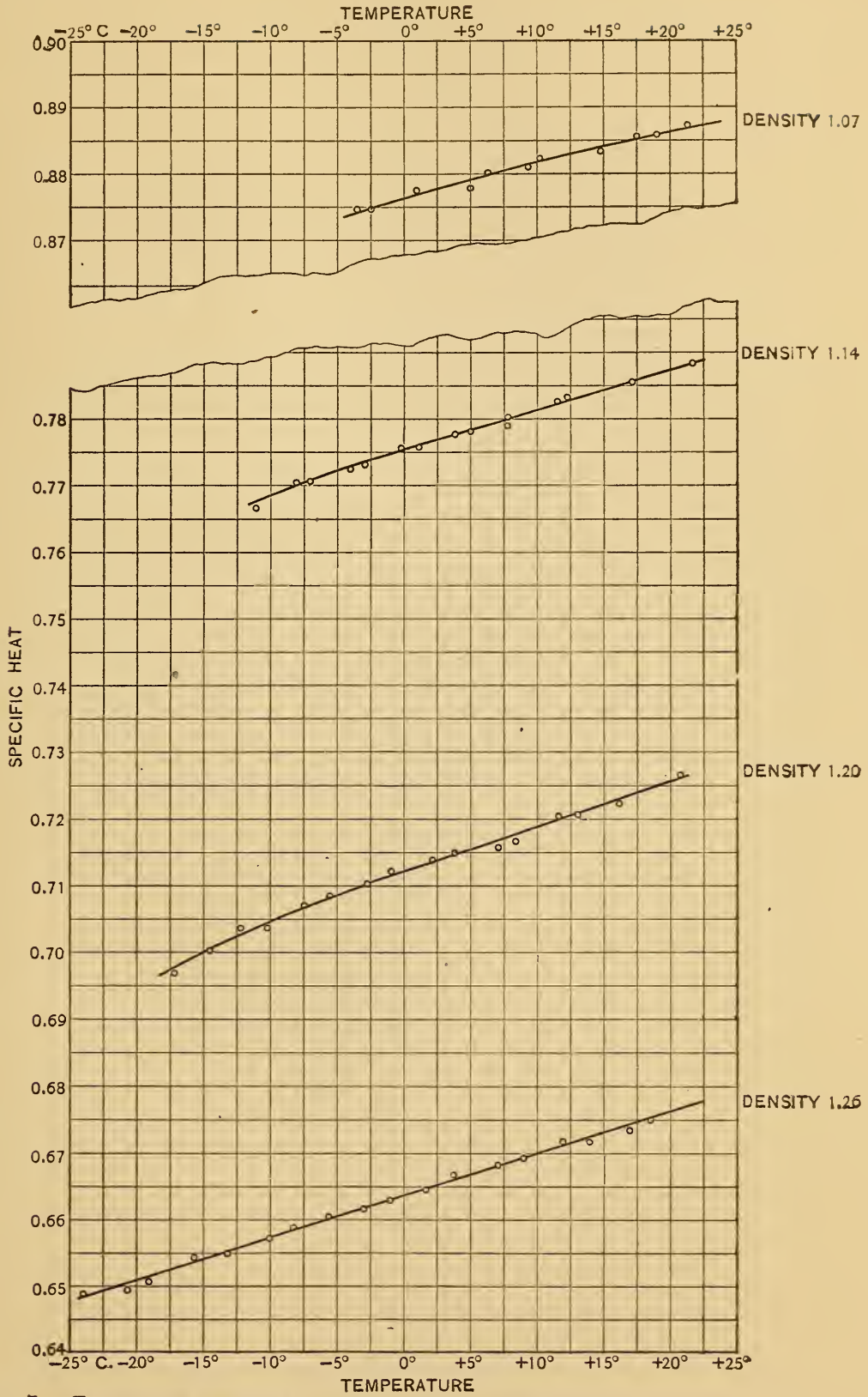
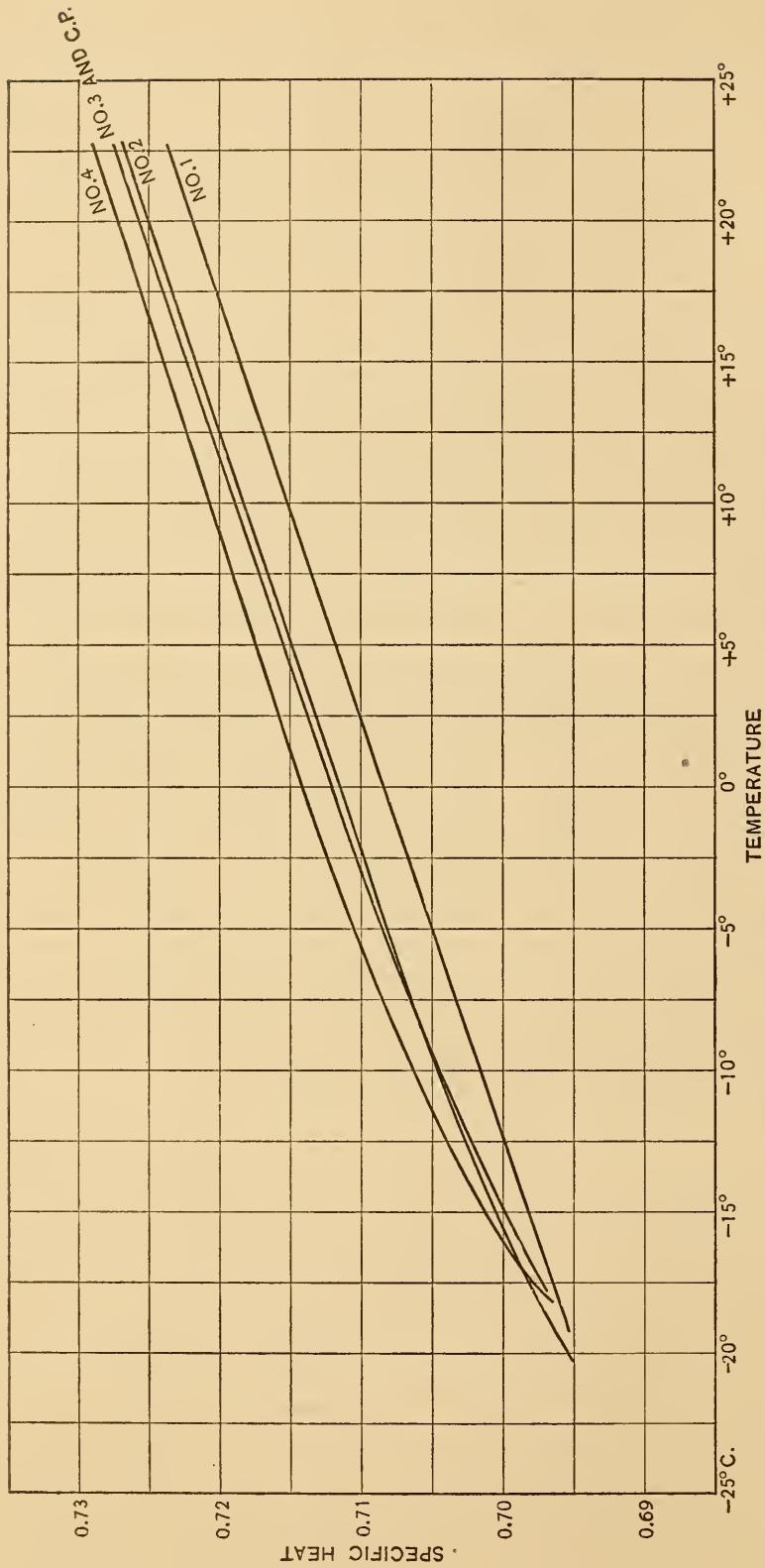Fig. 7.—*Temperature-specific-heat curves, showing observations for densities 1.070, 1.140, 1.200, 1.260.*

Fig. 8.—*Temperature-specific-heat curves for several commercial brines at density 1.200.*

ample, brine of a density 1.20 is to be used between temperatures
− 20° C and − 10° C. The specific heat for brine of this density
at − 20° is found to be 0.695 and at − 10° C, 0.705; the mean of
these is 0.700. Thus, if brine of this density be cooled to − 20° and
allowed to warm up to − 10° the heat absorbed is 0.700 times that
for water or 0.700 × 10 = 7.00 Calories per kilo. Or in B. T. U.,
since the temperature range is 18° F., the amount of heat is .700 ×
18 = 12.60 B. T. U. per pound.

TABLE VIII.

Showing Variation of Specific Heat with Temperature for Chemically
Pure Brine of Several Densities in Common Use.

Temperature	Densities			
	1.175	1.200	1.225	1.250
−25° C				0.653
−20°		0.695	0.674	.657
−15°	0.725	.700	.679	.661
−10°	.730	.705	.683	.665
− 5°	.734	.709	.687	.668
0°	.737	.712	.690	.671
+ 5°	.740	.715	.693	.674
+10°	.743	.719	.697	.677
+15°	.746	.722	.700	.680
+20°	.749	.725	.703	.683
−10° F			.670	.654
0°	.722	.697	.676	.659
+10°	.728	.703	.681	.663
+20°	.733	.708	.685	.667
+30°	.736	.711	.689	.670
+40°	.740	.715	.693	.674
+50°	.743	.719	.697	.677
+60°	.746	.722	.700	.680
+70°	.750	.726	.704	.684

Several observations were made on the freezing points of the
solutions tested and the results are given for solutions of C. P.
calcium chloride in the following table:

TABLE IX.

Density	Freezing temperatures
1.12	− 9° C
1.14	−13°
1.16	−16°
1.18	−20°
1.20	−24°
1.22	−29°
1.24	−34°
1.26	−40°

The freezing point is taken as the temperature at which crystals begin to form. It is not definite to nearer than 1° and the above results are not reliable to better than 1° or 2°. The solutions of commercial calcium chloride of the same density differ only by 2° or less from the above values, and are in general lower.

III. COMPARISON OF THE TWO METHODS.

By the use of the flow calorimeter an accurate determination of the water equivalent is avoided, so that it is adapted to the fundamental determination of specific heats of fluids, especially the specific heat of water, in terms of the electrical units. Further, there is no loss by radiation, and these two advantages appeared at first to be very important. With the vacuum calorimeter, on the other hand, a radiation constant and a water equivalent must be determined, and as shown in the discussion, the latter is difficult to determine accurately. When, however, the vacuum calorimeter is used to determine the heat capacity of a substance as compared with that of water, the error in determination of the water equivalent becomes of very small importance, as may be seen from the note on page 393. In the present case the total correction for water equivalent and for radiation was reduced to less than 4 per cent. The flow calorimeter is subject to a large error in the measurement of the temperature difference, particularly when the liquid has high viscosity, on account of the necessity of measuring the temperature at certain points in the flowing stream. Any system of mixing which tends to eliminate this error increases the difficulty of obtaining constant flow.

In actual working, the vacuum calorimeter is distinguished by greater simplicity, convenience, and accuracy. The amount of solution required for working is from one-tenth to one-twelfth that necessary for the flow calorimeter, and the time required for a set of observations is in almost the same ratio.

The greater accuracy of the results obtained with the vacuum calorimeter is best seen from the fact that the curvature of the specific heat temperature lines was found from these observations, while the best that could be done with the flow calorimeter observations was to establish a linear relation. In this connection it is to be noted that the vacuum calorimeter is better adapted to giving the variation of specific heat with temperature, since the results of a single series of observations give the complete curve for one solution.

IV. SUMMARY.

Two calorimeters—a continuous-flow calorimeter and a Dewar flask calorimeter—have been adapted to the determination of specific heats of liquids over a temperature range of a few degrees in the interval between $-35°$ C to $+20°$ C.

Measurements of temperature were, in both cases, made with platinum resistance thermometers.

Heat was supplied electrically and accurately measured by the potentiometer method.

The flow calorimeter was used for determinations of the specific heat of a single sample of commercial calcium chloride. The results obtained by this method showed individual variations as large as 1 per cent. The final results are probably accurate to 0.2 per cent or 0.3 per cent.

The inconvenience of the flow calorimeter and the time required for observations led to the adoption of another method. A calorimeter was built using a 6-liter Dewar flask containing a heating coil, thermometer, and stirring device. The individual results obtained by this calorimeter are in agreement to better than 0.2 per cent. Determinations of specific heat have been made with this calorimeter for chemically pure calcium chloride solutions of densities 1.07, 1.14, 1.20, and 1.26, and for three samples

of commercial calcium chloride of density 1.20. The solution used in the flow calorimeter was also used at densities 1.20 and 1.26. The results by the two methods are in agreement to within the accuracy of the observations with the flow calorimeter.

Freezing points of several solutions between densities 1.12 and 1.26 were also determined.

In conclusion, the authors wish to acknowledge their indebtedness for many valuable suggestions to Dr. C. W. Waidner, at whose suggestion the work was undertaken.

WASHINGTON, November 4, 1909.