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A METHOD FOR ACCURATE DETERMINATION OF THE SPECIFIC HEATS OF SALT SOLUTIONS UP TO 80°; INCLUDING RESULTS FOR POTASSIUM NITRATE AND CHLORIDE SOLUTIONS

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Introduction

The object of this research was to test the interesting theory which F. Zwicky[2] has advanced to account for the abnormally small heat capacity of electrolytic solutions at room temperature. Assuming complete ionization of the salt, he treats by the methods of mathematical physics the several factors influencing the heat capacity of such a solution. By far the most important of these he finds is the attraction exerted upon the rigid electric dipoles of the water molecules in the inhomogeneous field of the ions. This attraction produces a very high pressure in the vicinity of each ion. Since at room temperature increasing pressure decreases the heat capacity of water, that of an electrolytic solution is correspondingly diminished. The same result is not, however, to be expected at all temperatures. Bridgman's[3] work upon the pressure-volume relations of water has shown that with rising temperature the heat capacity of compressed water increases. The change is at first gradual; then much more rapid until, between 60 and 80°, pressure actually increases the heat capacity of water. If Zwicky's theory is correct, at these temperatures the heat capacity of salt solutions should show a corresponding increase.

The few data to be found in the literature are integral values of the heat capacity from high temperature down to that of the room, and are not sufficiently accurate to decide whether or not such an increase generally occurs. The physical conceptions upon which Zwicky's theory is based, if correct, are a very important contribution to our understanding of electrolytic solutions. This research was therefore undertaken to determine accurately the heat capacity of a number of electrolytic solutions over small temperature intervals, up to 80°. The results so far obtained do not suffice to settle the question, but so many experimental difficulties arose and had to be overcome that a description of the final apparatus seems advisable. The work will be continued during the winter, and more complete results will be published shortly.

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[1] National Research Fellow in Chemistry.

[2] Zwicky, *Physik. Z.*, **27**, 271 (1926). Summarized in *Physik. Z.*, **26**, 664 (1925) and *Proc. Nat. Acad.*, **12**, 86 (1926).

[3] P. Bridgman, *Proc. Amer. Acad. Arts Sci.*, **48**, 310 (1912–13).

Apparatus and Method

The apparatus was a further modification of the "twin calorimeter" method of Joule and Pfaundler, which may be outlined thus.[4] Two similar calorimeters, one containing water and the other the solution under investigation, are placed side by side in a uniform environment. Starting from the same temperature, they are heated by means of two similar electric resistances (one in each calorimeter) connected in series. The difference between the final temperatures of the calorimeters is measured, as well as the total rise in temperature. Knowing the ratio of the resistances, and the weights of water and of solution, the heat capacity of the latter is easily calculated.

For accurate work at high temperatures, where the vapor pressure of water becomes very large and the loss of heat by evaporation correspondingly great, the first requisite was a closed calorimeter system.

At first, Dewar flasks were tried. Into these were ground evacuated glass lids which restricted evaporation to a very small and definite space immediately above the liquid. This arrangement did not, however, prove satisfactory. Too great a heat capacity was evidently involved in the lids, into which the heat penetrated but slowly, requiring at least forty-five minutes to attain thermal equilibrium after an experiment. To remedy this fault, the glass calorimeters were replaced by others made entirely of copper and fitted with copper lids.

Fig. 1 gives an idea of the apparatus as a whole. The two calorimeters CC were suspended within a "submarine" jacket B, immersed in the water-bath A. The calorimeters were fitted with copper lids DD, screwed down upon the gaskets EE (represented by cross-hatching) to give a vapor-tight joint. They were heated by means of two resistance coils (not shown in the drawing);[5] and the difference in temperature between them was measured by the thermel FF. The two thermels GG, connected in series, measured the difference between the mean temperature of the calorimeters and that of the water-bath. The different parts of the apparatus will now be described in more detail.

Environment of Calorimeters.—The adiabatic method had been used previously[4] in order to increase the accuracy of the twin calorimeter apparatus. Each calorimeter was placed in a separate "submarine" jacket, both of which were immersed in a rather large water-bath maintained at the temperature of the calorimeters. In the present research both calorimeters were put inside a single jacket. This made the apparatus much more compact. The resulting reduction in the volume of the water-bath facilitated its temperature control and its stirring and so reduced the chance of error from inhomogeneity in the environment of the calorimeters. Each calorimeter was completely surrounded by a 2-cm. air space, which adequately insulated it from the jacket and the other calorimeter.

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[4] For a description of a somewhat similar apparatus and references to the literature of the subject, the reader is referred to an article by Richards and Gucker, THIS JOURNAL, 47, 1876 (1925).

[5] Shown in detail in Fig. 2. The coils would be directly in front of the stirrers, if shown in Fig. 1.

In addition to the thermal advantage gained by the new arrangement, the calorimeters were placed so much nearer together that the length (and hence the resistance) of the main thermel was greatly reduced and its sensitivity correspondingly increased.

The submarine jacket was constructed in the same manner which had proved satisfactory before[6] from No. 14 B. and S. gage copper, with a lid of the same material clamped down upon a rubber gasket by means of a number of studs and wing nuts.

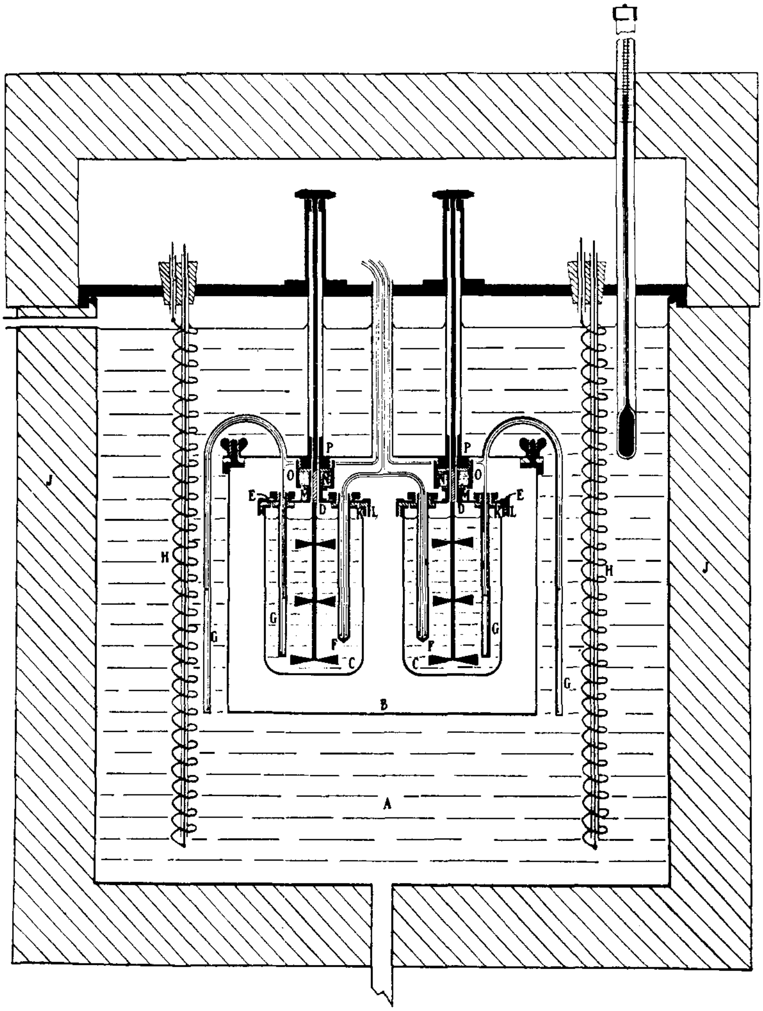

Fig. 1.

The water-bath was heated by four equally spaced coils of bare chromel wire (two of which are shown, HH) connected in series to the lighting circuit. Each coil was wound very loosely around a supporting piece of Pyrex tubing through which one of the heavy copper lead wires was carried. This tube, together with the smaller one used to

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[6] Ref. 4, p. 1880.

insulate the upper lead, was held in a two-holed rubber stopper fitting into the brass cover of the water-bath. The water was agitated vigorously by two rotating stirrers (not shown in Fig. 1) each having three propellers mounted on a vertical shaft and run at about 220 r.p.m.

The top layer of an open water-bath, no matter how vigorous the stirring, is always slightly cooler than the rest of the bath, because of evaporation from the surface. In order to prevent this inhomogeneity in the calorimetric environment, a heavy brass lid was fitted completely over the water-bath, leaving an air space of only about 2 cm. above the surface of the water. A two inch layer of plumbers' felt J was fastened around the outside of the container and over the cover on top of the apparatus in order to minimize heat conduction to the room, which otherwise would have caused considerable annoyance and possible errors at the high temperatures.

Calorimeters.—These were spun from No. 14 B. and S. gage copper, with copper lids of the same thickness (1.6 mm.) and were identical throughout. An externally threaded brass ring K was soldered to the top of each, while an internally threaded ring L was soldered to each lid so that it could be screwed down tight upon the calorimeter. A rubber gasket E was used to give a tight joint.[7]

The calorimeters were buffed on the outside and heavily nickel plated and polished. The surface was protected by a thin coating of transparent lacquer which preserved the polish very satisfactorily. The inside of the calorimeter and lid was heavily gold plated but, as usual, this was only partly satisfactory. A gold lining would be preferable and will be used in the later work.

The calorimeters were not supported from beneath in the usual fashion, but were suspended by their lids. This arrangement proved advantageous for its strength and simplicity and for the ease with which it allowed the apparatus to be assembled. The calorimeters were held rigidly and perfect alignment of the stirrers was assured.

A small threaded tube M was soldered to the center of each lid, with a hole drilled through it of sufficient size to allow the free passage of the stirrer shaft. On this tube was screwed a small cylinder N of "micarta"[8] held in place by a lock-nut at the top (not shown in the figure). This micarta cylinder in turn was supported by a large nut O threaded to a tube extending up through the top of the submarine jacket and soldered to the latter. The micarta section acted as thermal insulation from the jacket. Thin washers of gasket rubber were put on either side of the micarta to make a vapor-tight joint.[9]

The calorimeters were made with a capacity of about 250 cc. to reduce the quantity of solution required for an experiment. Although this decreased the heat capacity of

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[7] Some difficulty was at first experienced with this gasket, which had a tendency to stick to both calorimeter and lid and twist out of position before the lid was tightly in place. The thread had probably too fine a pitch and a coarse thread would be preferable. Satisfactory results were finally obtained by lubricating the gasket with a small amount of talc, well rubbed in. Other types of gasket (cork and steam packing) were tried, but could not be made air tight.

[8] A material made by impregnating a suitable base with a synthetic resin made by phenol condensation. Hard rubber was first tried but proved unsatisfactory. It softened at 80° and was deformed by the weight of the calorimeter, thus loosening the joint. Not only was the chance of evaporation thus increased, but the stirrer was thrown out of alignment. The micarta proved very satisfactory and showed no tendency to warp even at the highest temperatures.

[9] These washers, of course, did not carry the weight of the calorimeters, as a glance at Fig. 1 will show. When the lid was put in place they were compressed sufficiently so that they did not loosen during an experiment.

the system and so magnified any errors due to thermal leakage, other refinements more than compensated. As good agreement was obtained between experiments as previously, with calorimeters of 600cc. capacity.

Electric Heaters.—The reliability of the method depends upon that of the resistances used to heat the calorimeters, which therefore require careful construction. Satisfactory heaters had been made before[10] from asbestos-insulated constantan wire, threaded through thin brass tubing which was then bent into a convenient shape and gold plated. No asbestos-insulated wire being available for this work, cotton-insulated wire was first tried. The cotton should not have been affected by the temperature to which the resistance wire was heated but, after proving satisfactory for some time, it charred in one place and made the coils unreliable. Several other arrangements were then tried before a successful one was found. It is illustrated in Fig. 2.

The case consisted of a piece of half-inch copper tubing F into the bottom of which a copper disk was silver soldered. The top was threaded internally and fitted with a threaded brass plug G, having a hole drilled through the center. The whole case was heavily gold plated on the outside to protect it from the salt solutions.[11]

No. 28 Chromel "A" wire was used for the resistance. This has a low temperature coefficient of resistance change and is unaffected by a current much larger than that used. A piece of the bare wire having a resistance of slightly over 10 ohms was cut and strung with very fine glass beads, which formed a flexible insulation. No. 20 B. and S. copper wires were used as leads. The end of each was drilled centrally to a depth of about 3 mm. The resistance wire was slipped into this hole and silver soldered, making a strong and reliable connection. The resistance of the wire and leads was then measured and the length of the chromel wire adjusted until it was 10.00 ohms (±0.02).

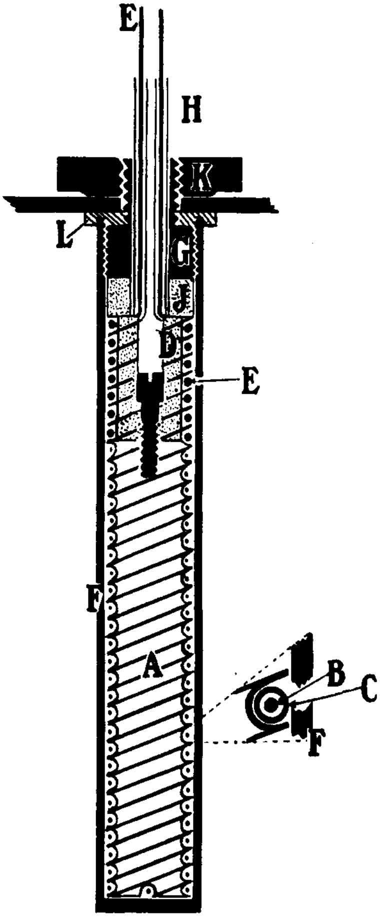

Fig. 2.

A double thread (6 per inch) was now cut in a piece of round copper stock A, Fig. 2. The slot was wide enough to hold the resistance wire B with its beads C and its depth was such that the beads came slightly below the surface of the cylinder. A similar slot was cut across the bottom and the wire was wound bifilar on the copper core. The ends just reached the top, to which was screwed a micarta cylinder D. The micarta carried a square thread (also 6 pitch, double) the width of the copper lead E and deep enough so that the latter, when wound into place, came just below the surface. The lead was

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[10] Ref. 4, p. 1879.

[11] The gold plating has now been replaced by a layer of sheet gold, spun on. This insures protection from any chemical action of the solutions.

painted with several coats of celluloid varnish, which held it in place and provided electrical insulation from the case.[12]

The copper and micarta core was then slipped into the copper case, which it fitted closely. The lead wires were bent toward each other, over the top of the micarta section, and insulated by fine pieces of "spaghetti" tubing H (such as is used in the construction of radio sets). A micarta washer J was put on top, with a hole in the center through which the leads passed. It insulated them from the brass plug G. Its thickness was such that the plug screwed down about 0.5 mm. below the end of the copper tube. The top of the plug fitted through a hole in the lid of the calorimeter where it was firmly held in place by the nut K. A rubber washer L made an air-tight connection. The projecting edge of the copper tube pressed tightly into this and excluded all moisture from the inside of the heater.

Such a heater is rugged and reliable. The case completely protects the wire from the solutions and also from strains which might change its resistance during the course of the experiments. Permanence is essential, since the failure of a heater necessitates not only the construction of a new one, but also the lengthy standardization of the apparatus. The only disadvantage experienced[13] does not seem inherent in the construction of the heater. The use of wire insulated with a thin layer of asbestos, instead of the relatively much thicker glass beads, would probably eliminate most of this lag and will soon be tried.

Thermels (Thermo-Elements).—These were all constructed of copper-constantan according to the design of White,[14] and were multiple-junction. The main thermel was made in two opposable sections of 9 junctions each, from No. 34 copper wire and No. 28 "Advance" (constantan), specially tested for homogeneity by White's method. The junctions were distributed over about 3 cm. The total resistance of the thermel was 24.9 ohms. The small thermels were made of finer wire, not specially tested since they were used as a zero instrument. The four junctions of each were spaced far apart, at equal distances, in both calorimeter and water-bath, so as to register the average temperature of each.

Either the main thermel or the two small ones (in series) could be connected to a high sensitivity Leeds and Northrup galvanometer of the all-copper circuit type. This galvanometer was carefully tested and found to have no appreciable zero shift, even after it had been deflected twice as much as in any actual experiment. In reading temperature differences it was therefore reversed by a suitable switch, thus eliminating the effect of any thermo-electric strays in the galvanometer circuit and at the same time doubling its sensitivity. The sensitivity of the main thermel, used in this way, was about 0.0006°/cm. on a scale a little over a meter away from the galvanometer, while that of the two small ones in series was about 0.0012°/cm.

The galvanometer and thermel circuits were protected by a complete equipotential shield and no difficulty was experienced from stray currents.

The thermel cases were metal tubes which reduced the lag in responding to a changing temperature.[15] They were fastened to the calorimeter lids by means of a nut

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[12] This arrangement was, however, designed to minimize the *thermal* insulation. Each lead was held in close proximity to the copper case for 7 cm., so that it might be brought to the temperature of the latter before leaving the calorimeter.

[13] Note 17, p. 1013.

[14] White, THIS JOURNAL, *36*, 2292 (1914).

[15] White (ref. 14, p. 2304) found that the substitution of a metal tube for a glass one reduced the lag by about one-half. Dr. L. P. Hall and Dr. B. J. Mair, working in the Gibbs Laboratory, have recently compared a thermel enclosed in a platinum tube with one enclosed in a glass tube and find a ratio somewhat more in favor of the metal case.

threaded to the top of each (see Fig. 1). A shoulder near the top supported a rubber washer which was drawn up against the calorimeter lid to make a tight joint. The thermel wires fitted the tubes rather closely but they were easily removed for inspection and pushed back into the case. The central portion of the wires (above the calorimeter lid) was completely inside the air jacket surrounding the calorimeters and hence required no other enclosure; this was a great improvement over the usual glass or metal case, with its uncertain heat capacity and conductivity to the surroundings.

Calorimeter Stirrers.—These were rotating stirrers with three propellers on each shaft. They were synchronized by a sprocket wheel and chain drive from an induction motor which also drove the stirrers in the outer water-bath. The shafts each ran in two reamed bearings. The upper was just below the sprocket wheel and the lower (P, Fig. 1) just above the submarine jacket, to avoid unnecessary frictional heat in the calorimeter itself. A 2cm. section of bone was threaded in just above the calorimeter lid to prevent thermal conduction along the metal shaft. This section is represented by cross hatching in Fig. 1.

Materials and Solutions.—The potassium nitrate was twice recrystallized and dried as well as possible at 150°. The solution was made up with slightly less than the calculated quantity of water. It was analyzed by evaporating weighed 10cc. samples to dryness in small Erlenmeyer flasks and heating them to constant weight at 200°. A small amount of water was then added to make the solution $KNO_3 \cdot 25.00H_2O$.

The potassium chloride was a good grade of analytical salt. There was not time to recrystallize it, but the small quantities of impurities listed should not have had any appreciable effect upon the heat capacity of the solution. It was fused in small quantities in a platinum crucible to drive off the last traces of water, and the solution was made up to determinate $KCl \cdot 25.00H_2O$.

Method of Standardization.—As before, the apparatus was standardized by means of water, but the procedure was slightly modified. The method was as follows. The same weight of water (W_0) was always put into the left-hand calorimeter (which may be called the "tare"). Enough water (W_1) was then weighed into the other ("working") calorimeter to make the heat capacity of the two systems nearly the same. They were then raised through a 2° temperature interval and the resulting galvanometer deflection was determined. Due correction was made for the slightly different heating effect of the two stirrers, etc., as will presently appear. When a second experiment had been made with the same weight of water in the working calorimeter, a pair of experiments was carried out with a slightly different weight. In this way the galvanometer deflections were determined corresponding to values of W_1 over a 1.5 g. range (the exact balancing weight falling near the center of the range). A solution was then substituted for the water and the galvanometer deflection corresponding to a certain weight (W_2) was determined. The weight of water (W_1) corresponding to this galvanometer deflection was found by interpolation and the specific heat of the solution obtained by dividing the latter by the former. With this method of standardization neither the heat capacity of the calorimeters nor the sensitivity of the thermel-galvanometer circuit need be determined.

The results of the water standardization are given in Table I.

TABLE I

WATER STANDARDIZATION DATA

	Expt.	Av. temp., °C.	Weight of water (in vacuo), g.	Galvanometer deflection, cm.	Average deflection, cm.
20°	3a	20.04	243.90	+ 5.4	+ 5.4
	4a	19.98	243.90	+ 5.4	
	1a	20.03	244.90	− 4.7	− 4.9
	2a	20.02	244.90	− 5.1	
	5a	20.00	245.40	−10.7	−10.7
	6a	20.04	245.40	−10.7	
50°	3b	50.00	243.90	+ 6.4	+ 6.1
	4b	50.02	243.90	+ 5.8	
	1b	50.00	244.90	− 3.9	− 4.1
	2b	50.00	244.90	− 4.2	
	5b	49.97	245.40	−10.7	−10.8
	6b	50.00	245.40	−10.8	
80°	3c	80.04	243.90	+ 7.9	+ 8.1
	4c	80.02	243.90	+ 8.3	
	1c	79.99	244.90	− 2.0	− 2.2
	2c	80.02	244.90	− 2.4	
	5c	80.02	245.40	− 9.9	−10.1
	6c	80.02	245.40	−10.2	

Experimental Procedure.—To facilitate assembly, the calorimetric apparatus was fastened rigidly to the heavy brass cover of the water-bath which, being counter-weighted, was easily raised or lowered. It carried the heaters and stirrers of the water-bath and also the lid of the submarine jacket; to which in turn were fastened the calorimeter lids, with stirrers, heaters and thermels all in place.

In preparing for an experiment the water and solution were cooled several degrees below the desired temperature, to allow for heat leakage from the room while assembling the apparatus. The calorimeters were then weighed to centigrams and 245.00 g. of water was weighed into the tare which was quickly screwed to its lid. The desired quantity of solution was immediately weighed into the working calorimeter and it was similarly screwed into place. The submarine jacket was then bolted tightly to its lid and the brass cover was lowered, immersing the submarine in the water-bath.

When the motor driving the stirrers was started, the water-bath was brought to the initial temperature of the experiment and the two calorimeters were then raised to the same temperature. In making the final adjustments the current through the calorimeters was cut down by an external resistance and sent through either one, or both, as occasion demanded.

It is impossible to eliminate the heat effect of stirring in the two calorimeters; hence the temperature trend was observed before and after each experiment and a suitable correction applied. With the open calorimeters previously used discrepancies had been observed between the trend before and after an experiment,[16] but with the closed calorimeters a great improvement was noted. In almost every case the two calorimeters tended toward the same temperature.

Ten minutes after the initial temperature adjustments, readings of the galvanometer deflection were made every two minutes, until the temperature trend was uniform for six minutes. Then the experiment was started by passing a current of 0.9 ampere through the heaters; raising the temperature of the calorimeters 2° in about five minutes. The temperature of the water-bath was raised simultaneously and at the same rate, so as to maintain as nearly adiabatic conditions as possible. After the heating current had been turned off, nine or ten minutes were allowed to insure thermal homogeneity in each calorimeter before the galvanometer deflection was read again.[17] The readings were then repeated at two minute intervals for an "after" period of six minutes, to make sure that a steady state had been reached.

During an experiment, the thermels which registered the difference in temperature between calorimeters and water-bath were connected to the galvanometer. By noting the deflection and adjusting the heating currents slightly from time to time, the temperature of the water-bath was kept within about 0.01° of that of the calorimeters (which themselves never differed by more than 0.005°). Somewhat closer agreement was easily maintained during the "fore" and "after" periods, by slightly heating or cooling the water-bath. In this way the heat transfer between the calorimeters and their surroundings was made practically negligible, as is shown by the agreement of the results.

When an experiment was concluded, the apparatus was heated to the temperature desired for the next one. It was thus possible to use the same sample of solution for experiments at 20, 50 and 80°.

A Typical Experiment.—The following is a complete record of a typical experiment, which will illustrate the procedure.

6/24/27	$KNO_3.25H_2O$	(Experiment 2a)
Calorimeter + contents	442.14 g.	489.99 g.
Calorimeter	197.14 g.	196.32 g.
Contents	245.00 g. (water)	293.67 g. (solution)

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[16] Ref. 4, p. 1886.

[17] The length of time required was evidently due to the poor heat conduction of the glass beads insulating the heating wires, since equilibrium had been reached much more rapidly when the cotton insulated coils were used. This delay was a disadvantage in that it increased the correction applied for the temperature trend, but fortunately the correction itself was small and no great error was introduced.

Time of reading	Difference	Galvanometer readings		Time factor[b]
		Deflection in cm.[a]	Observed change	
10:13.0	7.0	+1.28	+0.02 (Fore)	1
10:15.0		+1.29		
10:17.0		+1.30		
10:20.0		+1.30		
	14.0		−5.56 (Experiment)	
10:34.0	8.0	−4.26	+0.30 (After)	7/8
10:36.0		−4.16		
10:38.0		−4.08		
10:40.0		−4.04		
10:42.0		−3.96		

Initial temperature	19.00 °C.	
Final temperature	21.02 °C.	Av. temp. 20.01 °C.
Total rise (ΔT)	2.02 °C.	

[a] The deflection caused by reversing the galvanometer.

[b] The ratio by which the observed trend must be multiplied to correspond to half the experimental time.

The observed trends, multiplied by the corresponding time factors, become

Trend (fore) = +0.02 cm. Trend (after) = +0.26 cm.
Total trend (corrected to the experimental time) = +0.28 cm.

The corrected change in the galvanometer reading during the course of the experiment was therefore −5.56 − (+0.28) = −5.84 cm. This change was over a range of 2.02°. Corrected to 2.00° it becomes −5.79 cm. The figures are rounded off to the nearest millimeter (corresponding to 0.00006°) $\Delta G = -5.8$ cm.

By interpolation from Table I, the weight of water which at 20° gives this galvanometer deflection is $W_1 = 244.99$ g. (*in vacuo*). The weight of solution, corrected to the vacuum standard, is $W_2 = 293.90$ g., so that the specific heat of the solution is $S_{20°} = 244.99/293.90 = 0.83358$.[18]

The Experimental Results

The specific heats of potassium nitrate and chloride solutions at 20, 50 and 80° are given in the following table.

The accuracy of the method can be gaged by the agreement between duplicate experiments. In the standardization the average difference is

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[18] As was pointed out before (ref. 4, p. 1882) the results are subject to a slight correction because the volume of the air space in the calorimeter, above the surface of the liquid, is not the same during the standardization and during an experiment when the thermally equivalent amount of solution is substituted for the water. Also, the vapor pressure from the solution is less than that from the water, so that the heat absorbed by evaporation is slightly different in the two cases. The air space in the calorimeters used in this work was reduced as much as possible and calculations showed that the correction was negligible at room temperature and, although it became noticeable at the higher temperatures, it amounted to only about 0.06% or less.

TABLE II

SUMMARY OF RESULTS

(Specific heat referred to water over the same temperature range)

Expt.	Av. temp., °C.	W_2 (vac.), g.	ΔG, cm.	W_1 (vac.),[a] g.	Specific heat
$KNO_3.25H_2O$					
1a	20.00	293.90	−5.4	244.95	0.83345
2a	20.01	293.90	−5.8	244.98	.83355
					.83350 (Av.)
1b	50.01	293.90	−8.9	245.31	.83468
2b	50.00	293.90	−9.9	245.38	.83491
					.83480 (Av.)
1c	80.00	293.90	−0.4	244.85	.83311
2c	80.00	293.90	−1.1	244.91	.83332
					.83322 (Av.)
$KCl.25H_2O$					
1	20.00	293.97	+2.2	244.21	.83073
2	20.01	294.59	−3.3	244.75	.83082
					.83078 (Av.)
3a[b]	49.98	291.96	−0.2	244.57	.8377
3b[b]	80.01	291.96	−1.3	244.96	.8390

[a] Corrected for evaporation.

[b] Unfortunately time did not permit performing a duplicate experiment with the KCl solution at the higher temperatures; but the results listed should be as reliable as any other single experiments.

only 0.1 per mille, and in the experiments 0.2 per mille. The agreement was practically the same at high temperatures as at that of the room, although calorimetric difficulties are greatly increased. Even if the evaporation corrections were considerably in error (which seems most unlikely), the results should be accurate at least to 0.5 per mille.

Discussion of the Results

The results so far obtained certainly show no such increase in the specific heat of the solutions at high temperature as Zwicky's theory would lead us to expect. In the case of the chloride solution, there is a decided increase (1%), but nine-tenths of it occurs between 20 and 50°, which is not to be expected from the prediction of the theory. In the case of the nitrate solution, the specific heat is actually slightly less at 80° than at 20°—a result which is quite surprising since all the solutions previously studied[4] by the writer showed an increase in specific heat of about 2 per mille from 16 to 20°. Evidently a further study of the heat capacity–temperature curves of other salt solutions would be of interest, to see if they are of an entirely different type from that of water.

It may be, as Dr. Zwicky pointed out during a conversation, that not all electrolytic solutions show an increase in heat capacity between 60 and 80°, because in some cases the effect of the pressure caused by the ions is masked by that of hydration, which is doubtless different at different temperatures and cannot be predicted theoretically. A study of a number of different salt solutions should make it possible to settle this question; and this will be undertaken during the next few months.

Summary

An adiabatic twin calorimeter apparatus for the determination of specific heats of aqueous solutions up to 80° has been developed. It is similar in many ways to the apparatus previously used by Richards and Gucker[4] for work at room temperature, but there are many mechanical improvements. The apparatus has been made very compact, allowing the environment to be kept more uniform and the thermel circuit to be made more sensitive. Thermal insulation between the apparatus and the room has been made more effective. The use of closed calorimeters greatly improves the thermometric stability of the system.

The method of standardization has been improved and greatly simplified. It is no longer necessary to determine the sensitivity of the thermel-galvanometer system or the heat capacity of the calorimeters.

The volume of the calorimeters has been reduced from 600 cc. to 250 cc. and the temperature range from 4 to 2°, but other refinements have more than compensated. The accuracy of the method is at least 0.5 per mille, even at the highest temperatures.

The specific heats of solutions of potassium nitrate and chloride have been studied at 20, 50 and 80°. They show no great change over this range. The results so far obtained do not, therefore, confirm F. Zwicky's theory of the specific heat of such solutions. The work is being continued, and more conclusive and detailed results should soon be available.

The writer wishes to thank Professor A. A. Noyes for extending to him the privileges of the Gates Chemical Laboratory and for his generosity in allowing him to take the apparatus East in order to complete the research. He also wishes to thank Mr. E. H. Searle for many mechanical suggestions and for his help in constructing the apparatus.

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