[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

A Differential Method Employing Variable Heaters for the Determination of the Specific Heats of Solutions, with Results for Ammonium Nitrate at 25°

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Introduction

The adiabatic twin-calorimeter method is admirably suited to the precise measurement of the specific heats of solutions. A "thermal balance" employing this method has been in use for some time in this Laboratory.[1] In preparation for a new series of experiments, several modifications and improvements were introduced and a method was worked out whereby the electrical energy input in the calorimeters could be changed by means of variable resistance heating coils. This made the new apparatus much more flexible and convenient; and also increased its accuracy somewhat, as the new experimental results indicate. After a brief summary of the experimental method the significant new features of the present apparatus will be considered in more detail. For experimental details which were not appreciably changed, the reader is referred to the earlier articles mentioned above.

The apparatus consists of two similar calorimeters, one containing a solution, the other a fixed tare weight of water, enclosed side by side in a submarine jacket contained in an adiabatic water-bath. Starting at the same initial temperature, the calorimeters are heated one degree by means of a pair of variable resistance coils connected in series. The resistance ratio of these coils is adjusted until the two calorimeters are heated at the same rate, as determined by a multiple thermel connected to a high sensitivity galvanometer. The heat capacity of the solution is then calculated from the measured resistance ratio and the known heat capacity of the calorimeter.

Apparatus

General Description.—A general idea of the apparatus may be obtained from the simplified drawing, Fig. 1. The two calorimeters, C, C, of 280-ml. capacity, are enclosed in a water-tight submarine jacket, J, which is completely immersed in the water-bath, B. The stirrers, S, S, are rotated at 215 r. p. m. by a sprocket chain driven from a synchronous motor. The Bakelite thermal insulators (indicated by cross-hatching) in the stirrer shafts prevent leakage of heat into the calorimeters from the bearings above. The water-bath, B, is mounted on a motor-operated, vertical jack-screw so that it can be raised or lowered easily, even when filled with water. It is agitated by two stirrers (not shown in the diagram) which are driven at 215 r. p. m. by the same sprocket chain which operates the calorimeter stirrers. The bath is heated by four bare nichrome coils (not shown in Fig. 1) each of five ohms resistance, connected in series to the 110-volt a. c. circuit. Each coil is 30 cm. long, loosely wound around a heavy copper wire serving as one of the leads, from which it is insulated by a length of glass tubing. The coils are equally spaced and mounted on the brass plate, P, by means of standard attachment plugs so that they project vertically down into the water. A cover, F, and lid, L, fit over the top of the bath. The entire apparatus is insulated with a 5-cm. layer of felt, H. Bare chromel wires, insulated between thin sheets of asbestos, are wound around the cover, lid and bath, under the felt. These surface heaters, connected through a rheostat to the 110-volt a. c. circuit, compensate for loss of heat when working at temperatures higher than that of the room. To maintain temperatures below that of the room, a regulated stream of cold water is allowed to drip into the bath. The surplus water escapes through the outlet tube, R, and the sight glass and overflow, D.

Submarine Jacket.—The heavy copper submarine jacket, J, was nickel plated and burnished on the inside. The bottom was detachable in order to expedite the process of plating and burnishing. Once this was accomplished, a gasket was put in place and the bottom was bolted on permanently. The top of the jacket was rigidly attached to the lid of the bath, P, by the heavy brass tubes through which the stainless steel stirrer shafts extended. The calorimeters were suspended entirely from this top plate, so that the lower part of the submarine jacket was easily detached at the point indicated by the gasket, G.

Calorimeters.—The calorimeters and lids were spun from an alloy of 20% platinum and 80% gold,[2] which combines chemical inertness with adequate mechanical strength. The lids were ground to fit their respective calorimeters and the joints were made vapor-tight by a thin coating of vaseline. Three wells for the thermel and heater cases were gold-soldered to each lid. Only the wells for the main and adiabatic thermels are shown in the horizontal section in Fig. 1. The third well, for the heater, was located directly behind the stirrer. Each lid was also provided with two conical openings. Into the center one was ground the lower end of a glass tube, E, through which passed the stirrer shaft. Toward one side was a second opening, not shown in Fig. 1, fitted with a ground plug. The calorimeter was filled through this second opening. All the ground joints were made vapor-tight by means of a thin coating of vaseline. The 3-stage propeller stirrers, S, S, made of platinum, were screwed into insulating sec-

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[1] (a) Richards and Gucker, THIS JOURNAL, **47**, 1876 (1925); (b) Gucker, *ibid.*, **50**, 1005 (1928); (c) Gucker and Schminke, *ibid.*, **54**, 1358 (1932); (d) **55**, 1013 (1933).

[2] The calorimeters were made by J. Bishop & Co.

tions machined from transparent Bakelite, indicated by cross-hatching in Fig. 1. This material has a low thermal conductivity. Since tests showed it is almost impervious to water, it is superior to the ivory sections used previously in this Laboratory. Unfortunately, it softens so much that it cannot be used above 40 or 50°. The lower end of the Bakelite was conical to fit a 60° conical seat in the bottom of the glass tube, E.

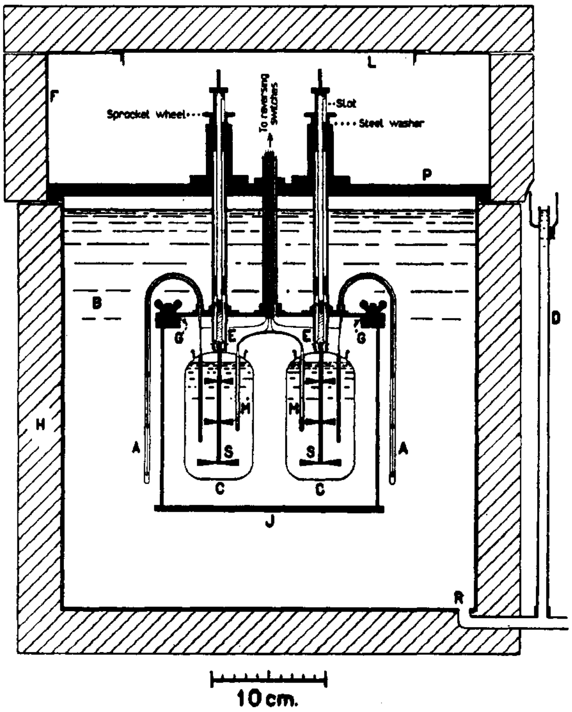

Fig. 1.—Calorimetric assembly.

In assembling the apparatus, the glass tube, E, was fitted into the lid of the calorimeter. The Bakelite section next was put in place and the stirrer screwed to it. The lid, carrying the stirrer, was put on the calorimeter, into which water or solution was then weighed. The conical joint between Bakelite and glass prevented evaporation during this process. The calorimeter was then raised until the top of the glass tube, E, fitted the conical base of the brass tube in the submarine lid, into which it had been ground. A temporary supporting frame held the calorimeter rigidly in this position. The bottom of the stainless steel shaft which carried the sprocket wheel was now screwed into the upper end of the Bakelite section, which was kept from turning by the friction between it and the conical seat in E. Finally the knurled knob above the sprocket wheel was screwed down, raising the shaft to the position shown in Fig. 1, where the Bakelite section is clear of the glass.

Each calorimeter was suspended from the top of the submarine jacket by four equally-spaced pieces of dental floss. The lower ends of these were tied to small wire loops, gold-soldered to the sides of the calorimeters near the top. The upper ends were slipped over small adjustable wire hooks which projected down from the top of the submarine jacket. Above the hook, each wire passed through a hole in the axis of a small machine screw, the lower end of which was knurled so that it could be turned with the fingers. Each screw was threaded vertically into a support fastened to the submarine lid. The top of the wire was bent horizontally, to fit into a vertical slot in the support, so that the hook did not rotate when the screw was turned. When the screws were tightened and the hooks raised, the calorimeters were held tightly against the glass tubes, E, E. Finally the temporary supporting frame was removed, leaving the calorimeters suspended with a very small avenue of heat exchange to the submarine jacket.

Two features in the calorimetric design are important. First, the air space above the liquid level in each calorimeter, including that inside the glass tube, E, is reduced to about 10 ml. This volume is so small that no trouble is caused by evaporation of water when the calorimeter is heated one degree. Second, since the stirrers are easily detachable at the bakelite–stainless steel joints, Fig. 1, the calorimeters and their contents can be removed completely and weighed with no loss of solution or water. The actual evaporation losses determined by this method are usually found to be only 2 or 3 mg. and hence completely negligible.

Thermels.—The constantan wire used in constructing the thermels was tested for homogeneity according to the method recommended by W. P. White[3] and only those sections were used which showed an e. m. f. of less than 1 μ v. over a thermal gradient of 70° in about 3 cm. The 20-junction copper–constantan main thermel, M, M, Fig. 1, was constructed in two halves of 10 junctions each so that the halves could be opposed in the usual manner. The general design is shown in Fig. 2a. Each junction was insulated from the others in a slot cut in a mica form, the No. 34 copper wires running up on one side of the mica and the No. 26 constantan on the other. The mica forms, 0.13 mm. thick, were about one centimeter longer than the corresponding wells in the calorimeter lid. Each 10-

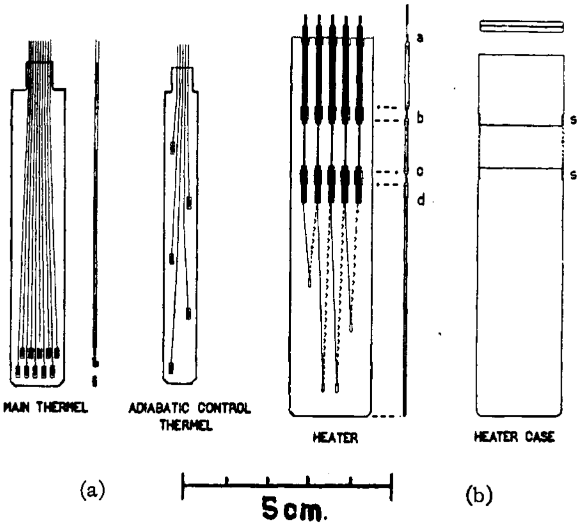

Fig. 2.—Details of thermels and heaters.

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[3] W. P. White, THIS JOURNAL, 36, 2292 (1914).

junction unit was dipped in "razo-glass"[4] and sandwiched between two mica insulating strips about 0.08 mm. thick. Snugly fitting copper cases, thick enough for good thermal contact with the calorimeter well and long enough to cover the mica, were then slipped over each pair of completed units. The resistance of the insulation between the thermel wires and the copper cases was found to be about 100,000 megohms (50% relative humidity).

The five junctions of each adiabatic control thermel (A, A, Fig. 1) were staggered as shown in Figs. 1 and 2a in order to obtain a comparison of the average bath temperature with the average temperature inside the calorimeters.

The thermels were connected to the galvanometers through copper reversing switches by which parasitic currents in the galvanometer circuit could be eliminated.

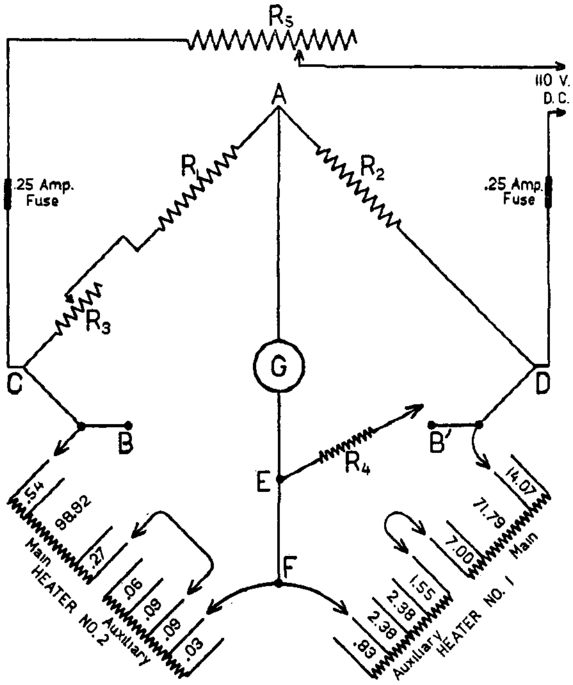

Fig. 3.—Bridge for measuring resistance ratio.

Variable Resistance Heaters.—The design of these heaters, allowing a measurement of the resistance ratio during an experiment, was the most important innovation in the present apparatus. Each consisted of 7 units with a total resistance of about 100 ohms. A large resistance, with a smaller one connected to each end, formed the *main heater* which was supplied with 4 leads. Four much smaller units, connected in series and supplied with 5 leads, formed the *auxiliary heater*. This arrangement gave a satisfactory flexibility in resistance with a minimum number of leads. In each main heater, connection could be made to the large resistance alone or in combination with either or both end coils. In order to keep the lead resistance constant, at least one unit of the auxiliary heater was always connected in series with the main. The 9 possible combinations of the auxiliary, combined with the 4 of the main, gave 36 resistances in each heater and 1296 resistance ratios for the two heaters. The values of the individual units, shown in Fig. 3, were so chosen as to give a series of resistance ratios progressing uniformly from 0.9800 to 1.3700 in steps of 0.0003 to 0.0004. In order to obtain a smooth progression, with no gaps, all the smaller steps were put in one heater (No. 2) and the larger in the other (No. 1).

The main and auxiliary heaters were mounted on separate strips of clear mica 0.13 mm. thick. The construction of auxiliary heater number 1 is shown in Fig. 2b, which is a scale drawing. The constantan resistance wires were No. 36 B and S gage, while those in auxiliary heater number 2, were No. 24 B and S gage, bent to shape and flattened to form a ribbon of the same thickness, 0.13 mm. These ribbons were annealed before assembly by the passage of a current of 6 amp. The large resistances of the main heaters were No. 40 B and S gage constantan. All the constantan wires were confined to the lower parts of the mica strips, 2.5 cm. or more below the surface of the liquid in the calorimeter.

The leads to the outside were No. 24 B and S gage copper wires. The lower end of each, flattened to form a ribbon 0.13 mm. thick, was carried down one side of the mica strip. It was fastened to the mica by means of a second copper strip carried down the opposite side and soldered to it in two slots at a and b, Fig. 2b. This arrangement ensured good thermal contact with the walls of the heater case, so that the heat generated in the coils is delivered to the calorimeter. One-centimeter lengths of flattened No. 36 B and S gage copper wire interposed between b and c, Fig. 2b, minimized the conduction of heat to the leads.

The heating units were made with slightly less than the desired resistance, mounted on the mica strips and soldered to the leads, using rosin flux. They were then annealed by passing through them a current appreciably larger than that which was used in the later experiments. The wires were then alternately scraped cautiously with a sharp knife and annealed until they were adjusted to within 0.01 ohm of the calculated value. Finally the heaters were washed thoroughly with carbon tetrachloride, to remove any rosin flux or grease from the hands, and rinsed several times in distilled water, to remove any salts which would increase the surface conduction of the mica. They were carefully dried and sandwiched between insulating strips of clear mica 0.08 mm. thick which had been cleaned in the same way. The total thickness of the heater with its two insulating strips was 0.9 mm. or less. Each heater was pushed into one side of a double case made from sheet copper 0.25 mm. thick, bent in the shape of a flattened S as shown in Fig. 2b and soldered together at the edges. A 1-cm. opening in the case, coinciding with the small wires bc of the heater leads, reduced conduction of heat up the heater case. The two copper sections of the case were held rigidly together by strips of stainless steel, s, s, 0.25 × 1.25 mm., soldered to shallow recesses filed in the edges of the case as shown in Fig. 2b.

The Resistance Ratio.—The heaters were incorporated in a conventional Wheatstone bridge circuit, Fig. 3, the measuring arms of which, AC and AD, consisted of much higher resistances than the heaters. R_1 and R_2 were 4000-ohm coils and R_3 consisted of a series of coils totaling 2000 ohms in series with a precision resistance box, variable in

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(4) "Razo-glass" is the trade name of a polymerized coumarone resin, obtained from the Marbro Products Corporation through the courtesy of the late Professor Eric von Gebauer-Fuelnegg. When dissolved in toluene, razo-glass is an excellent insulating varnish.

steps of 0.01 ohm. The individual Leeds and Northrup resistance coils, wound on metal spools, were mounted on brass rods in the usual manner. The coils were calibrated to within 0.01 ohm, using a set of Bureau of Standards type standard resistors as a basis of comparison. Calibration at intervals of several months showed no significant changes except in the 4000-ohm coils.

By means of this Wheatstone bridge, the resistance ratio was measured *during an experiment*, with a current of 0.19 ampere passing through the heaters, but only 0.005 ampere passing through the measuring arms—a current which they were designed to dissipate without an appreciable change in their calibration. The Leeds and Northrup pointer-type galvanometer G was sensitive to a change of 0.0003% in the resistance ratio.

The resistance ratio measured by the bridge is, of course, the ratio of the total resistances of the heater arms, from C to F and from F to D, respectively. The ratio of the resistances *effective in heating the calorimeters* can only be determined by applying a correction for the lead resistance. For this reason, every effort was made to keep the lead resistance small and constant. The 18 lead wires from the heaters were cut equal in length, and their upper ends were soldered to radio tip-jacks mounted on a shielded Bakelite disk immediately above the bath lid, P, Fig. 1. Connection between the jacks was made by short pieces of heavy stranded wire, soldered to phone tips, indicated by arrows in Fig. 3. Potentiometric measurement showed that the contact resistance of a pin-jack and phone-tip combination was about 0.0010 (±0.0002) ohm. This variation was negligible for the four contacts in each heater arm. Plugging all of the phone tips in and out several times in succession never produced a change in the measured resistance ratio of more than 0.0005%. In finding the value of the lead resistance, we assumed that only the lower half of the exposed leads within the air gap of the submarine jacket belonged to the heater and contributed to raising the temperature of the calorimeter. The resistance from this mid-point through the lead wires, phone connectors and external wires to the corners of the bridge made up the lead resistance, l, which we found by potentiometric measurement was 0.103 ohm for each heater. If the effective end of the heater is within 2 cm. of the center of the 9-cm. length of the lead wire in the gap, the uncertainty in l is not more than ±0.006 ohm. It can be shown easily that the *effective* resistance ratio, x' ($= r_2/r_1$) can be calculated from the *measured* resistance ratio X by the equation

$$x' = X + [l(X - 1)]/r_1 \qquad (1)$$

where r_1 is the resistance of heater 1. This equation shows that the effective ratio equals the measured ratio when that ratio is unity, and differs by an increasing amount as the lead resistance and the resistance ratio increase. The lead correction amounts to +0.04% with the maximum ratio of 1.37, and the value of l found above. If l is known to 0.005 ohm and r_1 to 2 ohms, the maximum error in the lead correction will not exceed 0.002%.

Theory of the Measurements

In principle, the method consists in finding the balance point of the apparatus, first with equal weights of water (268.330 g. *in vacuo*) in the two calorimeters, and then with the same weight of water in the tare (number 2) and an equal *volume* of solution of known weight in the working calorimeter (number 1). The balance point is the effective resistance ratio for which the two calorimeters rise exactly the same amount when heated over an interval of 1°. Since the resistance ratio cannot be set *exactly* at the balance point, the small galvanometer deflection, Δg (due to a slight difference in temperature rise over a 1° range) is found by the graphical method used in our previous work.[1c] After two or more experiments, the values of Δg are plotted against the corresponding resistance ratios and the balance point is read from the graph, as shown in Fig. 4.

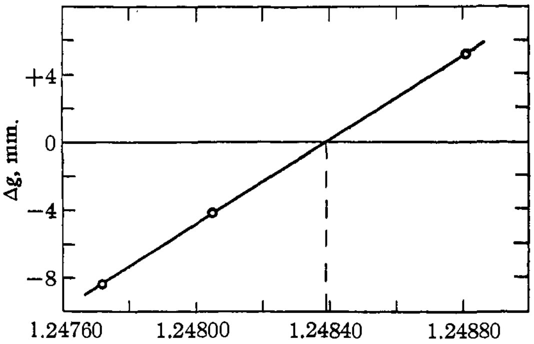

Fig. 4.—Graphical estimation of balance point: ($\Delta g = 0$ at $x = 1.24839$).

If the balance points corresponding to water and solution are designated respectively by x_0 and x, they are defined by the equations

$$x_0 = T/(C_w + c_1) \qquad (2)$$

and

$$x = T/(C_s + c_1) \qquad (3)$$

where T is the total heat capacity of the tare calorimeter and water, c_1 is the heat capacity of the working calorimeter and C_w and C_s the heat capacities of the weights of water and of solution in calorimeter 1 at balance. Dividing (2) by (3), and rearranging terms gives for the heat capacity of the solution

$$C_s = C_w x_0/x - c_1(x - x_0)/x \qquad (4)$$

This equation shows that the effective heat capacity of the working calorimeter, c_1, must be known with an accuracy which becomes greater the more x increases—*i. e.*, the lower the heat capacity of the solution. If x_0 is unity and x has the extreme value of 1.37, c_1 must be known to 0.07 cal. per degree if C_s is to be determined to 0.01%. As the value of x decreases, the error in C_s caused by an error in c_1 becomes correspondingly less. In our experiments, the largest value of x was 1.25, hence an error of 0.1 calorie unit in c_1 causes an error of only 0.004% in C_s.

Although the value of c_1 need not be known more closely than 0.1 calorie unit, it must *remain constant* to 0.01 calorie unit or better. Preliminary experiments showed that the effective heat capacity c_1 decreased nearly linearly by about 0.015 calorie unit per ml. for the first 30 ml. of water removed from the calorimeter. In calculating the results of these experiments a correction was applied for the evaporation of water into the increased air space. The decrease in c_1 was probably due to a lag in the heat reaching the lid of the calorimeter, and an increased heat leakage down the heater leads to the calorimeter. In order to keep c_1 constant, the same volume of liquid (± 0.5 ml.) was always put into the working calorimeter.

In determining c_1, a hollow air-tight copper shell, displacing about 33 ml. of water, was fastened below the surface of the water in the calorimeter, which was then filled up to the usual level. From the balancing ratio x_0', the heat capacity of the water, C_w', and that of the displacer, the value of c_1 was found by eliminating T between equation (2) and a similar equation for x_0'. The heat capacity of the solid parts of the displacer was found by opening it, immersing the parts in the calorimeter filled to the usual volume with water, and finding the balancing ratio. The heat capacity of the air in the displacer was added to this value in calculating the value of c_1. The values of c_1 corresponding to the working volume of 268.3 ml. in the calorimeter, were 10.83 and 10.89 25°-calorie units—an average of 10.86 being used in subsequent calculations in experiments 1–5 inclusive. A slight alteration in one of the heater cases, made before the second series of measurements was started, necessitated a new set of calibration experiments. The new average value of c_1 was found to be 10.73 25°-calorie units. This value was used in all calculations following experiment number five.

The determination of the heat capacity of the calorimeter from the difference of two large heat capacities necessarily increases the percentage error in the value of c_1. However, the effect of this error upon the final results is reduced to negligible proportions, as we have already shown.

A Typical Experiment.—As an indication of the manner in which the measurements were carried out, the important data taken in connection with a typical experiment are given in Table I. The solution used in this experiment was the most concentrated of the series (23.998 molal). The change in galvanometer deflection, Δg, was found as before[1c] by recording the galvanometer deflections at one-minute intervals before and after the experiment and estimating the change graphically. The individual galvanometer deflections are not tabulated here.

TABLE I

Experiment Number 7, 12/24/35–12/26/35

Weight NH_4NO_3 231.670 g.
Weight solution 352.272 g.
$m = 23.9978$

Heater settings (Nominal values) $\begin{cases} \text{No. 1} = 71.79 + 7.00 + 0.83 \text{ ohms} \\ \text{No. 2} = 98.92 + 0.54 + 0.06 \text{ ohms} \end{cases}$

	Time	Resistance
Balancing resistance during heating time ($R_1 + R_3$, Fig. 3)	9:43	4992.79 ohms
	44	.78
	45	.75
	46	.74
	47	.73
Average =		4992.76 ohms

Fixed resistance (R_2, Fig. 3) = 4002.47 ohms
Ratio = 4992.76/4002.47 = 1.24741 = X
Ratio, corrected for lead resistance
$= 1.24741 + [0.10(1.2471 - 1)]79.6 = 1.24772 = x_1$
$\Delta g' = -8.4$ mm. (galvanometer deflection for experimental temperature rise)

Platinum resistance thermometer $\begin{cases} \text{Final } R = 28.0808 \text{ ohms} \\ \text{Initial } R = 27.9799 \end{cases}$
$\Delta R = 0.1009$ ohm

$\Delta t = 9.957\Delta R = 1.005° =$ experimental temperature rise
Mean temperature = 24.99°
Δg_1, galvanometer deflection for 1° temperature rise $= -8.4/1.005 = -8.4$ mm.

Similarly, for two additional experiments using different heating ratios

$$\Delta g_2 = +5.2 \text{ mm.}, x_2 = 1.24881$$
$$\Delta g_3 = -4.2 \text{ mm.}, x_3 = 1.24805$$

From Fig. 4, $\Delta g = 0$, at $x = 1.24839$

$$C_s = \frac{1.00009(268.330) + (1.00009 - 1.24839)(10.73)}{1.24839}$$
$$= 212.826$$

$s = 212.826 \div 352.272 = 0.60481$ 25°-cal./deg.
$\Phi(C_{p_2}) = 31.945$ 25°-cal./deg.

Preparation of Ammonium Nitrate.—The ammonium nitrate used in these experiments was synthesized from pure ammonia and nitric acid by two slightly different methods, both based upon the procedure recommended by Archibald[5] for ammonium chloride. In both cases, C. P. nitric acid was distilled through a quartz condenser and the middle third was placed in quartz or platinum dishes. The first portions of ammonium nitrate were prepared by T. R. Rubin, who also measured the heat capacities of the corresponding solutions. The ammonia was obtained as follows. A hot solution of C. P. ammonium sulfate, dissolved in an equivalent weight of pure sulfuric acid, was treated with a few grams of finely powdered potassium permanganate and heated until it was colorless. This treatment ensures the oxidation of any organic matter. The purified ammonium bisulfate was cooled, dissolved in water and neutralized with a suspension of C. P. calcium oxide. It was then put in the bottom of a vacuum desiccator and mixed with excess lime, giving a slow evolution of ammonia. This was absorbed in the dishes of pure nitric acid which were placed on the shelf of the desiccator.

Subsequent tests showed that there were no oxidizable impurities in ammonium hydroxide of synthetic origin; hence the remaining portions were prepared by Robert Mueller using solutions of ammonium hydroxide made from synthetic ammonia in place of the lime and ammonium bisulfate mixture. The heat capacities of these solutions were measured by F. D. Ayres.

The ammonium nitrate resulting from either procedure was twice crystallized from water and dried *in vacuo* at 70–80°. The Hyvac pump was connected through a trap immersed in a mixture of carbon dioxide snow and acetone (about −78°). Pumping was continued until no more moisture collected in the trap. The salt was then ground in an agate mortar and dried again *in vacuo* at the same temperature for about six to ten hours. It was stored in a desiccator.

Experimental Results.—The results for all the ammonium nitrate solutions are collected in

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[5] E. H. Archibald, "The Preparation of Pure Inorganic Substances," John Wiley and Sons, Inc., New York, 1932.

TABLE II

THE SPECIFIC HEATS AND APPARENT MOLAL HEAT CAPACITIES OF AMMONIUM NITRATE SOLUTIONS AT 25°

Expt.	m	c	$c^{1/2}$	s	$\Phi(C_{p_2})$ obsd.	$\Phi(C_{p_2})$ calcd.	Δs in (0.001%)
	0.0	0.0	0.0	1.00000		−3.64	
3	.1012	.1004	.3169	0.99211	1.5	0.8	− 7
2b	.1928	.1905	.4365	.98534	2.82	2.46	− 5
1a	.4065	.3975	.6305	.97044	4.96	5.14	+ 8
6	.5771	.5599	.7483	.95960	6.81	6.75	− 3
1	.8433	.8079	.8988	.94361	8.66	8.79	+10
2a	1.5093	1.4020	1.1841	.90907	12.52	12.58	+ 7
4b	2.4323	2.1672	1.4721	.87000	16.20	16.24	+ 9
2	3.2385	2.7855	1.6690	.84228	18.724	18.592	−35
9	3.2533	2.7962	1.6722	.84157	18.667	18.629	−10
5a	5.4142	4.2555	2.0629	.78362	22.761	22.790	+11
4a	7.5672	5.4761	2.3401	.74185	25.269	25.286	+ 8
8a	9.8764	6.5834	2.5658	.70781	27.074	27.081	+ 4
4	12.6314	7.6923	2.7735	.67681	28.590	28.596	+ 4
5	13.4508	7.9855	2.8258	.66918	28.971	28.961	− 6
7a	17.4353	9.2207	3.0366	.63850	30.376	30.385	+ 6
8	21.0845	10.1337	3.1833	.61792	31.341	31.337	− 3
7	23.9978	10.7495	3.2786	.60481	31.945	31.943	− 2

Table II. The experiments are numbered chronologically. Each solution made from weighed quantities of salt and water is given a consecutive number, while those made by quantitative dilution are designated by letters following the number of the concentrated solution from which they came. Experiments one to five inclusive were carried out by T. R. Rubin; the rest by F. D. Ayres. The molality, m, of the solution (moles solute per kg. water) was determined directly from the weights of the constituents. The molarity, c (moles solute per liter of solution) was then calculated from the equation[6]

$$\frac{c}{m} = d_1\left[1 - \frac{c\Phi(V_2)}{1000}\right]$$

The values of $\Phi\ (V_2)$, the apparent molal volume of ammonium nitrate, were calculated from the equation

$$\Phi(V_2) = 47.558 + 0.966\ c^{1/2} + 0.0474c$$

which was derived[6a] (p. 314) from the accurate density measurements of Adams and Gibson.[7] Successive approximations were made until two consecutive values of c agreed within 0.0001. The process was expedited, especially when successive values diverged, by taking the *average* of the two preceding values of c in making the later approximations. The value of the apparent molal heat capacity $\Phi(C_{p_2})$ was calculated from the usual equation

$$\Phi(C_{p_2}) = \left[\frac{1000}{m} + M_2\right]s - \frac{1000}{m}$$

where M_2 is the molecular weight of ammonium nitrate, 80.047 g. Since s is the specific heat at 25°, $\Phi(C_{p_2})$ is expressed in 25°-calories per degree.

One of our objects in studying ammonium nitrate was to compare the plots of the apparent molal heat capacity against $m^{1/2}$ and $c^{1/2}$ and to see if it was as nearly a linear function of the latter over the whole concentration range as we had already[6a] (p. 314) shown the apparent molal volume to be. Ammonium nitrate is particularly suitable for such a study. Its high solubility and large apparent molal volume give a great difference between the volume and weight concentrations. A plot of $\Phi(C_{p_2})$ against $m^{1/2}$, reproduced in Fig. 5, showed that up to 1.5 m the results could be reproduced with an accuracy of ±0.005% in s by means of the equation

$$\Phi(C_{p_2}) = -2.90 + 12.56m^{1/2}$$

Above 1.5m the experimental points lay along a smooth curve which was concave downward.

A plot was next made, using $c^{1/2}$ as abscissa, but a linear equation reproduced the specific heat data adequately to no higher concentration than before. The equation

$$\Phi(C_{p_2}) = -3.30 + 13.37c^{1/2}$$

reproduced the specific heats within ±0.004% on the average, up to $c = 1.4$. At higher concentrations the experimental points again lay along a smooth curve, concave downward, although the curvature was considerably less than in the plot against $m^{1/2}$.

In order to calculate values of the specific heat of the solution and of the partial molal heat ca-

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[6] (a) Gucker, *J. Phys. Chem.*, **38**, 312 (1934); (b) see also Geffcken, *Z. physik. Chem.*, **A155**, 1 (1931).

[7] Adams and Gibson, THIS JOURNAL, **54**, 4520 (1932).

pacities of the salt and the water at any desired concentration, an equation connecting the apparent molal volume and the concentration was next sought. Calculations involving the weight concentration are simplest to make, so that we first attempted to obtain the apparent molal heat capacity as a function of the molality. Various equations giving $\Phi(C_{p_2})$ as an explicit function of $m^{1/2}$ were first tried, but none was found to reproduce the curve successfully. The large curvature near the center, with nearly straight portions at each end, suggested a section of a hyperbola.

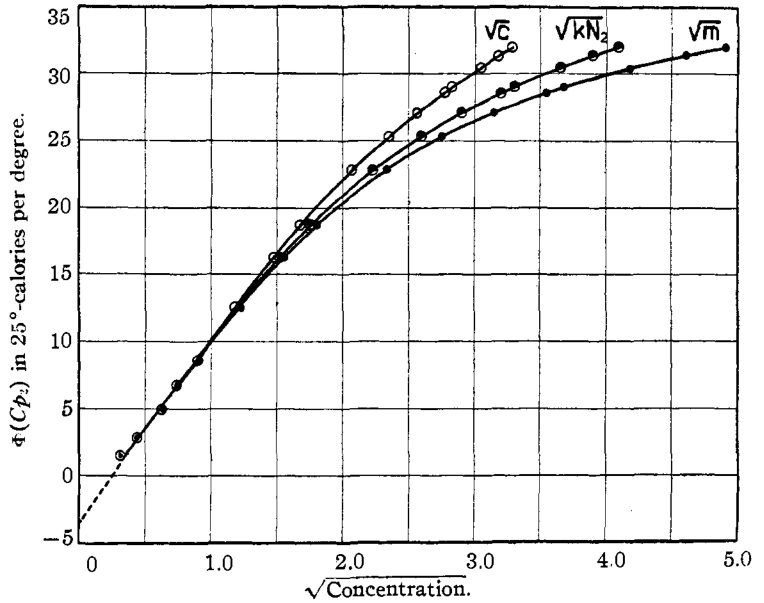

Fig. 5.—A comparison of abscissas.

Accordingly we tried a general equation of the second degree in $\Phi(C_{p_2})$ and $m^{1/2}$, and found that it gave a much better agreement. Such a function reproduced the curve with average deviations of ±0.0085% in s, but there were five deviations of more than 0.01% and the deviations were systematic at both ends of the curve. In order to reduce the curvature, still employing a function of the weight concentration, we next tried the same type of equation with the abscissa $\sqrt{1000\ N_2/M_1}$ where N_2 is the mole fraction of solute, and M_1 the molecular weight of water. This curve coincides with the previous one at low concentrations and in general lies about midway between the plot against $m^{1/2}$ and that against $c^{1/2}$ (see Fig. 5). The agreement was not appreciably improved. Finally we tried the equation

$$\Phi^2 + ac + b\Phi c^{1/2} + dc^{1/2} + e\Phi + f = 0$$

Substituting five values of the variables we evaluated the coefficients a, b, d, e, f. The equation was solved for Φ by the general algebraic formula. Calculated values of Φ were then compared with the experimental ones, and several successive solutions were tried to obtain the coefficients which gave best agreement at every point on the curve. The equation which we finally obtained was

$$\Phi(C_{p_2}) = 6.036 + 9.991c^{1/2} - [93.644 - 78.79c^{1/2} + 19.683c]^{1/2}$$

From this equation we calculated the values of Φ which are included in Table II. The average deviation in the specific heat, Δs, is ±0.0075%, with only one of the seventeen observations showing a deviation exceeding 0.011%. In order to check this value, a final experiment, No. 9, was made at almost exactly the same concentration. It gave a value of the specific heat about 0.02% higher than the former one, but still 0.01% lower than the curve at this point. Since this was the largest discrepancy in the whole series, we may conclude that the experimental results, obtained by two experimenters using different samples of ammonium nitrate and making up solutions independently, are in very satisfactory agreement.

Using the last equation, we calculated the values of the apparent molal heat capacity of the salt at even values of c, which are collected in Table III. We also included the corresponding values of the molality and of the partial molal

TABLE III

THE SPECIFIC HEATS OF AMMONIUM NITRATE SOLUTIONS AND VALUES OF $\Phi(C_{p_2})$, $\bar{C}_{p_2}$ AND $\bar{C}_{p_1} - \bar{C}^{\circ}_{p_1}$ AT EVEN CONCENTRATIONS

c	m	s	$\Phi(C_{p_2})$	$\bar{C}_{p_2}$	$\bar{C}^{\circ}_{p_1} - \bar{C}_{p_1}$
0.0	0.0	1.00000	−3.6	−3.6	0.0000
.25	.2538	0.98092	3.3	6.8	.0156
1.0	1.0541	.93205	10.15	16.50	.1205
2.0	2.2239	.87818	15.52	23.47	.3184
3.0	3.5319	.83277	19.313	27.631	.5292
4.0	5.0066	.79314	22.171	30.146	.7194
5.0	6.6842	.75766	24.392	31.752	.8862
6.0	8.6120	.72539	26.179	32.927	1.0469
7.0	10.8529	.69586	27.678	33.893	1.2151
8.0	13.4928	.66874	28.979	34.726	1.3969
9.0	16.6522	.64379	30.142	35.452	1.5930
10.0	20.5044	.62083	31.203	36.083	1.8026
11.0	25.3099	.59966	32.183	36.624	2.0249

heat capacities of the solute and solvent. The partial molal heat capacity of the solute, $\overline{C}_{p_2}$, was obtained from the general equation which had been derived previously,[6a] namely

$$\overline{C}_{p_2} = \Phi(C_{p_2}) + \left[\frac{1000 - c\Phi(V_2)}{2000 + c^{3/2}\dfrac{\partial\Phi(V_2)}{\partial c^{1/2}}}\right] c^{1/2}\,\frac{\partial\Phi(C_{p_2})}{\partial c^{1/2}}$$

Values of $\Phi(V_2)$ were calculated from the equation previously given, and $\partial\Phi(V_2)/\partial c^{1/2}$ from its derivative

$$\partial\Phi(V_2)/\partial c^{1/2} = 0.966 + 0.0948c^{1/2}$$

The values $\partial\Phi(C_{p_2})/\partial c^{1/2}$ were obtained from the derivative of our equation, which was

$$\frac{\partial\Phi(C_{p_2})}{\partial c^{1/2}} = 9.991 + \frac{39.395 - 19.683c^{1/2}}{[93.644 - 78.79c^{1/2} + 19.683c]^{1/2}}$$

The partial molal heat capacity of the water was obtained from the equation

$$\overline{C}_{p_1} = \overline{C}^{\circ}_{p_1} - \frac{M_1}{d_1}\left[\frac{c}{2000 + c^{3/2}\dfrac{\partial\Phi(V_2)}{\partial c^{1/2}}}\right] c^{1/2}\,\frac{\partial\Phi(C_{p_2})}{\partial c^{1/2}}$$

where M_1 is the molecular weight (18.0156 g.) of water and d_1 is its density (0.997077 g./ml.) at 25°. This equation is perfectly general, and would apply to any other partial molal property as well as to the heat capacity. In the case of the partial molal volume of the solute, it reduces to an equation analogous to that derived by Gibson[8] for the partial specific volume. Calculations involving the volume concentration are more complicated than those involving the weight concentration, but their use is justified when the apparent molal property may be expressed more exactly as a function of the volume than of the weight concentration.

In Fig. 6 we have plotted $\Phi(C_{p_2})$, $(\overline{C}_{p_2})$ and $\overline{C}_{p_1}$. The apparent molal heat capacity of the solute starts from the value −3.6 calories per mole per degree at zero concentration, with an initial slope of $\partial\Phi(C_{p_2})/\partial c^{1/2} = 14.06$, which decreases to 6.287 at $c = 11$. The corresponding partial molal heat capacity starts from the same point, with a slope half again as great. It is always greater than the apparent molal heat capacity, but the difference is greatest (8.3 calories per degree) at 3 molar and decreases steadily to 4.4 at 11 molar, where the *slope* of the curve is only about 55% of that of the apparent molal heat capacity curve.

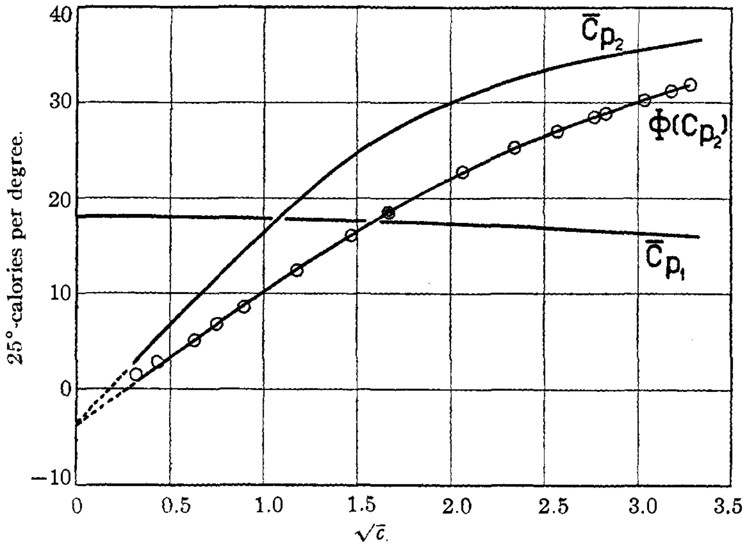

Fig. 6.—Apparent and partial molal heat capacities in solutions of ammonium nitrate at 25°.

The partial molal heat capacity of the water decreases regularly from the value in pure water, $\overline{C}^{\circ}_{p_1}$ = 18.0156 25°-calories per degree, to a value of 15.9907 in a saturated solution of ammonium nitrate (11 molar): a decrease of 11%.

Acknowledgments.—It is a pleasure to acknowledge our indebtedness to the National Research Council for a Grant-in-Aid which defrayed part of the cost of the apparatus used in this work; to Professor R. G. Bigelow and Mr. M. L. West of the Northwestern Engineering School for their advice and assistance in the construction of many parts of the apparatus; and to Mr. Robert J. Mueller who, working under an N. Y. A. project, assisted in the purification of much of the ammonium nitrate.

Summary

We have described the construction and operation of a new modification of the twin calorimetric apparatus for measuring specific heats. Special electrical heaters with resistances variable in small increments, mounted on mica strips, are used to supply energy proportional to the heat capacity in each calorimeter. The resistance ratio is measured during the experiment.

Solutions of ammonium nitrate were made from weighed amounts of purified dried salt and water, or from a single quantitative dilution. The specific heats of seventeen of these solutions, over

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[8] Gibson, *J. Phys. Chem.*, **38**, 319 (1934).

the concentration range 0.1 to 10.75 moles per liter, were measured at 25°.

The apparent molal heat capacity is a linear function of $c^{1/2}$ (or $m^{1/2}$ or $N_2^{1/2}$) only up to about a 1.5 molal solution, above which the relation found by Randall and Rossini fails. A hyperbolic second degree equation for the apparent molal heat capacity as a function of the square root of the volume concentration reproduces the specific heats with an average deviation of ±0.0075%. Values of the partial molal heat capacity of the salt at round concentrations were calculated from an equation previously derived and values of the partial molal heat capacity of the water were calculated from a new equation which is generally applicable to all molal quantities. These values are tabulated, along with those of the specific heats of the same solutions.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Thermodynamics of Aqueous Indium Sulfate Solutions[1]

BY ERWIN M. HATTOX AND THOS. DE VRIES

Very little work has been done on the activity coefficients and other thermodynamic properties of aqueous solutions of the ter-bivalent salts. Hovorka and Rodebush[2] determined the freezing point lowering of dilute solutions of lanthanum sulfate, and from these data calculated the activity coefficients. Since their results dealt only with dilute solutions, it seemed desirable to study the behavior of indium sulfate in aqueous solutions over a wider range of concentrations and at several temperatures. E. m. f. measurements were made on cells of the type In (s) | $In_2(SO_4)_3$ (*m*) | Hg_2SO_4–Hg at 0, 15, 25 and 35°, and freezing point lowerings were determined for a few dilute solutions of indium sulfate. The degree of hydrolysis was also determined at room temperature.

Materials and Apparatus

All materials used in this investigation were very carefully purified. The water used for making the solutions and for making ice was prepared by double distillation of the ordinary laboratory distilled water. The first distillation was made from alkaline permanganate and the second from barium hydroxide. The water thus purified was stored in glass-stoppered Pyrex bottles.

Commercially pure indium (98.9%), obtained from W. S. Murray, Ithaca, New York, was purified in the following manner. The metal was dissolved in concentrated nitric acid, the solution diluted, and precipitated as indium hydroxide with dilute ammonium hydroxide. This was washed several times and dissolved in dilute hydrochloric acid. Spongy indium was plated out from this solution, using platinum electrodes and a current of about 0.3 ampere. The washed, spongy mass then served as an anode in another dilute hydrochloric acid solution, the indium being redeposited by electrolysis on a platinum cathode.[3] Indium sulfate was prepared from this indium by slowly evaporating a strong sulfuric acid solution of it at about 50°, washing the crystals that separated out with glacial acetic acid, and then heating in a furnace to a temperature of 450–500° for six hours.[4] By gravimetric analysis the product was shown to be anhydrous indium sulfate.

The mercury was purified by washing for several days with dilute nitric acid and distilling twice under reduced pressure in a current of air.

Mercurous sulfate was prepared by electrolysis from dilute sulfuric acid using a mercury anode and a platinum cathode, and a current density of 0.5 ampere per square decimeter. In order to prevent the formation of a yellow basic salt due to hydrolysis, the mercurous sulfate, along with the finely divided mercury mixed with it, was washed first with alcohol, then with ether. The product was dried and kept in a desiccator until ready for use.

The most concentrated indium sulfate solution was made up by weight from the prepared anhydrous salt. All the solutions of lower concentrations were made by successive weight dilutions, using an analytical balance of 2-kg. capacity.

After experimenting with complicated cells in which the air could be replaced by hydrogen, a simple cell was developed, made by sealing a platinum wire in the bottom of a 16-mm. Pyrex tube, and having a side-arm in which the indium electrode was placed.

The thermostat temperatures were maintained within ±0.01°. A two-liter size Dewar flask with crushed ice served very satisfactorily for the 0° bath. All temperatures were established with standard thermometers.

Electromotive forces of the cells were measured on a Leeds and Northrup Type K potentiometer.

Apparatus for the freezing point measurements was

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[1] Based upon a thesis submitted by Erwin M. Hattox to the Faculty of Purdue University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1936. Presented before the American Chemical Society at its 92nd meeting in Pittsburgh, Pa., Sept. 7-11, 1936.

[2] Hovorka and Rodebush, THIS JOURNAL, **47**, 1614 (1925).

[3] Baxter and Alter, *ibid.*, **55**, 1943 (1933).

[4] Seward, *ibid.*, **55**, 2740 (1933).