[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY, HARVARD UNIVERSITY]

AN IMPROVED DIFFERENTIAL METHOD FOR THE EXACT DETERMINATION OF SPECIFIC HEATS OF AQUEOUS SOLUTIONS; INCLUDING RESULTS FOR VARIOUS SALTS AND ORGANIC ACIDS

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Introduction

This research was undertaken to provide data for further study of the heats of neutralization, similar to previous work in this Laboratory.[1] Specific heats are the foundation upon which is built the structure of thermochemistry. Obviously, refinements in measuring the rise of temperature produced by a chemical reaction are futile unless the pertinent heat capacity is known with equal accuracy.

The specific heats of aqueous solutions have been so often studied that a complete history of their determination would be too voluminous for this paper. Early work (chiefly rather crude in quality) was reviewed comprehensively by Hermann Kopp,[2] and later work (previous to 1905) has been described elsewhere.[3]

Subsequent contributions are noted below.[4]

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[1] Richards and Rowe, THIS JOURNAL, **44**, 684 (1922).

[2] Kopp, *Ann. Chem. Pharm.*, Suppl., **3**, 1 (1884–1885).

[3] Richards and Lamb, *Proc. Am. Acad. Arts Sci.*, **40**, 659 (1905).

[4] (a) Muller and Fuchs, *Compt. rend.*, **140**, 1639 (1905). (b) E. Bose, Müller and M. Bose, *Nachr. Kgl. Ges. Wiss. Göttingen*, p. 277 (1906); *Z. physik. Chem.*, **58**, 585 (1907). (c) Bose, *Chem. Zentr.*, **78**, 233 (1907). (d) Aufhauser, *Rev. Fett. Harz Ind.*, **14**, 57 (1907). (e) Magie, *Proc. Am. Phil. Soc.*, **46**, 138 (1908); *Phys. Rev.*, [1] **25**, 171 (1907). (f) Schlesinger, *Phys. Z.*, **10**, 210 (1909). (g) Swientoslawski, *Anz. Akad. Wiss. Krakaw*, 548–55 (1909); through *Chem. Zentr.*, **81**, 472 (1910). (h) Magie, *Z. physik. Chem.*, **71**, 636 (1910). (i) Schröder, *J. Russ. Phys.-Chem. Soc.*, **40**, 360 (1908). (j) Doroshevskii and Rakovskii, *ibid.*, **40**, 860 (1908); **41**, 1110 (1909). Doroshevskii, *ibid.*, **41**, 958 (1909). (k) Brillouin, *Ann. chim. phys.*, [8] **18**, 197 (1909). Mellecoeur, *ibid.*, [8] **23**, 556 (1911). (l) Louguinine, *Arch. Sci. Phys. Nat.*, **29**, 29 (1909). (m) Mills and MacRae, *J. Phys. Chem.*, **14**, 797 (1910). (n) Lussana, *Nuovo cimento*, [6] **4**, 207 (1912). Johnson and Hammer, THIS JOURNAL, **35**, 945 (1913). (p) Campetti, *Atti accad. sci. Torino*, **48**, 968 (1913). (q) Telkessy, *Chem.-Ztg.*, **35**, 724 (r) Magie, *Proc. Am. Phil. Soc.*, **51**, 235 (1912). (s) Hartung, *Trans. Faraday Soc.*, 11, 64 (1915). (t) Heydweiller, *Ann. Physik*, **46**, 253 (1915). (u) Bramley, *J. Chem. Soc.*, **109**, 496 (1916). (v) Keyes and Babcock, THIS JOURNAL, **39**, 1524 (1917). (w) Barus, *Proc. Nat. Acad. Sci.*, **5**, 340 (1919). (x) W. R. and C. E. Bousfield, *Phil. Trans.*, **218A**, 119 (1919). (y) Narbutt, *Z. Elektrochem.*, **24**, 42, 339 (1918). (z) Bailey and Edwards, *J. Ind. Eng. Chem.*, **12**, 891 (1920). (aa) Cohen and Moesveld, *Z. physik. Chem.*, **95**, 305 (1920). (bb) Tréhin, *Ann. phys.*, [9] **15**, 246 (1921). (cc) Werner, Koch, *Z. ges. Kalte-Ind.*, **29**, 37; *Chem. Zentr.*, **93**, 905 (1922). (dd) Blaszkowska, *Bull. soc. chim.*, **33**, 562 (1923). (ee) Pascal and Gainier, *Mem. Poudres*, **20**, 29 (1923).

One of the greatest improvements in experimental technique was the "twin calorimeter" method first invented by Joule and improved by Pfaundler.[5] Of two resistance wires, having equal value and connected in series, one was immersed in the liquid under investigation and the other in water. A given current through these resistances yielded a like quantity of heat in each calorimeter; hence, rise in temperature was inversely proportional to heat capacity. If the two heat capacities were very different, one of the resistances could be correspondingly altered so as to equalize the temperature changes. Thus, errors from heat interchange with the surroundings could be partly eliminated.

The method was further improved and elaborated by Magie[6] and has also been used with slight modification by Swientoslawski,[4g] Heydweiller,[4t] Koch,[4cc] Blaszkowska,[4dd] and Moureu.[4ff] It has been applied not only to solutions, but also to solids immersed in a suitably inert liquid. Lamb and Fairhall[7] substituted chemical (neutralization) heating[8] for electrical, which made easily possible the exact adjustment of the temperature rise in each calorimeter. Although this method is an excellent one and yielded very accurate results, the time needful for the preparation of each experiment was much greater than that required with the present apparatus.

The Apparatus

In the present research, "adiabatic calorimetry"[9] was applied to Joule's electrical method and comparison of specific heats was made by a new

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(ff) Moureu, Dufraisse and Landrieu, *Compt. rend.*, **176**, 1573 (1923). (gg) Keyes and Beattie, THIS JOURNAL, **46**, 1753 (1924). (hh) Wrewsky and Kaigorodoff, *Z. physik. Chem.*, **112**, 83 (1924); **113**, 490, Errata. (ii) Williams and Daniels, THIS JOURNAL, **46**, 903, 1569 (1924). (jj) Dickinson and Osborne, *Bur. Standards Sci. Paper*, Nos. 247, 248 (1915). (kk) Osborne, *ibid.*, **301**, 133 (1917). (ll) Cohen, Helderman and Moesveld, *Proc. Acad. Sci. Amsterdam*, **27**, 565 (1924). (mm) Busse, *Ann. Physik*, **75**, 657 (1924). (nn) Maass and Waldbauer, THIS JOURNAL, **47**, 1 (1925). See also Richards and Rowe, Ref. 8; Lamb and Fairhall, Ref. 7.

[5] Joule, *Mem. Manchester Lit. Phil. Soc.*, [2] 559 (Read 1845); *Scientific Papers*, 1, 192 (Taylor and Francis, London, 1884). Pfaundler, *Sitzsb. Akad. Wiss. Wien.*, **59**, 2145 (1869). We are indebted to Dr. W. P. White for knowledge of Joule's priority.

[6] Magie, (a) *Phys. Rev.*, **9**, 65 (1899); (b) **13**, 91 (1901); (c) **14**, 193 (1902); (d) **17**, 105 (1903).

[7] Fairhall, *Thesis*, presented to the Faculty of Arts and Sciences of Harvard University, for the degree of Doctor of Philosophy, 1918.

[8] Richards and Rowe, (a) *Proc. Am. Acad. Arts Sci.*, **43**, 475 (1908); *Z. physik. chem.*, **64**, 187 (1908); (b) *Proc. Am. Acad. Arts Sci.*, **49**, 173 (1913); *Z. physik. chem.*, **84**, 585 (1913); (c) THIS JOURNAL, **43**, 770 (1921).

[9] Attention should be called to the use of adiabatic calorimetry by Person, long ago [*Ann. chim. phys.*, [3] **27**, 270 (1849)]. Having been buried and forgotten, the method was again suggested in 1895 [S. W. Holman, *Proc. Am. Acad. Arts Sci.*, **31**, 252 (1895)], independently developed experimentally in 1905 [Richards, Henderson and Forbes, *ibid.*, **41**, 3 (1905)] and later improved with the help of other collaborators.

method of substitution. A general idea of the whole apparatus can be gained from Fig. 1.

The two calorimeters CC were each enclosed in a "submarine" jacket B, and supported on a light glass frame resting upon cork wedges which served for thermal insulation. A collar made of waxed paper M, fastened to the lid, fitted tightly over the lip of the calorimeter so as to prevent the evaporation of water into the air space between calorimeter and jacket.

The liquid in each calorimeter was agitated by the reciprocating stirrers EE, which were moved up and down at the rate of 50 strokes per minute. They were rigidly bolted to the cross bar H which was carried on a vertical reciprocating shaft and guided by a second shaft (not shown in the figure).

The resistance coils DD were connected in series to a source of direct current by means of heavy copper wires dipping into the mercury cups KK. The difference in temperature between the two calorimeters was measured by means of the thermo-element G. Two smaller thermo-elements FF, connected in series, measured the difference between the average temperature of the calorimeters and that of the outer water-bath A. Several details of the apparatus thus briefly outlined, now deserve description.

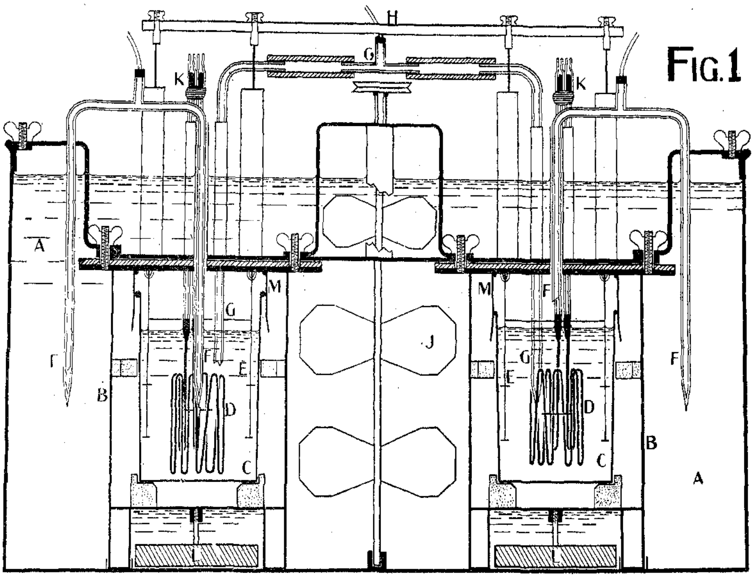


FIG. 1

Environment of Calorimeter.—By means of studs and wing-nuts the lids of the "submarine" jackets were clamped down upon rubber gaskets (represented by cross hatching). Two horizontal strips of heavy brass were secured by these same bolts, holding the jackets fixedly with respect to one another. Other similar strips, bent at right angles, clamped them rigidly within the large outer water-bath. This rigid construction allowed the apparatus to be taken apart and assembled in the same position without disturbing any of the adjustments. The stirrers, once carefully aligned, gave no trouble during the year. Lead weights LL fastened to the bottoms of the "submarines" overcame their buoyancy and allowed them to be handled more easily. The water-bath (heated by 4 electric lamps—two 500-watt heaters and two 40-watt elongated bulbs) was rapidly agitated by the propeller stirrer J, run at 360 r.p.m.

Quantitative Heating Coils.—The development of a satisfactory heating coil presents a difficult technical problem. The resistance wire must be insulated from the solution, if the latter is an electrolyte, and the insulation must be impervious to the solution in which it is immersed. Previous investigators experienced great difficulty in making a coil that would fulfil this condition.[10]

For the present research constantan wire (employed for obvious reasons), insulated by asbestos, was obtained through the kindness of Professor T. Lyman of the Jefferson Physical Laboratory of this University and yielded excellent service. Each wire was shielded from the solution by a fine brass tube, from which it was adequately insulated by its asbestos covering.

The arrangement was assembled as follows.

Fig. 2

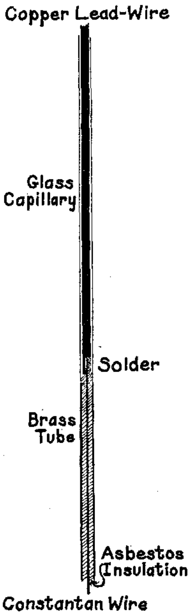
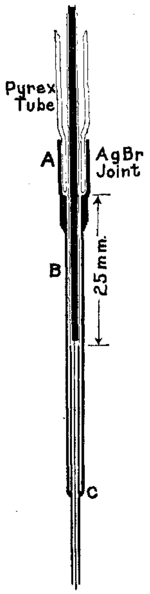


Fig. 3



Each of two exactly similar pieces (about 110 cm. and 10 ohms) of covered constantan wire was pulled into a snugly-fitting brass tube (1.6 mm. external diameter) which was then bent into somewhat the form of the tungsten wire in an ordinary lighting bulb. Copper lead wires were soldered to each end, as shown in Fig. 2, after which they were enclosed in glass capillaries. Brass collars (of the dimensions shown) previously fastened to 5mm. Pyrex tubes by means of fused silver bromide, were then soldered to the brass tubing at C (Fig. 3). Each entire brass coil was then heavily gold-plated, and the metal at the soldered joints was protected by a thin coating of celluloid cement (celluloid dissolved in acetone). The upper ends of the two lead wires were sealed into the Pyrex tubes with de Khotinsky cement and a mercury cup on the top of each formed a connection which was simple, convenient and constant. Each coil was mounted by cementing its Pyrex tubes within an enclosing brass one. These latter tubes fitted snugly into the "chimneys" of the "submarine" jacket. Suitable collars enabled the coils to be secured in exactly the same positions in successive experiments. Spring clips held

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[10] Pfaundler, *Sitzsb. Akad. Wiss. Wien*, 1002–**A**, 352 (1891) used capillary glass tubing filled with mercury, as did also Joule; but mercury is far from satisfactory because its resistance changes greatly with change of temperature. Magie[6c] used special German silver wire with a low temperature coefficient of resistance-change. He protected it by means of a coating of asphalt varnish and ozokerite. Blaszkowska[4dd] used a constantan wire with large copper leads. The wires were slipped into a glass capillary which was wound into a spiral. A silver mirror deposited on this was heavily plated with copper, which was protected by an outer layer of silver-plate. The metal tube thus formed provided mechanical strength, but the air space and the glass tube around the resistance wire delayed the dissipation of heat.

them in place. Each heating coil had a heat capacity of only about 2 cal. per degree, and the heated wire was in good thermal contact with the solution. The resistance wires ended 25 mm. below the glass tube; so that the lead wires, being in fairly good thermal contact with the solution for that distance, could not conduct from the calorimeter the heat generated in the coil. The lead wires were large and consequently had little resistance. The larger glass tubes acted not only as electrical, but also as thermal insulators. The coils had considerable mechanical strength, and were not affected by the solutions. For some reasons it would have been better to use larger resistances, (as W. P. White has suggested) but our method of substitution probably made this precaution unnecessary.

Calorimeters, Stirrers.—The calorimeter for the solutions was of platinum, whereas the tare-calorimeter was of spun copper, heavily silver-plated and gold-plated inside. The reciprocating stirrers were two-stage, made of platinum and gold-plated silver, respectively. Each carried a central disk (suspended from an upper cross-bar) which insured vigorous stirring even inside the heating coils.

"Submarine" Jackets.—The jackets were of the familiar type, constructed of sheet copper and nickel-plated. A ground joint for connecting the lids, advocated by Daniels[11] was not successful, because of warping of the castings from which the ground parts were made. A flat flange (with greased rubber gasket) was finally adopted and gave no trouble.

Thermo-elements (or "Thermels").—These were of copper-constantan (multiple-junction), constructed according to the design of W. P. White.[12] The largest (of low resistance) was made in two opposable sections of four junctions each, and could thus be tested at any time to insure its integrity. For the small thermo-elements finer constantan wire was used; and each contained only three junctions. All were enclosed in Pyrex glass (which has a higher coefficient of thermal conductivity than soft glass) and the junctions were embedded in naphthalene.

The galvanometer was a Leeds and Northrup instrument, having a sensitivity of 7 mm. per mv., with the scale 1.4 meters from the mirror. It was shielded electrically by enclosure in a metal box, which was made a part of the equipotential shield[13] protecting the whole electrical system. A wooden box fitted loosely over the metal one and the space between was packed with felt for thermal protection. White's clothes-pin "anti-thermo-electric" clips were used for all connections which were not soldered. Either the large thermo-element, or the two small ones (in series) could be connected to the galvanometer, by a suitable switch. In addition, each thermo-element was provided with an eliminating switch, by which it could be short-circuited. The polarity of the galvanometer could be changed by a reversing switch, the average of the two deflections always being taken to obtain the most accurate reading. These devices showed

[11] Daniels, This Journal, **38**, 1473 (1916).

[12] White, *ibid.*, **36**, 2292 (1914).

[13] Ref. 12, pp. 1856, 2011, 2480.

that the stray currents in the circuit were so small as to be almost negligible, and assisted in compensating for them.

The large thermo-element was standardized (after inserting a large extra resistance) by establishing a difference in temperature between the two calorimeters, read by means of two large standardized thermochemical thermometers. Allowing for the extra resistance, the sensitivity of the circuit was easily computed. Eight experiments, with varying temperature differences and extra resistances of 4000 and 9000 ohms, indicated a sensitivity of 0.000435° per mm. (±0.000003°). A 1% error could not affect the final results, since the thermo-element was used only for differences of temperature of less than 0.01°. The sensitivity of the two small thermo-elements in series was calculated to be 0.000672° per mm. The thermo-element is of course at its best when used (as in this research) almost as a zero instrument, for measuring very small differences of temperature.

Adiabatic Control.—Adiabatic calorimetry was peculiarly convenient since the "reaction" (electrical heating) could readily be accelerated or retarded, started or stopped.

Heat Leakage.—Heat interchange between calorimeters and surroundings due to radiation, conduction and convection was reduced to a minimum. Under a thermal head of 0.007° the interchange through the air gap should cause a change of 0.0002° in 20 minutes according to Barry's data[14] for a larger calorimeter. Conduction through solid parts (calculated from the thermal conductivities involved) was estimated to be only 0.0001°. A series of experiments, carried out under working conditions, showed that the leakage in the same time was practically identical for the two calorimeters and amounted to 0.0002° for a positive and 0.0006° for a negative thermal head of 0.007°. The difference is due to the effect of evaporation from the surface of the calorimeter in the latter case, and condensation upon it in the former.[15] Barry's data are for a closed calorimeter, with which the rate of leakage is the same for positive as for negative thermal heads. The calculated values for the leakage, based upon the latter's data, are somewhat larger than that herewith observed for a positive thermal head.

Since the rate of thermal leakage was found to be practically the same for the two calorimeters, the *difference* in their thermal heads alone is of moment. Unless this difference exceeded 0.006° for a continuous positive thermal head, or 0.002° for a negative one, thermal leakage would cause no appreciable error. In actual experiment, the difference in temperature between the two calorimeters never exceeded 0.006° and the average thermal head of the outer bath was kept slightly positive. Nevertheless, as a further precaution, the relative change in temperature of the two calorimeters was determined before and after each experiment. Thus a correction was applied for any heat leakage due to a difference in tempera-

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[14] Barry, This Journal, **44**, 899 (1922).

[15] Richards and Burgess, *ibid.*, **32**, 449 (1910).

ture between them, as well as for small thermal effects peculiar to the arrangement of any one experiment, such as the slight frictional heat developed by the reciprocating stirrers.

Errors from Evaporation.—In addition to the possible exchange of heat with the surroundings, there is an important thermal effect due to the evaporation of water from the liquid in the calorimeter. "Closed" calorimeters, with tightly fitting lids, are often employed to reduce this effect. Owing to the construction of the reciprocating stirrers in this apparatus, many changes would have been necessary for the adoption of this device. A coating of oil also prevents evaporation; but it must be fairly thick and involves other difficulties. Fortunately, another device, simpler than the closed calorimeter and neater than oil, was found to be adequate.

Tightly fitted collars of heavy paper, impregnated with paraffin and sealed to the "submarine" lids by a mixture of beeswax and rosin, restricted the evaporation to a space about 320 cc. above each calorimeter. The cooling effect due to evaporation into this space (assuming complete saturation before and after the experiment) was calculated to be 0.0012°. In the differential method employed, if this evaporation were the same from each calorimeter, its effect would be eliminated from the results. Since, however, the vapor pressure of a solution is less than that of pure water, an appreciable error might perhaps thus be introduced. Moreover, the solution, because it occupied a slightly larger volume than the thermally equivalent amount of water, reduced the volume of the air-space above its calorimeter, into which evaporation was possible. The maximum sum of the resulting corrections was computed and found never to exceed 0.0003°, or 1/13,000 of the temperature change. Since the attainment of complete saturation was doubtful, half the appropriate correction was applied. The error of this compromise could rarely have exceeded 0.0001°, even if the saturation had been complete.

Air Pumped by Stirrer-Rods.—Error from this source was negligibly small. The stirrers were supported by 1.5mm. hard-drawn brass rods; while packing members, similar to those used by Barry, gave additional security. The packing cotton was slightly moistened at the top.

Materials and Solutions

The materials of which the solutions were made were of sufficient purity. The best preparations available were further purified, the solids by a fractional crystallization followed by centrifugal drying, and the acetic acid by thrice freezing the "glacial" acid.

Sodium hydroxide was especially guarded against carbon dioxide. A solution of the best available preparation, saturated at about 150°, was allowed to cool in a platinum dish to room temperature, yielding long crystals. These were washed with a little pure water in platinum Gooch crucibles and drained centrifugally. A minimum amount of water (free from carbon dioxide) was used to dissolve the crystals and the saturated solution was transferred (through a Gooch-Munroe crucible) to an 8-liter bottle, lined with paraffin.[16] Carbon dioxide was excluded with reasonable care; moreover, sodium carbonate, being practically insoluble in the saturated sodium hydroxide solution, would have remained in the filtering crucible. A portion of the solution showed no precipitate when tested with clear barium hydroxide solution. It contained only a trace of chloride, which could have had no appreciable effect upon its specific heat and was evidently of a high degree of purity.

The other solutions were kept in 4-liter bottles of resistant glass, from which they were drawn off through appropriately fitted siphon tubes, and in which they were protected from evaporation by passing the entering air through a gas-washing bottle containing the same solution.

The organic substances could not be heated to a temperature high enough to insure removal of the traces of moisture, and were therefore dried as well as possible at 60–70°. From these specimens (which still included traces of water) solutions slightly too concentrated were prepared; these were analyzed and diluted to the desired concentration.

Analysis of Solutions

The salt solutions were simply and accurately analyzed by weighing 20- or 30g. portions from a weight buret into a flask, evaporating to dryness at 100° and heating the salt to a constant weight at the highest permissible temperature.

The acid solutions were standardized by comparison with standard sodium hydroxide solution, using phenol-phthalein. The alkali had been provisionally standardized against constant-boiling hydrochloric acid[17] (which did not give wholly satisfactory results) by means of weight burets. Final standardization was effected by evaporating weighed portions of the sodium hydroxide solution with an excess of distilled hydrochloric acid and weighing the resulting sodium chloride. Two sets of analyses by the latter method, made two months apart, agreed within 1/10,000, checking both the analytical method and the integrity of the hydroxide solution. They agreed equally well with the average result of the less concordant provisional standardizations.

Specific Gravity Determinations

During this work all weighings of solutions were referred to the vacuum

TABLE I

SPECIFIC GRAVITIES OF SOLUTIONS

Substance		
Name	Formula	d_{18}^{18}
Acetic acid	$HC_2H_3O_2.25H_2O$	1.0168
Sodium acetate	$NaC_2H_3O_2.25H_2O$	1.0816
Sodium hydrogen tartrate	$NaHC_4H_4O_6.200H_2O$	1.0272
d-Tartaric acid	$H_3C_6H_5O_7.25H_2O$	1.1366
Sodium citrate	$Na_3C_6H_5O_7.50H_2O$	1.1696
Sodium dihydrogen citrate	$NaH_2C_6H_5O_7.50H_2O$	1.1078
Disodium hydrogen citrate	$Na_2HC_6H_5O_7.50H_2O$	1.1388

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[16] Ref. 1, p. 689. For purification see Mathews and Germann, *J. Phys. Chem.*, **15**, 73 (1911).

[17] Hulett and Bonner, THIS JOURNAL, **31**, 390 (1909).

standard. The following specific gravities, which could not be found in the literature, were therefore determined with a 25cc. volumetric flask. The result (d^{18}_{18}) is in each case the mean of two experiments; the last figure in each case is uncertain.

These results are adequate for the purpose of calculating vacuum corrections.

Standardization of the Apparatus

When two calorimeters are heated by resistance coils connected in series, the following equation holds:

$$(C_1W_1 + e)/(C_0W_0 + c_0) = (R_1/R_0)(\Delta T_0/\Delta T_1) \qquad (1)$$

Here C_1 and C_0 are the heat capacities per gram of the liquids of which W_1 and W_0 grams, respectively, are taken; c_0 and e are the heat capacities of the calorimeters (including the apparatus immersed in them); R_1 and R_0 are the resistances of the heating coils and ΔT_1 and ΔT_0 the resulting temperature increments.

To solve this equation directly, the resistance ratio (R_1/R_0) and the heat capacities e and c_0 should be determined with great precision. The process would be analogous to the use of a balance with unequal arms. This complication may be eliminated in the latter case by the expedient of weighing "by substitution." An analogous procedure was here adopted; the apparatus was standardized by the use of pure water in each calorimeter. A fixed weight of water (designated W_0) was always put into the left calorimeter, which thus played the role of a "tare" heat capacity. Many experiments then determined the weight of water (W_1) in the right calorimeter which would just "balance" the "tare" heat capacity, that is, the weight which, when heated 4°, would rise through exactly the same temperature interval as that shown by the "tare." Next, the weight W_2 of a solution was found, which when substituted for water in the right calorimeter would also just "balance" the "tare." The specific heat of the solution, compared with that of water over the same range of temperature, was then obtained by dividing W_1 by W_2. The result is independent of R_1/R_0 and also of c and e, if all these remain constant.

The "balancing weight" of water or of solution was calculated from the data of any particular experiment by noting the very small difference between ΔT_1 and ΔT_0. This was measured directly by the thermoelement.

If, during the experiment with water alone, the temperature of the right calorimeter rose more than that of the tare, it obviously contained too little liquid, and vice versa. The weight of water ΔW_1, which should have been added to that actually in the right calorimeter w_1 to make $\Delta T_1 - \Delta T_0 = 0$, was determined, much as are the tenths of a milligram in using a balance. There, small differences in weight are ascertained from deflections of the pointer; here, from small differences in rise of temperature.

The value of ΔW_1 is given by the equation,

$$\Delta W_1 = (w_1 + e/C_1)(\Delta T_1 - \Delta T_0)/\Delta T_1 \qquad (2)$$

All the terms in the right member of this equation were known experimentally, most of them with an accuracy far exceeding that necessary. The crucial datum is $(\Delta T_1 - \Delta T_0)$; this was found to within 0.0001° by the large thermo-element. Having thus computed ΔW_1, the quantity W_1 was easily found from the equation,

$$W_1 = w_1 + \Delta W_1 \qquad (3)$$

In the case of a solution the "solution equivalent" (e/C_2) takes the place of the "water equivalent" (e/C_1) and W_2, w_2 and (ΔW_2) take the place of W_1, w_1 and (ΔW_1), respectively, in Equations 2 and 3. To determine ΔW_1, the heat capacity of the solution need be known only very roughly, because it here concerns only a small correcting term in the presence of much larger numbers.

Experimental Procedure

When preparing for an experiment, the left (tare) calorimeter, after receiving 590.00 ± 0.01 g. of water (cooled at least 0.5° below the intended initial temperature), was quickly transferred to its supporting glass frame, which had been placed beneath an iron tripod stand. The lid of the "submarine" jacket, with its paper collar beneath, was placed upon the stand, of which the height was so adjusted that the paper collar fitted over the calorimeter, and supporting wire loops from the glass frame could just be slipped over their respective hooks on the lid. Calorimeter and lid together were then transferred to their appropriate places in the jacket. The heating coil and stirrer had been previously assembled with the lid; hence, one side (the "tare") of the calorimetric balance was now complete.

Immediately, the solution, weighed to centigrams in the second calorimeter, was adjusted in its duplicate jacket exactly as the "tare" had been. The two jackets were bolted together by means of brass strips and wing-nuts, which at the same time clamped the lids tightly in place. The entire assembly was transferred at once to the outer water-bath and bolted in place.

The thermo-elements were then slipped into the proper tubes in the lids of the jackets. Next, moving parts were appropriately adjusted and connected by belt with the motor; the heavy wire connections were slipped into the proper mercury cups; the cotton at the tops of the packing members was moistened and the apparatus was ready.

After starting the motor, the experimenter adjusted the outer bath to the initial temperature desired for the experiment, and warmed the cooler of the two calorimeters by means of its heating coil (interposing a temporary additional resistance of 500 ohms to retard the heating) until the two calorimeters were equally warm (± 0.002°). Then the two coils were connected in series, and the two calorimeters heated until their average temperature was about 0.005° lower than that of the outer bath. It is easy thus to start the experiment within 0.02° of the desired temperature, the manipulations taking five or ten minutes at the most.

The heat of stirring was found to be inevitably somewhat different on different occasions. Hence, it was determined for each individual experiment. As an experiment lasted for about 20 minutes, the temperature drift was observed for ten minutes beforehand and ten minutes afterward; and the algebraic sum of the two drifts (appropriately corrected to the exact time concerned) was taken as the drift during the experiment. During these tests the temperature of the outer bath was regulated as carefully as during the actual experiment.

The pre-experimental and post-experimental drifts were often different, so that some uncertainty is involved in the assumption that the change during the experiment was the algebraic sum of the two. This correction probably caused the largest part of the fortuitous "experimental error" in the result of an individual experiment. Nevertheless, the error introduced was not of serious magnitude; the concordance of the results of successive experiments is as satisfactory as could reasonably be expected.

The main experimental process occurred as follows. When the pre-experimental drift had been determined, a current of about 1 ampere was passed through the heating coils. This raised the temperature of the two calorimeters 4° in about 16 minutes. The temperature of the outside bath was simultaneously raised by means of the heating lamps. The adiabatic control during the first half minute was rather difficult to attain, although even then a thermal head exceeding 0.015° was rarely observed for even a few seconds. During the rest of the heating period, the control could easily be kept within ± 0.007°. As was previously mentioned, the thermal head was at all times kept positive, rather than negative.

When the carefully watched thermometer in the outer water-bath registered a temperature a few hundredths of a degree below the desired final point, the heating currents were stopped. Because of a slight delay in the dissipation of heat from the heating apparatus and because of the lag in registering the true temperature of the bath, inherent in all thermometers, the mercury thread continued to rise for some seconds after the supply of heat had ceased. If necessary, the heating circuits were both closed for a few seconds more, until the desired temperature was reached. Practice enabled the experimenter to allow for the lag to a nicety. The thermometer-column usually attained the desired final temperature within 0.01°. After this consummation, a full minute was allowed (to insure perfect thermal homogeneity) before the third reading of the difference in temperature between the calorimeters.

As a specific illustration, the data of a typical experiment are given in full, together with the necessary calculations.

A TYPICAL EXPERIMENT

3/25/24 $H_2C_4H_4O_6.25H_2O$ Expt. 4

	Water G.	Solution G.
Calorimeter + contents	740.91	805.20
Calorimeter	150.91	106.81
Contents	590.00 (W_0)	698.39 (w_2)

TABLE II

GALVANOMETER READINGS

Time Reading	Diff.	Scale reading[a] Cm.	Observed difference Cm.	Time factor[b]
4:05.0		+0.29		20.5/22.0
	11.0		−0.38	
4:16.0		− .09		
(C. on)	20.5		− .33	
4:36.5		− .42		
(C. off)	10.5		− .18	
4:47.0		− .18		20.5/21.0
Initial temp.	15.99°			
		Av. temp.	18.00°	
Final temp.	20.01°			
Total rise (ΔT)	4.02°			

[a] The average of two galvanometer deflections, using the reversing switch, "parasitics" having been thus eliminated from each reading as previously explained.

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

Multiplying the observed difference by the corresponding time factors gives the following corrected values.

Trend (before) = −0.354 cm. Trend (after) = −0.176 cm.

Total trend (corrected to time of heating) = −0.53 cm.

The corrected change in the galvanometer reading in the course of the heating was, therefore, —0.33 − (—0.53) = +0.20 cm. Since 1 cm. on the galvanometer scale corresponded to a difference in temperature of 0.00435°, the difference in temperature $\Delta T_1 - \Delta T_0 = (0.00435)\ (0.020) = +0.0009°$.

The positive sign indicates that the solution had risen more in temperature than the "tare," and therefore had a smaller heat capacity. The amount of solution which should be added to this calorimeter to make the rise of temperature of the two identical is calculated from the appropriate modification of Equation 2, thus:

$$\Delta W_2 = (w_2 + e/C_2)(\Delta T_1 - \Delta T_0)/T_1 \qquad (4)$$

$C_2 = 0.853$ (determined by a preliminary experiment).

$$\Delta W_2 = +\ (0.0009/4.02)\left(698.4 + \frac{6.34}{0.853}\right) = +0.15 \text{ g.}$$

W_2 (weighed in air) $= w_2 + \Delta W_2 = 698.39$ g. + 0.15 g. = +698.54 g.

This preliminary value of W_2 still needs two small corrections as follows.

Vacuum correction[18] = +0.093%, or +0.65 g.
Correction for evaporation = −0.003%, or −0.02 g.
W_2 (corr., in vacuum) = 698.54 g. + 0.63 g., = 699.17 g.
W_1 (in vacuum) = 596.50 g.
Specific heat = W_1/W_2 = 0.85315

The integrity of the apparatus, during the whole time of its use, is well shown by the repeated water standardizations. Seventeen experiments were made, at frequent intervals; the extremes differed by only 0.26 g., while the average of the first nine agreed with that of the last eight to within 0.02 g. These tests were carried out at three different temperatures (16°, 18° and 20°). The results were

At 16° (av. of Expts. 5, 7, 9, 17)	596.49 g.
18° (av. of Expts. 1, 4, 11, 13, 14, 15, 16, 20, 21)	596.49 g.
20° (av. of Expts. 6, 8, 10, 18)	596.52 g.
General average of all (W_2)	596.50 g.

They are seen to agree within experimental error. Evidently (as might be supposed) the heat capacity of the solid parts of the apparatus remained essentially constant, and the apparatus functioned consistently over the range of temperature explored.

All of the several results for the specific heat of $NaOH.25H_2O$ are given in full to illustrate the agreement among individual experiments.

TABLE III

SPECIFIC HEAT OF $NaOH.25H_2O$[a]

Expt.	Av. temp.	W_2 (vac.) G.	Specific heat
5a	15.97	654.03	0.91204
6a	16.02	654.07	.91198
7a	15.95	654.10	.91194
	Av. 15.98		.91199
1	18.00	653.11	.91332
2	18.00	653.24	.91314
3	18.00	653.14	.91328
4	18.00	653.07	.91338
	Av. 18.00		.91328
5b	19.97	652.17	.91464
6b	19.96	652.22	.91457
7b	19.96	652.18	.91462
	Av. 19.96		.91461

[a] Analysis gave the exact concentration = $NaOH.25.03H_2O$, density of the solution = 1.09, therefore vacuum correction = +0.00096 g./g. This correction and that for evaporation are included in W_2. W_1 = 596.50 g. (in a vacuum).

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[18] According to Thomsen ["Thermochemistry," trans. by K. A. Burke, Longmans, Green and Co., London, **1908**, p. 162] the density of this solution is 1.123.

Tabulation of Results for all Solutions

In all, thirteen different solutions were investigated. The first three (which had been previously determined by another method at Harvard[8c]) were studied at the beginning of this research, as a check upon the behavior of the new apparatus. The differences between the results obtained by the two methods are no greater than might be expected, considering the increased sensitivity and precision of the differential method herewith employed.

The atomic weights used in calculating the concentrations of the solutions were C, 12.00; N, 14.008; Na, 22.997; Cl, 35.458; O, 16.00; H, 1.008; K, 39.095.

Table IV contains averaged results, similar to those just detailed, depending upon 113 individual determinations of relative heat capacity. The last figure is in each case uncertain.

TABLE IV

SUMMARY OF RESULTS FOR THIRTEEN SOLUTIONS

Average specific heats referred to water over identical temperature ranges[a]

Solution	Av. temp. °C.	Specific heat
$NaCl.25.00H_2O$	18.04	0.87777
$NaNO_3.25.01H_2O$	18.01	.86842
$KNO_3.24.99H_2O$	18.01	.83284

Solution	16.00°	18.00°	20.00°
$HC_2H_3O_2.24.97H_2O$	0.95405	0.95445	0.95523
$NaC_2H_3O_2.24.99H_2O$	.90003	.90102	.90212
$H_2C_4H_4O_6.25.00H_2O$	.85200	.85328	.85445
$Na_2C_4H_4O_6.50.01H_2O$	.86615	.86711	.86808
$NaHC_4H_4O_6.200.04H_2O$	.96354	.96394	.96443
$H_3C_6H_5O_7.25.00H_2O$	.82080	.82193	.82327
$Na_3C_6H_5O_7.50.02H_2O$	.83556	.83659	.83747
$NaH_2C_6H_5O_7.50.00H_2O$	.87689	.87754	.87852
$Na_2HC_6H_5O_7.50.00H_2O$	.85804	.85894	.85977
$NaOH.25.03H_2O$[b]	.91200	.91328	.91464

[a] The specific heats of the last ten solutions here summarized are corrected to average temperatures of exactly 16°, 18° and 20°, so as to be strictly comparable.

[b] Reduction to exactly $NaOH.25H_2O$ would decrease each of these values by 0.0001.

Absolute Heat Capacities

The values summarized in Table IV are specific heats (over a 4° range) relative to water over the same range. Since the heat capacity of a gram of water changes with temperature, the values do not immediately show the changes of heat capacity of the solutions with changing temperature. For this purpose all results should be in absolute units. Unfortunately, the heat capacity of water is not as well known as its importance demands. Neither the relative heat capacities at different temperatures, nor the absolute heat capacity at any one temperature has been determined as accurately as have these specific heats. Considering the best values at present available,[19] Oscar C. Bridgeman, who has made an especial study of the matter, has concluded that the following values represent the best knowledge concerning the heat capacity of a gram of water at the temperatures named. The values are expressed in mayers (joules per centigrade degree); 10°, 4.1902; 15°, 4.1843; 20°, 4.1805; 25°, 4.1780; 30°, 4.1763. The following quadratic equation derived from these values has been found to represent these instantaneous values of heat capacity within the limit of error.

$$C_t = 4.1902 - (1.25)(10^{-3})(t^\circ - 10) + (2.7)(10^{-5})(t^\circ - 10^\circ)^2$$

From this equation by integration the following values have been computed for the mean heat capacities for the several ranges involved in the present research.

TABLE V

HEAT CAPACITY OF ONE GRAM OF WATER

Range, °C.	14–18	16–20	18–22
Mean temperature, °C.	16	18	20
Mean heat capacity, Mayers	4.1837	4.1820	4.1805

The mean heat capacities of the different solutions (obtained by multiplying the specific heats given in Table IV by the mean heat capacity of water over the same range) are given in Table VI. Δ_1 and Δ_2 are the differences between the heat capacities at 16° and 18° and at 18° and 20°, respectively.

TABLE VI

MEAN HEAT CAPACITIES OF A GRAM OF EACH OF THE SOLUTIONS

Over a range of 4°

Solution	Av. temp. °C.	Heat capacity Mayers
$NaCl.25.00H_2O$	18.04	3.6705
$NaNO_3.25.01H_2O$	18.01	3.6317
$KNO_3.24.99H_2O$	18.01	3.4829

HEAT CAPACITIES (MAYERS)

Solution	16°	$\Delta_1 \times 10^4$	18°	$\Delta_2 \times 10^4$	20°
$HC_2H_3O_2.24.97H_2O$	3.9915	0	3.9915	18	3.9933
$NaC_2H_3O_2.24.99H_2O$	3.7655	26	3.7681	32	3.7713
$H_2C_4H_4O_6.25.00H_2O$	3.5645	39	3.5684	36	3.5720
$NaHC_4H_4O_6.200.04H_2O$	4.0312	0	4.0312	6	4.0318
$Na_2C_4H_4O_6.50.01H_2O$	3.6237	25	3.6262	28	3.6290
$H_3C_6H_5O_7.25.00H_2O$	3.4340	33	3.4373	44	3.4417
$NaH_2C_6H_5O_7.50.00H_2O$	3.6686	13	3.6699	28	3.6727
$Na_2HC_6H_5O_7.50.00H_2O$	3.5898	23	3.5921	22	3.5943
$Na_3C_6H_5O_7.50.02H_2O$	3.4957	29	3.4986	24	3.5010
$NaOH.25.03H_2O$	3.8155	39	3.8194	42	3.8236

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[19] (a) Marks and Davis, "Steam Tables," (1909, republished 1910) give the mean of the best work before 1910. (b) Dickinson and Osborne, *Bur. Standards, Bull.*, **12,** 47 (1915). (c) Jaeger and von Steinwehr, *Ann. Physik.*, **64,** 305 (1921).

Evidently some of the heat capacities show considerable change, even with a 2° change in temperature. Moreover, the rate of change is far from constant: Δ_1 and Δ_2 often differ considerably. Hence, the true heat capacity at any temperature is not identical with the mean value (over a 4° range) at the same temperature. Assuming a quadratic change with temperature, instantaneous heat capacities may be calculated from these values by using a general equation: $C(t^\circ - 14^\circ) . = C_{14^\circ} + a(t^\circ - 14^\circ) + b\ (t^\circ - 14^\circ)^2$, similar to that employed in the case of water, in the reverse sense. The mathematical details needful for calculating *a* and *b* require too much space for presentation here. Like most other interpolation formulas, this equation can be safely employed only near the temperatures actually observed. The values of *a* and *b*, and of the instantaneous heat capacities, are recorded in Table VII.

TABLE VII

VALUES OF *a* AND *b*, AND OF THE INSTANTANEOUS HEAT CAPACITIES

Solution	Coefficients		True heat capacity (in mayers)				
	a	*b*	14°	16°	18°	20°	22°
$HC_2H_3O_2.24.97H_2O$	−131	22	3.9929	3.9912	3.9912	3.9930	3.9965
$NaC_2H_3O_2.24.99H_2O$	83	8	3.7634	3.7653	3.7680	3.7712	3.7751
$H_2C_4H_4O_6.25.00H_2O$	218	−4	3.5604	3.5646	3.5685	3.5720	3.5753
$NaHC_4H_4O_6.200.04H_2O$	−40	7	4.0316	4.0301	4.0311	4.0317	4.0329
$Na_2C_4H_4O_6.50.01H_2O$	111	3	3.6213	3.6236	3.6262	3.6290	3.6321
$H_3C_6H_5O_7.25.00H_2O$	89	13	3.4315	3.4338	3.4371	3.4417	3.4469
$NaH_2C_6H_5O_7.50.00H_2O$	−55	19	3.6688	3.6691	3.6700	3.6723	3.6769
$Na_2HC_6H_5O_7.50.00H_2O$	125	−2	3.5874	3.5899	3.5921	3.5942	3.5962
$Na_3C_6H_5O_7.50.02H_2O$	180	−6	3.4925	3.4958	3.4987	3.5011	3.5030
$NaOH.25.03H_2O$	164	5	3.8120	3.8154	3.8193	3.8236	3.8283

Plotted against temperature, most of the heat capacities are found to have minimum values, approximately as follows: water, 35°; $H_3C_6H_5O_7.25H_2O$, 11°; $HC_2H_3O_2.25H_2O$, 17°; $NaC_2H_3O_2.25H_2O$, 9° (?); $NaHC_4H_4O_6.200H_2O$, 17°; $NaOH.25H_2O$, —3° (?); $NaH_2C_6H_5O_7.50H_2O$, 13°; $Na_2C_4H_4O_6.50H_2O$, —4° (?).

Although meager and somewhat uncertain (since the small differences upon which they depend are dangerously near the experimental error), these data nevertheless show, as might be expected, that the minimum heat capacity of each solution occurs at a distinctly lower temperature than that of water. The lowering of the minimum is presumably dependent both on the concentration of the solute and on its strength as an electrolyte. It may well result from depolymerization of the solvent water, which the addition of a salt would cause. The shape of the curves would also be influenced by the heat capacity of the solute, and by the normal increase in heat capacity which is shown by nearly all substances, as the temperature rises.

Comparison with Previous Results

The specific heats of most of these solutions have not been previously determined; such results as have been found in the literature are given in Table VIII. The first three solutions here recorded were experimentally determined in this research for the purpose of testing the new method. Accordingly, the comparison of these is especially significant. The results in the last two columns have been corrected exactly to the temperatures and concentrations noted.

TABLE VIII

SPECIFIC HEATS AT 18°

	Thomsen[a]	de Marignac[b]	Others[c]	Richards and Rowe[d]	Richards and Gucker
$NaCl.25H_2O$	0.882 (?)	0.876	0.875 (?)	0.8776	0.8778
$KNO_3.25H_2O$	.832	.831	..	.8321	.8328
$NaNO_3.25H_2O$	.863	.868	..	.8695	.8684
$HC_2H_3O_2.25H_2O$	..	...	.946 (?)	...	.9546
$NaC_2H_3O_2.25H_2O$	.872 (?)	.9004	..	...	.9010
$H_2C_4H_4O_6.25H_2O$	.856	...	.844 (?)	...	.8533
$NaOH.25H_2O$	.909 (?)	...	..	...	.9132

[a] Thomsen's values for NaCl, $NaC_2H_3O_2$ and NaOH were found by graphic interpolation (Ref. 18, pp. 162–164).

[b] Only the value for NaCl was given at 18°. Those for KNO_3 and $NaNO_3$ were at 20.5° and that for $NaC_2H_3O_2$, at 22.5°. The correction to 18° is only approximate (*Oeuvres complètes*, Eggimann, Geneva, II, **1902**, 628).

[c] A value (0.8745) for $NaCl.25H_2O$ may be calculated from the data of Bousfield [*Phil. Trans.*, **218,** 135 (1919)]; 0.8754 from Blaszkowska's results at 21.4° (?) (Ref. 4dd). 0.946 for $HC_2H_3O_2.25H_2O$ may be obtained by interpolation from the data of v. Reis (Landolt-Börnstein, "Tabellen" 5th ed., **1923,** p. 1269; 0.844 for $H_2C_4H_4O_6.25H_2O$ may be calculated from the interpolation formula of Kalikinsky [*J. Russ. Phys.-Chem. Soc.*, **35,** 1215 (1903); abstracted in *J. Chem. Soc.*, **86,** ii 232 (1904)].

[d] The values given in the original paper were for $NaCl.(25.07)H_2O$; $KNO_3.(24.96)H_2O$ and $NaNO_3.(25.03)H_2O$. (Ref. 8c.)

Evidently the present results agree more satisfactorily with the earlier work in this Laboratory (obtained by a different method) than with that of any of the others. The remarkable success attained by de Marignac with his very simple method redounds to his credit. The most serious discrepancy is shown in the case of sodium hydroxide. Unfortunately, no earlier work was done in this Laboratory upon a concentrated solution of this substance, Richards and Rowe having used for their calculations involving dilution heats, the value 0.855 (derived from the work of others, which ranged from 0.84 to 0.89) for the specific heat of $NaOH.10H_2O$. Their values for $NaOH.25H_2O$ are seriously affected by this cause, but their values for the more dilute solutions of this substance are less affected. A full discussion of the matter will be given in a paper (almost ready for publication) presenting new exact determinations of the heat of dilution and heat capacity of sodium hydroxide solutions, together with the needful recalculations.

We are indebted to the Carnegie Institution of Washington and to an anonymous benefactor of this Laboratory, for generous financial support in this investigation.

Summary

The purpose of this research was to develop a precise method of determining specific heats and to obtain data that could be used in further thermochemical investigations.

1. The adiabatic principle has been applied to Joule's twin-calorimeter method. Measurement of the very small temperature differences involved was made by thermo-elements. One of the calorimeters was always used as a tare in the calorimetric balance; the other contained first water and then a solution, in alternate experiments. By this method of substitution many minor errors were avoided.

2. Electrical resistance coils were developed, with adequate mechanical strength and small heat capacity, in which the heated wire was in good thermal contact with the solution, yet protected from its chemical action, and in which there was a minimum of thermal leakage to the outside.

3. The results obtained with this apparatus are perhaps accurate to about one part in ten thousand, the method is expeditious, and the necessary calculation very simple.

4. The specific heats of three solutions were investigated at a mean temperature of 18°, and of ten solutions at mean temperatures of 16°, 18° and 20°.

5. These results were recalculated in terms of absolute heat capacity and also reduced to instantaneous heat capacities at 14°, 16°, 18°, 20° and 22°.

6. Most of the corresponding curves are similar to that for water; but the minimum values occur at lower temperatures.

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