

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

A New Micro-Calorimeter: the Heats of Dilution of Aqueous Solutions of Sucrose at 20 and 30° and their Heat Capacities at 25°¹

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Introduction

The study of heats of dilution of dilute aqueous salt solutions requires calorimetric apparatus capable of measuring small temperature changes to a millionth of a degree or better. The development of such a *micro-calorimeter*, begun in 1926 by Nernst and Orthmann,² has been chiefly the work of E. Lange and his collaborators from 1927 on. Lange's improved apparatus, which was described by Lange and Robinson³ with references to the original literature, consisted of a 2-liter unsilvered Dewar flask, divided into 2 similar calorimeters by a partition which carried a 1000-junction iron-constantan thermel. In one form of the apparatus the ends of the thermel projected a few mm. into the liquid, from which they were insulated by means of glass capillaries. This thermel, connected through a special potentiometer to a very sensitive galvanometer, enabled differential measurements to 1 microdegree or better. Each calorimeter contained a stirrer and a small pipet, the contents of which could be mixed with the surrounding liquid by pulling out suitable plugs. Heat liberated by a dilution in one calorimeter was balanced by quantitative electrical heating in the other. Lange and his co-workers investigated many salts in aqueous solutions and showed that the dilute solutions always *liberated* heat when they were diluted further. The heats of dilution changed linearly with the square root of the concentration and increased with increasing valence of the ions, in qualitative agreement with the Debye-Hückel limiting law. The major factor influencing the heats of dilution of very dilute aqueous solutions of electrolytes therefore is the electrostatic field of the ions.

A few scattered measurements of the heats of dilution of non-electrolytes indicate that they are much smaller than those of electrolytes, but do not show what limiting law they obey or what properties of the solute influence them. In order to investigate this subject we have developed a

(1) This paper was presented before the Division of Physical and Inorganic Chemistry at the Milwaukee Meeting of the American Chemical Society, September 7, 1938.

(2) Nernst and Orthmann, *Sitzber. preuss. Akad. Wiss.*, 51 (1926); *Z. physik. Chem.*, 135, 199 (1928).

(3) Lange and Robinson, *Chem. Rev.*, 9, 89 (1931).

new micro-calorimeter, embodying certain improvements in design and operation which will be explained later. We report in this paper studies of solutions of sucrose—chosen as a typical non-electrolyte for which the apparent molal volume⁴ and heat capacity⁵ already have been studied.

Apparatus

General Description.—A general idea of the apparatus can be obtained from the simplified section, Fig. 1, and plan, Fig. 2. It is a differential adiabatic apparatus, similar in many respects to that developed in this Laboratory for the precise measurement of specific heats of solutions.⁶ Two similar tantalum calorimeters, C, C, each containing a dilution pipet, P, are suspended from the lid of a water-tight submarine jacket, J, immersed in the water-bath, B. The submarine jacket is supported from an aluminum plate, R, by means of four brass tubes which accommodate the stirrer and lifter shafts. Two of these are shown in Fig. 1. The aluminum plate, suitably counterpoised, can be raised and clamped to a frame of iron pipe to permit the opening of the submarine jacket and the adjustment of the calorimeters. The large copper tank containing the water-bath, and the galvanized sheet-iron cover, L, are insulated by 5 cm. of hair-felt, indicated by cross-hatching. A sprocket-chain, driven from a synchronous motor, rotates the calorimeter stirrers at 180 r. p. m., two large 3-stage stirrers, W, W, in the water-bath at 270 r. p. m., and the large sprockets, F. The leakage of heat down the stirrer and lifter shafts is reduced by insulating sections of "Lucite."⁷ The calorimeter lids are spaced from the top of the submarine jacket by four tightly fitting cones of the same material, two of which are shown as D and E in Fig. 1.

The difference in temperature between the calorimeters is measured to 1 microdegree by means of a thermel, M, connected to a Paschen astatic galvanometer. The current sensitivity of this instrument is so great that a 60-junction thermel is adequate. Therefore, we are able to use a more conventional calorimetric arrangement than had been employed previously for this type of work. Fewer junctions and a 3-cm. gap between the calorimeters reduces thermal conduction between them to a small fraction of that in a calorimeter of Lange's type.

The air gap between our calorimeters and the walls of the jacket was 3 cm. The heat conductivity constant be-

(4) Redlich and Klinger, *Sitzber. Akad. Wiss. Wien.*, Abt. IIB, 143, 489 (1934); *Monatsh.*, 65, 137 (1934).

(5) Gucker and Ayres, *THIS JOURNAL*, 59, 447 (1937).

(6) Gucker, Ayres and Rubin, *ibid.*, 58, 2118 (1936).

(7) "Lucite" is the trade name of a methyl methacrylate resin made by the du Pont Company. Its coefficient of thermal conductivity, 4.3×10^{-4} cal./cm.²/sec./°C./cm., is about that of hard rubber. This and its other physical and chemical properties are summarized in an article entitled "Methacrylate Resins," *Ind. Eng. Chem.*, 28, 1160 (1936). Its heat capacity recently was measured in this Laboratory: Gucker and Ford, *THIS JOURNAL*, 60, 2563 (1938).

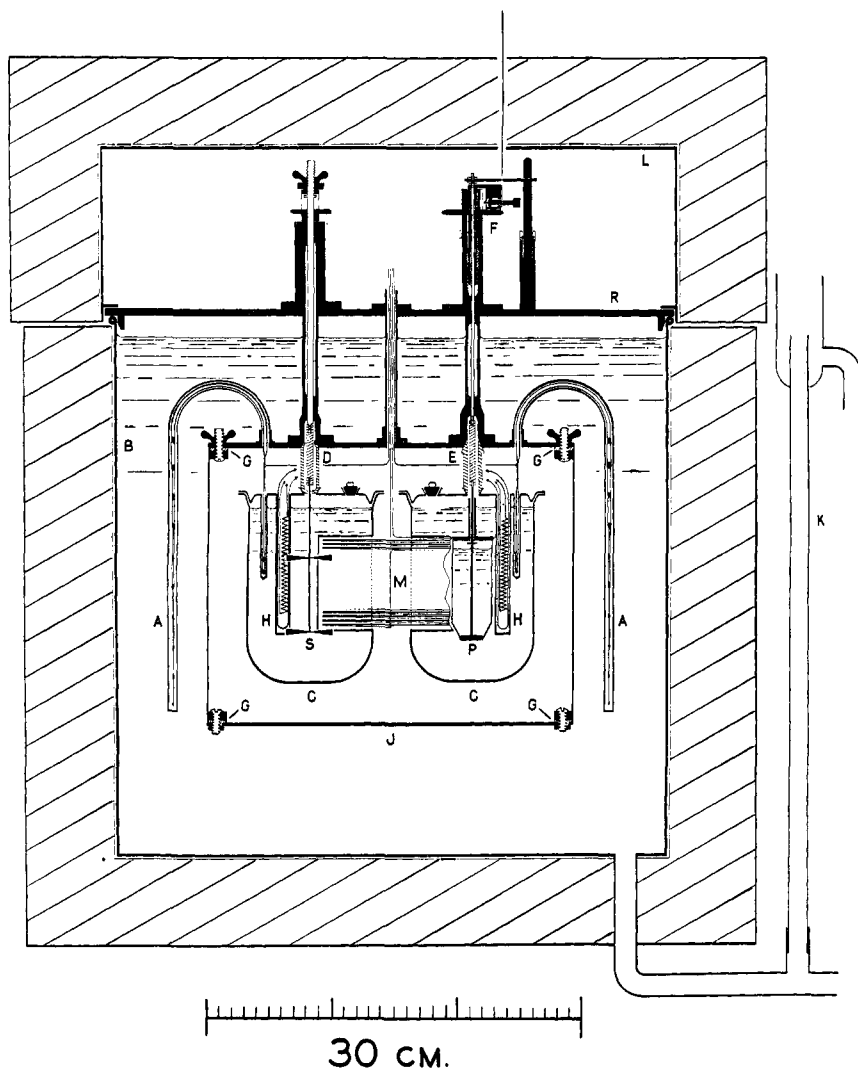


Fig. 1.—General view of the calorimetric apparatus.

tween each calorimeter and the outer bath was found to be 0.003/min. This is just half of the value given by Gulbransen and Robinson⁸ for an apparatus of Lange's type, employing an *unsilvered* Dewar flask, in which the black-body radiation is the controlling factor.

The difference in temperature between calorimeters and water-bath is determined by means of the adiabatic thermels, A, A, connected in series. These operate an automatic control which regulates the current through the four bath heaters, U (Fig. 2), so as to make the process practically adiabatic. Since the temperature changes involved in dilution are so small it is also practically isothermal. The advantages of the adiabatic method are well summarized in W. P. White's authoritative book⁹ and need not be described here.

Submarine Jacket.—The top and bottom of the submarine jacket were made of 3-mm. sheet copper, nickel-

plated and polished on the inner surfaces. The top plate was fastened tightly to the flanged lower ends of its supporting tubes. The monel metal walls of the jacket, burnished on the inside, were soldered to brass flanges which were bolted to the top and bottom through suitable gaskets, G, G. The bottom connection was made permanently with machine screws. After the calorimeters are installed, the upper flange of the jacket is attached by means of 12 wing-nuts.

Calorimeters.—The twin calorimeters, each holding about 1 liter, were made entirely of tantalum¹⁰ on account of its mechanical strength and its chemical inertness. A well was welded into the side of each calorimeter to receive the main thermel, M. The lid of each calorimeter was ground to fit and the joint was made tight with a grease consisting of 1 part paraffin to 3 of Vaseline. Wells in each lid received the electrical heater, H, and one end of the adiabatic control thermel. An opening in the lid, fitted with a ground plug, allowed the introduction of the diluting liquid without removing the entire lid. Each calorimeter was suspended by four loops of dental floss from adjustable hooks fastened to the top of the submarine jacket. A

similar arrangement was described fully in connection with the specific heat apparatus.⁶ Four Lucite spacers, two of which, D, E, are shown in Fig. 1, were machined to the proper length with conical ends fitting snugly into the calorimeter lids and the top of the jacket. Lucite is preferable to glass, which was first used, since its coefficient of thermal conductivity⁷ is only one-fifth as great, it is easily machined to the proper length and taper and it does not crack or break so easily.

Each dilution pipet, P, having a capacity of 60 ml., was suspended from the lid of the calorimeter by three rods (not shown) and could be removed easily for washing and drying, preparatory to re-loading. Each pipet was closed with heavy valves ground into the top and bottom. The valves were sealed with the best available grade of commercial Vaseline. Careful tests were made to see whether this contained any electrolytes which might dissolve in the water. Distilled water that stood in contact with this

(8) Gulbransen and Robinson, *THIS JOURNAL*, **56**, 2638 (1934).

(9) W. P. White, "The Modern Calorimeter," Chemical Catalog Co., New York, N. Y., 1928.

(10) The calorimeters were made by the Fansteel Metallurgical Co. of North Chicago, Ill.

Vaseline for several days failed to show any increased conductance due to electrolytes leached from it.

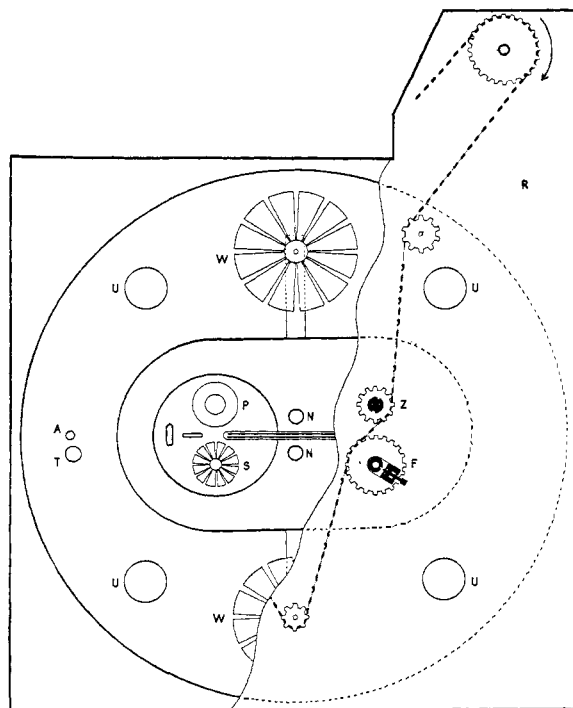


Fig. 2.—Plan of calorimetric apparatus.

Lifting Devices.—A uniform method of opening the dilution pipets was necessary to ensure the constancy of any heat effects due to opening, so that a correction could be made for them. The device adopted is shown in Fig. 3. The brass rod, *b*, was drilled to slip over the stainless steel lifter shaft, *i*, and its lower end was threaded into the trigger support, *z*. To the top of *b* was fastened a trigger-head. The trigger, *t*, pulled outward against a small spring (not shown), was held in place by the piece of stiff piano-wire, *x*. The sprocket, *F*, then revolved on *b* as an idler. The hub of this sprocket was replaced by a tall collar with a slot milled along its length. When the wire, *x*, was pulled out, the tip of the trigger was forced into this slot. The shaft, *b*, then turned with the sprocket and was screwed upward, carrying the lifter shaft with it. When the tip of the trigger had risen out of the slot, it disengaged the sprocket, which once more acted simply as an idler. The rotation of the lifter shaft was prevented by a brass bar, *p*, fastened securely with two nuts, and resting against a stop, *s*, consisting of a short section of brass rod which fitted into the top of a larger rod, *r*, fastened permanently to the aluminum plate. The upper section, *s*, could be removed while the lifting head was being lowered for another run. With this device the ground plugs of the dilution pipet were raised approximately 10 mm. in ten seconds in a uniform manner. This eliminates any variation in the way in which the solutions are allowed to mix, which might occur if the pipets were opened by hand, as in the work of Lange.

Main Thermel.—The difference in temperature between the calorimeters was measured by a 60-junction copper-

constantan thermel of 12 ohms resistance connected to a Paschen astatic galvanometer with a guaranteed sensitivity of 14.6 m. per microamp. at 1 meter scale distance, and with a period of six sec. It was usually operated at a sensitivity of 6 m. per microamp., or 1.8 microdegrees per mm. Our thermel extended directly across the 3-cm. air gap between the calorimeters and projected 3.4 cm. into the wells in the calorimeters. Preliminary studies by Mr. K. H. Schminke showed that this arrangement was adequate to register the true temperature of the calorimeter, since this type of thermel gave the same e. m. f. as a conventional U-shaped thermel immersed to a greater depth in the same calorimeter. The straight thermel, however, has only a third of the resistance of the U-shaped one, and delivers a correspondingly larger current. It has a distinct advantage over the short thermels used by Lange since it gives a true reading of temperature differences even when these are relatively large.

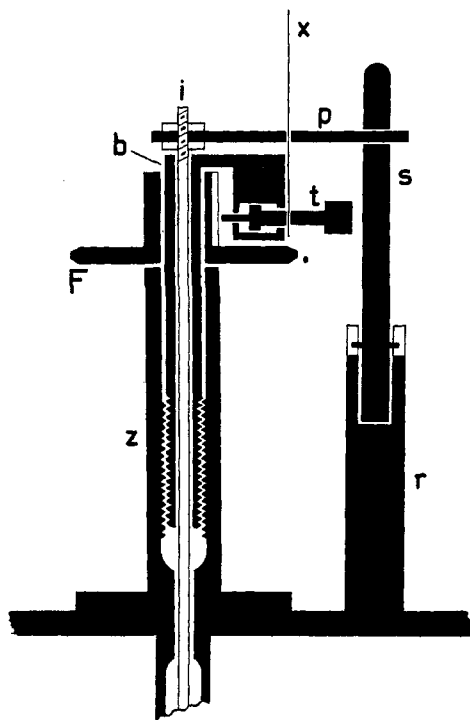


Fig. 3.—Lifting device for opening pipet.

We originally set 0.001 per minute for the heat conductivity constant along the thermel. Thus a temperature difference of 0.001° (over 3 times the greatest temperature rise in the present measurements) would be reduced by 2 microdegrees per minute. Since each calorimetric system has a heat capacity of almost 1000 cal. per degree, the heat transfer would be 0.001 cal. per minute. We can calculate the best size and number of wires as follows:

To give the maximum ratio of electrical to thermal conductance, W. P. White¹¹ calculated that the cross section of the constantan wire should be 21.4 times that of the copper. From the known thermal conductances of the metals and the distance between the calorimeters, we find the allowable cross sections are 0.0257 sq. cm. for the copper and

(11) W. P. White, *THIS JOURNAL*, 36, 2292 (1914).

0.549 sq. cm. for the constantan. Taking into account the specific resistivities of the two metals and the length of each wire, the total resistance of n pairs of wires turns out to be $1.602 \times 10^{-8} n^2$ ohms. The galvanometer resistance is 12 ohms. Since each pair of junctions develops 43 microvolts per degree, the thermal current is

$$I = \frac{E}{R} = \frac{43 \times 10^{-6} n}{12 + 1.602 \times 10^{-8} n^2}$$

Inspection of the graph of this equation (Fig. 4) shows that 86 junctions give the maximum current, but that 60 junctions are practically as good, since the last 26 junctions increase the current by only 8%.

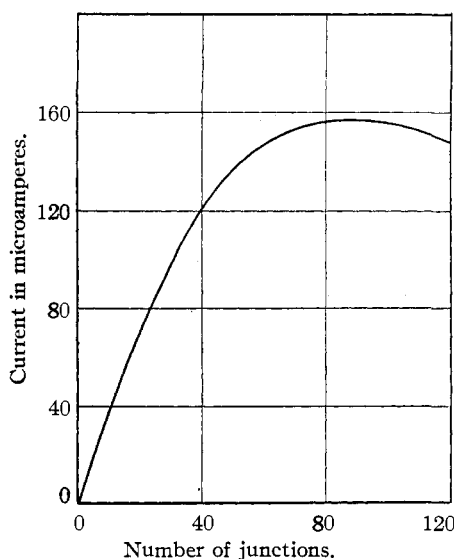


Fig. 4.—Thermel sensitivity curve for constant thermal conduction.

The main thermel (M in Fig. 1) consisted of two identical halves of 30 junctions each, made from double silk-covered no. 17 B. and S. gage constantan wire and no. 30 copper, the cross sections of which were as nearly as possible those indicated in the above calculations. An attempt to test the constantan for homogeneity by the method of White¹¹ proved difficult because the wire was so stiff. Since no unsatisfactory portions appeared in about eight feet (2.4 meters), further testing was discontinued.

The arrangement of the wires is shown in Figs. 1 and 2. The thickness of the junctions was reduced by bending the thin copper wire over a V-shaped notch in the end of the heavy constantan wire, instead of wrapping it around the latter. A rosin flux was used in soldering the wires as recommended by White.¹¹

Each half of the thermel was mounted on a rectangular card of mica 0.2 mm. thick, notched along the ends to space the junctions properly. After being coated with resoglass the two halves were placed between thinner sheets of mica to provide electrical insulation.

The copper case was made in two sections, each slightly longer than the depth of the thermel-well in the calorimeter. To prevent contact between the junctions and the case, a sheet of mica, less than 0.02 mm. thick, was folded around each end of the thermel as it slipped into its

half of the case. After both halves of the case were in place, they were connected by short sections of constantan wire of low thermal conductivity, flattened at the ends, and soldered to the top and bottom of the cases. The measured heat conductivity constant of the completed thermel was 0.0011 per minute.

Four-lead cable,¹² of the type used on platinum resistance thermometers, was employed for the leads. The insulation resistance between two leads was found to exceed 500 megohms. The silk insulation is much more permanent than rubber. The leads were carried out of the submarine jacket through a copper tube as shown in Fig. 1. The leads of both thermels were connected to their galvanometers through copper reversing switches submerged in a well-insulated oil-bath to eliminate parasitic currents in the galvanometer circuits. These switches, shown in Fig. 5 as S_1 to S_4 , were similar to those described in detail by Rubin.¹³ By means of shunt resistances, C, F, the sensitivity of each galvanometer could be decreased in several steps to 0.1% of its full sensitivity. The cross-hatched arrows represent the knobs of the reversing switches. The thermel and galvanometer leads were sheathed in flexible woven-copper tubing, forming an equipotential shield to eliminate stray external currents.

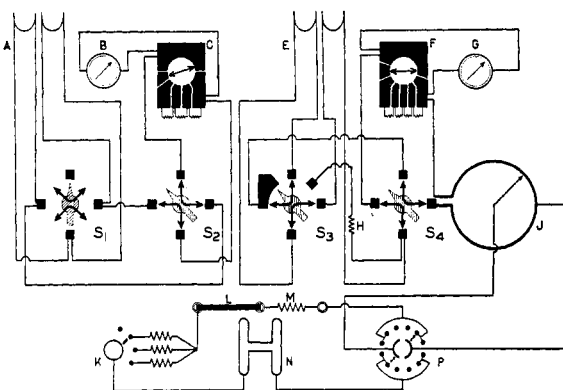


Fig. 5.—Thermel and potentiometer circuits.

Recording Potentiometer.—Since the sensitivity of the Paschen galvanometer, G, was not constant across the full length of the scale and since the temperature changes caused by the dilution frequently exceeded the full scale deflection, the thermel e. m. f. had to be balanced and the galvanometer used as a null instrument. To accomplish this we constructed a recording potentiometer, the wiring of which is shown in Fig. 5. The no. 18 manganin slide-wire, J, was mounted in a small groove machined in the edge of a circular disk of bakelite, immersed in the same oil-bath which held the reversing switches. One end of this wire was soldered directly to the proper contact of the reversing switch, as shown in the drawing. The other end was soldered to one of the galvanometer leads. This junction was clamped directly above the first one, from which it was insulated by pieces of mica 0.05 mm. thick. Thus, the two copper-manganin junctions were maintained at practically the same temperature. Any para-

(12) "Code R" stranded cable, obtained from the Leeds and Northrup Company.

(13) T. R. Rubin, Thesis, Northwestern University, 1935.

sitic effects due to them would be eliminated by the method of double deflections.

The source of the potential was a large saturated Weston cadmium cell, N, in series with a resistance of 100,000, 400,000 or 1,000,000 ohms selected by the switch, K. The size of the series resistance determined the magnitude of the potential applied to the slide wire and hence the sensitivity of the potentiometer. The potential produced by the standard cell was reversed by means of a modified two-circuit, six-point switch, P, mounted directly beneath the bakelite panel forming the top of the reversing switch box, and connected to the same shaft which reversed the galvanometer circuit. Pairs of adjacent contacts on the switch were connected by soldering thin copper strips across them as shown. Thus as the knob S_1 is turned clockwise from the position shown in the diagram to reverse the thermel and the Weston cell, the galvanometer circuit is broken before the potentiometer circuit and closed after it. This avoids violent galvanometer deflections that would occur if this circuit were closed while the cell circuit was open. One of the potentiometer circuit leads, consisting of no. 24 enameled copper wire, was silver-soldered to the middle of the resistance wire, making as narrow a joint as possible. With this arrangement the potential could be applied to the slide wire in either direction. The sliding contact was made by means of a short piece of manganin wire, soldered to a brass arm, which exerted an inward pressure against the resistance wire. The arm was fastened to a brass rod which made contact through a bushing to which the second lead was soldered. A short collar of Lucite served to insulate the lower section of this rod from the upper section, which carried a large dial.

In order to test the sensitivity of the Paschen galvanometer, a known potential was applied to the circuit, with the switch S_2 turned to the vertical position, so that the thermels were replaced by a coil of copper wire, H, having the same resistance.

A 100-ohm resistor, M, in the potentiometer circuit allowed the potential of the standard cadmium cell to be checked from time to time. In order that the resistor itself might be standardized, the brass bar, L, held between two binding posts, could be removed and a standard resistor put in its place. The ratio of the two resistances could then easily be determined potentiometrically.

The position of the sliding contact was automatically recorded by the potentiometer. A large gear, fastened to the shaft directly beneath the dial, was connected through a pinion to a rack which moved in a closely-fitting section of square brass tubing and carried a recording pen mounted on one end.

A typewriter platen, mounted on top of the potentiometer box, was driven by a Telechron electric clock motor through a train of reducing gears and carried the record paper forward at the rate of 12.5 mm. a minute. The pen moved across the paper along the top of the platen and made a permanent record of the potential applied to the slide-wire, which was proportional to the temperature difference of the two calorimeters. A displacement of 1 mm. on the paper corresponded to a temperature change of from 0.3 to 3 microdegrees, depending on the resistance in the circuit. A large part of the work was done with a sensitivity of 0.6 microdegree per mm.

Paschen Galvanometer Suspension.—Because of its extreme sensitivity, the Paschen galvanometer¹⁴ required a support that was free from vibration. A Julius suspension hung from the ceiling proved inadequate. A solid concrete pier weighing about 8 tons then was built upon the ground free from the floor and walls of the building. A heavy iron pipe-frame, 2 m. high, rested solidly on the pier and supported a modified Julius suspension¹⁵ by means of a single wire.¹⁶ A set of vanes on the bottom plate of the suspension extended into a tank filled with transformer oil and aided in damping out any mechanical vibrations. To avoid disturbances due to air currents, the pipe-frame was surrounded with a Celotex housing having a door in one side to permit galvanometer adjustments and a narrow open window in the front through which the light beam passed.

Adiabatic Control.—In order to maintain adiabatic conditions, the temperature of the water-bath was kept the same as that of the calorimeters by an automatic control of the current supplied to the bath heaters. The temperature difference between the bath and each calorimeter was measured by means of a 10-junction copper-constantan thermel. These thermels, similar in construction and mounting to the adiabatic control thermels in the specific heat apparatus to which reference has already been made,⁸ are shown at A in Fig. 5. The wires were no. 34 copper and sections of no. 26 constantan which passed White's test for homogeneity.¹¹ The leads were the same type of silk-insulated cable used for the main thermel. By means of switch S_1 , the thermels could be connected either individually (for testing) or in series (for operating) through the reversing switch, S_2 , to the Leeds and Northrop type-HS galvanometer, B.

Light from a 32 C. P. lamp was reflected from the galvanometer mirror onto a photocell which was part of a "Fotoswitch" unit¹⁷ that operated a two-circuit relay. This relay was connected to a Variac¹⁸ and to a reversible Telechron clock motor which was geared to the shaft of the Variac. When the calorimeters and bath were at the same temperature and there was no deflection of the galvanometer, light fell upon the photocell and the clock motor slowly turned the shaft of the Variac to reduce the voltage output. When the bath temperature dropped below that of the calorimeters the light moved off the photocell, the current through the bath heaters was turned on, and the clock motor was reversed so that it slowly increased the voltage delivered by the Variac. In this way the Variac was adjusted to such a voltage that the heaters were on and off for equal intervals of time, giving the best regulation.¹⁹ When the calorimeters were heated and

(14) Made by the Cambridge Instrument Co., Cambridge, England.

(15) The Brevoort modification of the Julius suspension, made by the G-M Laboratories, Chicago, Ill.

(16) Johnson and Nottingham, *Rev. Sci. Instruments*, **5**, 191 (1934), have shown the advantage of a heavy cage, suspended by a single wire. This simplification eliminates the necessity of equalizing the tension in the three wires of the Julius suspension and of adjusting the center of gravity of the system and the plane of the knife edges to coincide with the point of suspension of the galvanometer mirror.

(17) Made by the G-M Laboratory, Chicago, Ill.

(18) A variable transformer made by the General Radio Co., Cambridge, Mass.

(19) A similar control described by Kistiakowsky, *et al.*, *This Journal*, **57**, 65 (1935), employed a magnetic reversing clutch. The reversible motor was suggested to us by one of his co-workers at Harvard.

thermal balance between the bath and calorimeters was disturbed, the heater current was automatically turned on until balance was again restored, maintaining adiabatic conditions within $\pm 0.0003^\circ$. The output voltage was stepped down by a transformer in the ratio of 1/11 so that the potential applied to the heaters varied from 4 to 10 v. This low voltage caused no deflections of the Paschen galvanometer as the full 110 v. had done.

When the experimental temperature was below that of the room, a steady ice-water drip was used in conjunction with the automatic control. The temperature of the bath was measured with Beckmann thermometers which had previously been standardized against a platinum resistance thermometer.

Calorimeter Heaters.—Each main calorimeter heater, having a resistance of about 50 ohms, was made of no. 38 manganin wire, wound on a thin strip of mica and annealed. It was enclosed in a flat copper case made in two sections connected by two flattened pieces of constantan wire. The resulting 15-mm. opening in the case reduced thermal conduction to the lid of the calorimeter. The heater was sandwiched between two thin mica strips to insulate it from the case.²⁰ Each heater had two no. 24 copper leads to carry the current and two potential leads of no. 30 wire, fastened to the current leads half-way between the calorimeter lid and the top of the submarine jacket. To raise the temperature of the calorimeters rapidly, alternating current from a Variac was passed through the heaters either separately or in series. For a quantitative heating period the source of current was a 3-volt heavy-duty dry cell. The potential was determined with a Leeds and Northrop type K₂ potentiometer and the current by measuring with the same instrument the potential drop across a standard 100-ohm resistor in series with the heater. The current was passed through a 50-ohm substitute resistance for at least twenty minutes before a quantitative heating period, since the current drawn from the dry cell decreases appreciably for the first few minutes. In timing the heating period a Cenco impulse-counter was used as a super-sensitive stop watch. One side of a double-pole, double-throw switch turned the current from the substitute resistance into the heater while the other side started 60-cycle a. c. through the impulse-counter. This arrangement counted the half-cycles and measured the heating periods with a sensitivity of $1/120$ second and an accuracy of 0.1% with which the frequency was regulated. Preliminary experiments showed that the closing and opening of the two circuits was simultaneous (within one half-cycle). The resistance of the heater was determined in nearly every experiment after the heating, by measuring the potential drop across it and across the standard resistor. The resistance of the heaters did not vary more than 0.04% over a period of several months. Previous tests of the resistance of heaters made from the same spool of manganin wire showed that the resistance varied less than 0.01% as the current was increased from 0.005 to 0.015 amp., the latter being the current used in the experiment.

Each heater case contained, beside the main heater, a short section of no. 30 "salamander"-coated constantan

(20) Details of the construction of a somewhat similar heater are given in reference 6. We have found recently that flat heaters of this general type were described by Sligh in THIS JOURNAL, 43, 470 (1921).

wire, having a resistance of about 1.5 ohms. This was used as an auxiliary heater to balance out, within a micro-degree per minute, any temperature trend between the calorimeters due to unequal stirring or evaporation. A 1.5-volt dry cell was connected through two rheostats so that the current could be varied from 0 to 20 m. a. and could balance out a trend of 10 microdegrees per minute, which might be caused by the evaporation of 0.08 mg. of water per minute from one calorimeter.

Theory of the Measurements.—When the dilution of a solution absorbs heat, an equivalent amount of electrical energy must be supplied to the calorimeter in which the dilution takes place in order to restore thermal balance. This quantity can be found easily from Joule's equation

$$\Delta E = I^2 R t \text{ joules}$$

where ΔE is the energy added, I the current, R the resistance of the heater, and t the time. When heat is evolved upon dilution and the other calorimeter must be heated to restore balance, the computations involve also the heat capacities of the two calorimeters.

If a current be passed through both the heaters in series, the heating in the two calorimeters is proportional to the resistances.

$$\Delta E_1 / \Delta E_2 = R_1 / R_2$$

Now $\Delta E_1 = \Delta T_1 \times C_1$ and $\Delta E_2 = \Delta T_2 \times C_2$ where ΔT_1 and ΔT_2 are the temperature changes and C_1 and C_2 are the heat capacities of the calorimeter systems. If we set $(\Delta T_1 - \Delta T_2) = \delta T$

$$\frac{\Delta E_1}{\Delta E_2} = \left(\frac{\Delta T_2 + \delta T}{\Delta T_2} \right) \frac{C_1}{C_2} = \frac{R_1}{R_2}$$

or

$$\left(1 + \frac{\delta T}{\Delta T_2} \right) \frac{C_1}{C_2} = \frac{R_1}{R_2}$$

We shall let

$$\left(\frac{C_2}{C_1} \times \frac{R_1}{R_2} \right) = \left(1 + \frac{\delta T}{\Delta T_2} \right) = K$$

where K is a constant which must be determined for every experiment. The ratio $(\delta T / \Delta T_2)$ is the same as the ratio of the displacement of the pen actually produced by the series heating to that which would be produced if the same current were passed through heater no. 2 alone for the same period. The latter quantity is calculated readily by dividing the time in seconds by the sensitivity of the record in terms of seconds per mm. displacement.

Knowing K we can evaluate the heats of dilution. If a dilution in the first calorimeter is balanced exactly by electrical energy in the second

$$\Delta T_1 = \frac{-q_1}{C_1} = \Delta T_2 = \frac{\Delta E_2}{C_2}$$

where q is the heat *absorbed*. Therefore

$$-q_1 = \left(\frac{C_1}{C_2}\right) \times \Delta E_2 = \left(\frac{C_1}{C_2}\right) \times I_2^2 R_2 t_2 \text{ joules}$$

or

$$-q_1 = 0.2389 I_2^2 R_2 t_2 / K \text{ cal.}_{15}$$

Similarly, if the dilution takes place in calorimeter no. 2 and heat is supplied to no. 1

$$-q_2 = 0.2389 K I_1^2 R_2 t_1 \text{ cal.}_{15}$$

Assembling the Apparatus.—After the calorimeters had been loaded they were placed on a temporary holder hung from the lid of the submarine. First the main thermel was inserted in the wells provided for it and the calorimeters were pushed together. Then the holder was screwed up by means of four threaded rods at the corners, connected together by a chain and sprocket. As the calorimeters were raised slowly into position, the heater and adiabatic thermel cases were slipped into their respective wells. After the stirrer and lifter shafts had been screwed into the Lucite sections, the dental floss loops were slipped over the hooks and the lids were drawn tightly against the Lucite cones. When the holder was removed, the position of the calorimeters was adjusted so that the stirrer shafts did not scrape. Finally, the submarine jacket was fastened on, the bath stirrers and heaters were installed, and the assembly was submerged in the water-bath.

Obtaining the Time-Temperature Record.—The calorimeters were brought to the working temperature by means of their heaters and the automatic control was started. The temperatures of the two calorimeters then were equalized, gradually increasing the sensitivity of the Paschen galvanometer as thermal balance was approached. When the galvanometer deflection was small enough to be balanced by the potentiometer, the clock motor was started and a permanent record was begun. Such a record is reproduced in Fig. 6.

The temperature difference between the calorimeters was followed for at least ten minutes, reversing the galvanometer circuit every ten or fifteen seconds and turning the potentiometer knob when necessary to reduce the deflection to zero. If there was a definite temperature trend of more than 2 microdegrees per minute between the two calorimeters, current was passed through the 1.5-ohm heater in the cooler calorimeter and adjusted to reduce the temperature trend below 1 microdegree per minute, giving a line on the potentiometer record with only a slight slope or none at all.

After a satisfactory line had been obtained for about ten minutes, the current was switched from the substitute resistance to one of the calorimeter heaters for a measured interval of time. When the heating current was turned off, the temperature difference was followed on the record until the line resumed a steady slope. By extrapolating the slopes before and after the heating period and measuring the displacement the record could be calibrated for that calorimeter in terms of seconds of heating time per mm. displacement. This same procedure was followed for the other calorimeter.

When the slope again had become sufficiently constant, one of the dilution pipets was opened by means of its automatic lifter and the current was switched into the heater in the other calorimeter. The time of heating which would balance the dilution was not known exactly, but after some experience it could be estimated within two or three seconds. After thermal equilibrium had been restored, the temperature difference was followed for at least ten minutes. The slope was extrapolated back to the time of the dilution and the displacement was measured. Since the heating time equivalent to a displacement of 1 mm. already had been determined, the correction was calculated easily and added to the actual heating period to obtain the corrected heating time. This same procedure was followed with the other calorimeter.

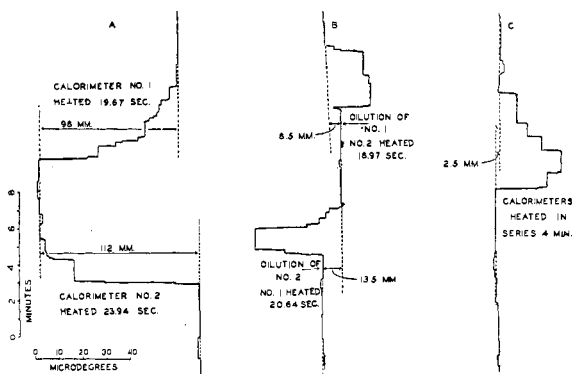


Fig. 6.—Potentiometer record for a typical experiment. (The original record was cut in three sections which were mounted side by side and photographed.)

The current and resistance were determined as explained before. Knowing these and the time, it was a simple matter to calculate the electrical energy supplied to each calorimeter. Finally both calorimeters were heated in series for several minutes to evaluate the constant K , after which

the heats of dilution were calculated as explained before.

Blank Experiments.—Before calculating any results from experimental data, it was necessary to determine whether or not the opening of the pipets caused any thermal effect. Experiments in which the calorimeters and pipets both contained water showed a slight cooling effect due to the opening of the pipets. When the pipets held 50 ml., the average of thirteen experiments was a drop of 6 (≈ 2) microdegrees, while the average of ten experiments with 60 ml. in the pipets was a drop of 8 (≈ 2) microdegrees. Since the cooling was approximately proportional to the volume of liquid contained in the pipet, apparently it was caused by a slight lag in the pipet, so that the heat produced by stirring in the outer portion had not been distributed uniformly throughout the contents of the pipet. It was necessary to apply a correction of $\delta q = -0.006$ cal. when the pipets contained approximately 50 ml. In the occasional experiments where the volume of solution was less than 50 ml., correspondingly smaller corrections were applied.

A Typical Experiment

To indicate how the experiments were carried out, the data recorded for a typical experiment are given in Table I. Fig. 6 is a photograph of the potentiometer record.

TABLE I

Experiment No. 12, May 16, 1938

Dilution of sucrose from 0.1000 *m* to 0.0050 *m* at 20°Preparation of 0.1 *m* solution:

Weight sucrose 11.6141 g. $m = 0.1000$
 Weight water 339.32 g.

	Calorimeter no. 1	Calorimeter no. 2	
0.1 <i>m</i> soln. in pipet, g.	52.817	50.412	
Water in calorimeter, g.	970.34	926.16	
Concn. of soln. after diln., <i>m</i>	0.00500	0.00500	
Moles of sucrose	.005107	.004874	
	Time of heating, sec.	Potential drop across standard 100-ohm resistance, v.	Net displace- ment on record, mm.
Heating No. 2	23.94		112.0
Heating No. 1	19.67		98.0
Diln. of No. 2, heating No. 1	20.64	1.4967	13.5
Diln. of No. 1, heating No. 2	18.97	1.5238	8.5
Heating both in series	240		2.5

Determination of heater resistances during series heating

Potential across 100-ohm standard, v.	1.4911
Heater No. 1, v.	0.8010
Heater No. 2, v.	.7627
100-ohm standard (check), v.	1.4914

	No. 1	No. 2
Heater resistance, ohms	53.71	51.15
Displacement factor, sec./mm.	0.201	0.214
Correction to heating time, sec.	-1.82	-2.71
Corrected heating time, sec.	17.15	17.93
Heating current, amp.	0.01524	0.01497

$$K = [1 + 2.5/(240 \div 0.214)] = 1.002$$

$$q_1 = -[53.71 \times (0.01524)^2 \times 17.15 \times 0.2389] \div 1.002 = -0.051 \text{ cal.}_{15}$$

$$q_2 = -51.15 \times (0.01497)^2 \times 17.93 \times 0.2389 \times 1.002 = -0.049 \text{ cal.}_{15}$$

Making the correction of -0.006 cal. due to the heat of opening,

$$q_1 = -0.057 \text{ cal. and } q_2 = -0.055 \text{ cal.}$$

$$(\Delta H)_1 = -0.057/0.005107 = -11.2 \text{ cal./mole}$$

$$(\Delta H)_2 = -0.055/0.004874 = -11.3 \text{ cal./mole}$$

Since $\Delta m = -0.095$

$$\left(\frac{\Delta H}{\Delta m}\right)_1 = 118 \quad \left(\frac{\Delta H}{\Delta m}\right)_2 = 119$$

Preparation of Solutions.—The sucrose used in these experiments was c. p. material²¹ furnished by the Bureau of Standards through the courtesy of Dr. F. J. Bates, Director of the Polarimetry Section. The distilled water used in making up the solutions had a specific conductance of 3×10^{-6} reciprocal ohm or less. The solutions used in experiments 1–13, 16, 24, 27, 29 were made up determinate in specially designed glass-stoppered Pyrex flasks of 500 ml. or one liter capacity. The solutions for experiments 14, 15, 17–23, 25, 26, 28, 30–37 were the products of previous dilutions.

Experimental Results.—Two general types of dilution were made. Young and Vogel²² have shown that the best way to determine the integral heat of dilution curve is to determine its slope accurately at a number of concentrations and to integrate the slope curve. Therefore, at each temperature, a series of dilutions was performed between 0.2 *m* and 0.1 *m*, in which a comparatively large amount of solution was diluted with a small amount of water. The ratio was approximately 20:1 giving a decrease of 0.01 to 0.006 in the value of *m*. The results of this type of dilution are given first in Tables II and III.

A second group of experiments was carried out in which a small amount of solution was diluted

(21) Standard Sample No. 17 purified as described in "Polarimetry" Circular No. 44 of the Bureau of Standards.

(22) Young and Vogel, *THIS JOURNAL* **54**, 3030 (1932).

TABLE II^a

HEATS OF DILUTION OF SUCROSE SOLUTIONS AT 20°							
Expt.	Initial concn., m_1	Final concn., m_2	$-q(\text{cal.}_{15})$ (obsd.)	$-q(\text{cal.}_{15})$ (calcd.)	$10^3 \Delta q$ (obsd.-calcd.)	ΔH cal. $_{15}$ /mole	$\Delta H/\Delta m$
29	0.2000	0.1900	0.236	0.229	-7	1.33	133
	.2000	.1900	.232	.224	-8	1.33	133
30	.1900	.1800	.220	.223	3	1.27	127
	.1900	.1800	.214	.213	-1	1.30	130
31	.1800	.1700	.210	.212	2	1.28	128
	.1800	.1700	.205	.202	-3	1.30	130
32	.1700	.1600	.203	.200	-3	1.31	131
33	.1600	.1500	.179	.180	1	1.28	128
	.1600	.1500	.169	.173	4	1.26	126
34	.1240	.1180	.089	.087	-2	0.78	131
	.1240	.1180	.085	.084	-1	.78	131
35	.1180	.1120	.086	.083	-3	.80	133
	.1180	.1120	.078	.080	2	.75	126
36	.1120	.1060	.077	.079	2	.76	126
	.1120	.1060	.074	.076	2	.76	126
37	.1060	.1000	.070	.075	5	.72	120
	.1060	.1000	.069	.071	2	.75	125
3	.2000	.0050	.132	.128	-4	26.0	133
	.2000	.0050	.126	.120	-6	26.4	136
4	.2000	.0100	.245	.248	3	24.2	127
	.2000	.0100	.229	.233	4	24.1	127
8	.1500	.0050	.090	.089	-1	19.0	131
	.1500	.0050	.088	.086	-2	19.3	133
11	.1000	.0050	.054	.059	5	11.1	117
12	.1000	.0050	.057	.063	6	11.2	118
	.1000	.0050	.055	.060	5	11.3	119
6	.2000	.0200	.227	.224	-3		
	.2000	.0200	.215	.210	-5		

^a In Tables II and III the pairs of experiments are numbered chronologically. All experimental results are included except five which gave very small heat effects, presumably due to leakage of the pipet valves, and one of pair 11 which, for some unknown reason, gave a result 18 microdegrees higher than the other and the check experiments of pair 12.

with a large amount of water or (in Expts. 2 and 6) 0.01 m solution. The results of these dilutions are also given in Tables II and III. Chords are plotted in Fig. 7 for both types of dilution, the ordinate in each case being the chord of the integral heat of dilution curve and the abscissas of the extremities of the chord being the initial and final concentrations.

The most probable value of $\Delta H/\Delta m$ at each temperature was obtained by taking the mean of the values for both the long and short chords, weighting each value according to the actual heat liberated in the dilution. The results, indicated by the heavy lines in Fig. 7, were

$$\left. \begin{aligned} \Delta H/\Delta m &= 128.9 = d\Phi_{H_2}/dm & (20^\circ) \\ \Delta H/\Delta m &= 140.2 = d\Phi_{H_2}/dm & (30^\circ) \end{aligned} \right\} (m < 0.2)$$

TABLE III

HEATS OF DILUTION OF SUCROSE SOLUTIONS AT 30°							
Expt.	Initial concn., m_1	Final concn., m_2	$-q(\text{cal.}_{15})$ (obsd.)	$-q(\text{cal.}_{15})$ (calcd.)	$10^3 \Delta q$ (obsd.-calcd.)	ΔH cal. $_{15}$ /mole	$\Delta H/\Delta m$
13	0.2000	0.1900	0.258	0.255	-3	1.42	142
16	.2000	.1900	.237	.238	1	1.40	140
14	.1900	.1800	.236	.239	3	1.38	138
	.1900	.1800	.231	.230	-1	1.41	141
17	.1900	.1800	.237	.239	2	1.39	139
	.1900	.1800	.228	.231	3	1.38	138
18	.1800	.1700	.226	.226	0	1.40	140
19	.1700	.1600	.209	.212	3	1.38	138
	.1700	.1600	.205	.201	-4	1.43	143
15	.1600	.1500	.189	.198	9	1.34	134
	.1600	.1500	.189	.190	1	1.40	140
20	.1600	.1500	.196	.198	2	1.39	139
	.1600	.1500	.190	.188	-2	1.42	142
21	.1500	.1420	.154	.148	-6	1.17	146
	.1500	.1420	.144	.142	-2	1.14	142
22	.1420	.1340	.140	.141	1	1.11	139
	.1420	.1340	.135	.135	0	1.12	140
23	.1340	.1260	.135	.133	-2	1.14	143
	.1340	.1260	.128	.127	-1	1.13	141
24	.1200	.1140	.091	.090	-1	0.85	141
	.1200	.1140	.084	.086	2	.82	137
25	.1140	.1080	.084	.089	5	.80	133
	.1140	.1080	.081	.085	4	.80	133
26	.1080	.1020	.081	.081	0	.84	139
	.1080	.1020	.077	.077	0	.84	139
1	.2000	.0100	.259	.254	-5	27.2	143
	.2000	.0100	.258	.252	-6	27.3	144
5	.2000	.0050	.137	.138	1	27.1	139
	.2000	.0050	.135	.136	1	27.3	140
7	.1500	.0050	.100	.096	-4	20.9	144
	.1500	.0050	.087	.091	4	19.6	135
9	.1500	.0050	.093	.093	0	20.3	140
10	.1000	.0050	.068	.068	0	13.4	141
	.1000	.0050	.066	.065	-1	13.5	142
27	.0400	.0020	.012	.011	-1	6.1	160
	.0400	.0020	.013	.010	-3	7.0	185
28	.0020	.0001	-.002	.000	2		
	.0020	.0001	-.001	.000	1		
2	.2000	.0200	.250	.243	-7		
	.2000	.0200	.233	.224	-9		

Integration then gives for the apparent molal heat content of the sucrose below 0.2 m

$$\begin{aligned} \Phi_{H_2} &= \Phi_{H_2}^\circ + 128.9 m & (20^\circ) \\ \Phi_{H_2} &= \Phi_{H_2}^\circ + 140.2 m & (30^\circ) \end{aligned}$$

where $\Phi_{H_2}^\circ$ is the apparent molal heat content in the infinitely dilute solution. The heat q to be expected for each dilution was calculated from these equations and is tabulated in column 5 of Tables II and III. The difference between this figure and the experimental value is given in

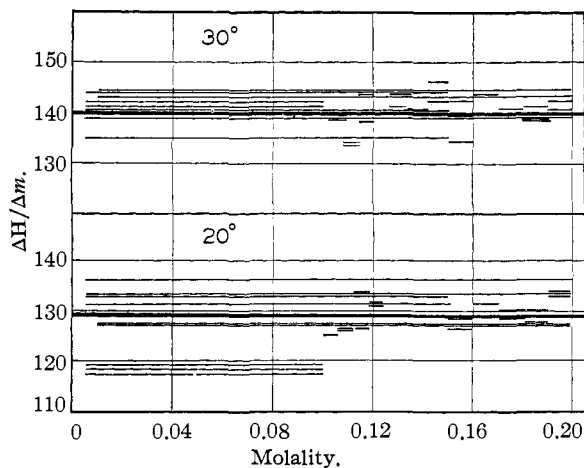


Fig. 7.—Slopes of dilution curve for sucrose.

column 6. The average deviation corresponded to a temperature difference of 3.4 microdegrees at 20° and 2.6 microdegrees at 30°. We also used the method of least squares to determine the best coefficients of the second degree equations

$$\Phi H_2 = \Phi H_2^\circ + am + bm^2$$

but we found that these were no improvement over the simpler linear ones.

Since, by definition, the apparent relative heat content

$$\Phi L_2 = \Phi H_2 - \Phi H_2^\circ$$

we have for the region below 0.2 m

$$\Phi L_2 = 128.9 m \quad (20^\circ)$$

$$\Phi L_2 = 140.2 m \quad (30^\circ)$$

The graphs of these equations are given in Fig. 8. By calculating from the equations values of ΦL_2 for the initial concentrations $m = 0.20, 0.15, 0.10,$ and $0.04,$ values for the concentrations $m = 0.2, 0.01, 0.005,$ and 0.002 were determined from the data of the experiments of the second type. These values are plotted in Fig. 8 and justify the assumption that the slope is constant within experimental error from 0.2 m down to 0.002 m . The experiments in the very dilute range at 30° were carried out to make certain that there was no sudden change in the slope of the curve in this region.

The apparent relative heat content of the solute is related to the relative heat content of the solution, L , by the equation

$$\Phi L_2 = \frac{L - 55.51 \bar{L}_1^\circ}{m}$$

Since \bar{L}_1° is zero, we have

$$L = m\Phi L_2$$

Differentiating with respect to m gives the partial relative molal heat content of the solute as

$$\bar{L}_2 = \frac{\partial L}{\partial m} = \Phi L_2 + m \frac{\partial \Phi L_2}{\partial m}$$

Substituting the values of ΦL_2 and $(\partial \Phi L_2 / \partial m)$ into this equation gives

$$\bar{L}_2 = 257.8 m \quad (20^\circ) \\ \bar{L}_2 = 280.4 m \quad (30^\circ) \quad \left\{ (m \leq 0.2) \right.$$

Moreover, since $L = m\Phi L_2 = 55.51 \bar{L}_1 + m\bar{L}_2$

$$\bar{L}_1 = \frac{m(\Phi L_2 - \bar{L}_2)}{55.51}$$

$$\bar{L}_1 = -2.322 m^2 \quad (20^\circ) \\ \bar{L}_1 = -2.525 m^2 \quad (30^\circ) \quad \left\{ (m \leq 0.2) \right.$$

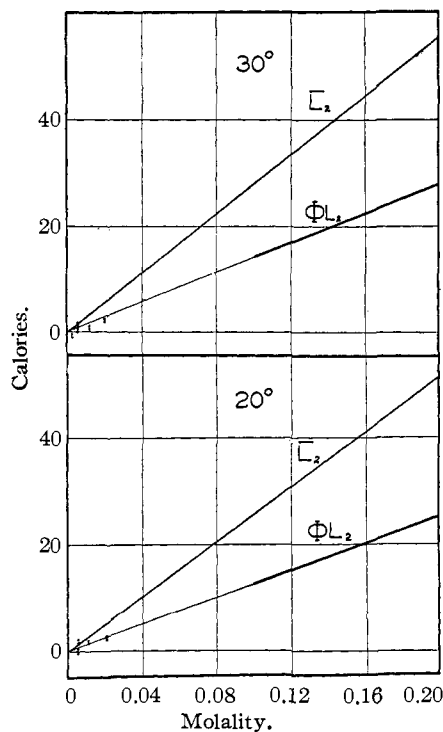


Fig. 8.—Apparent and partial relative molal heat contents for sucrose in dilute solutions at 20 and 30°.

Correlation of Previous Work on Sucrose

The heats of dilution of aqueous solutions of sucrose have been studied at moderately high concentrations, but little work has been done in the dilute region. Ewan²³ and Stackelberg²⁴ published a few heats of dilution, which are of little value since the experimental temperature is not given. Porter and Wood²⁵ measured the partial relative heat content per gram of solvent between 0.5 and 4.0 molal at 20° by adding small amounts of water to large amounts of solution.

(23) Ewan, *Z. physik. Chem.*, **14**, 409 (1894).

(24) Stackelberg, *ibid.*, **26**, 546 (1898).

(25) Porter, *Trans. Faraday Soc.*, **13**, 123 (1917).

We calculated the partial molal relative heat content, \bar{L}_1 , from their data, and integrated it graphically by the method of Lewis and Randall²⁶ to obtain \bar{L}_2 . From this quantity ΦL_2 was calculated. The second degree equation (obtained by the method of least squares) which best represented the data was

$$\Phi L_2 = 145.9 m - 10.58 m^2 \quad (20^\circ)$$

Pratt²⁷ employed the continuous flow method, with a mercury thermometer, to measure the heats of dilution of sucrose between 0.222 and 2.22 molal at several different temperatures. The equations which fit his data best were found to be

$$\Phi L_2 = 131.6 m - 7.50 m^2 \quad (20^\circ)$$

$$\Phi L_2 = 161.7 m - 15.7 m^2 \quad (30^\circ)$$

Naudé,²⁸ using Nernst's differential calorimeter and an iron-constantan thermel of 100 junctions, with a galvanometer sensitivity of 0.5 mm. per microdegree, made several dilutions at 18° in the region between 1 and 0.003 molar. These data were corrected to 20°, using the Person-Kirchhoff equation and the empirical equation given by Gucker and Ayres⁵ for the apparent molal heat capacity of sucrose at 20°. The best equation in this case was

$$\Phi L_2 = 135.9 m - 21.5 m^2 \quad (20^\circ)$$

Vallender and Perman²⁹ have made the most comprehensive study of sucrose, carrying out dilutions at five temperatures and at concentrations ranging from 0.34 to 5.88 molal. They introduced small amounts of water into large volumes of solution, reading the temperature changes to 0.001° on a Beckmann thermometer. We have calculated ΦL_2 as described above and find the following second degree equation to fit their data

$$\Phi L_2 = 131.0 m - 7.146 m^2 \quad (20^\circ)$$

The values of ΦL_2 calculated from the four sets of data have been plotted in Fig. 9. The values of Pratt and of Vallender and Perman at 20° fall along the same curve, as would be expected from the similarity of the corresponding equations. The values for the limiting slope agree within 0.5%, and are nearly the value which we obtained for the dilute region. We have therefore obtained by the method of least squares the best curve having the limiting slope of 128.9 which

(26) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, p. 90.

(27) Pratt, *J. Franklin Inst.*, **185**, 663 (1918).

(28) Naudé, *Z. physik. Chem.*, **135**, 209 (1928).

(29) Vallender and Perman, *Trans. Faraday Soc.*, **27**, 124 (1931).

would fit the combined data of Pratt and of Vallender and Perman. This equation was found to be

$$\Phi L_2 = 128.9 m - 6.917 m^2 \quad (20^\circ) \quad (m \leq 5.9)$$

The values of ΦL_2 calculated from this equation agree within 0.5% with the value obtained from the data of Vallender and Perman at 5.05 *m* and within 0.3% at 3.70 *m*. The value calculated for 1.332 *m* agrees within 1.5% with that obtained from Pratt's data.

Similarly, the equation having our limiting slope of 140.2 which best fits Pratt's data at 30° was found to be

$$\Phi L_2 = 140.2 m - 7.08 m^2 \quad (30^\circ) \quad (m \leq 2.2)$$

Agreement between experimental and calculated values is satisfactory although not so good as at 20°.

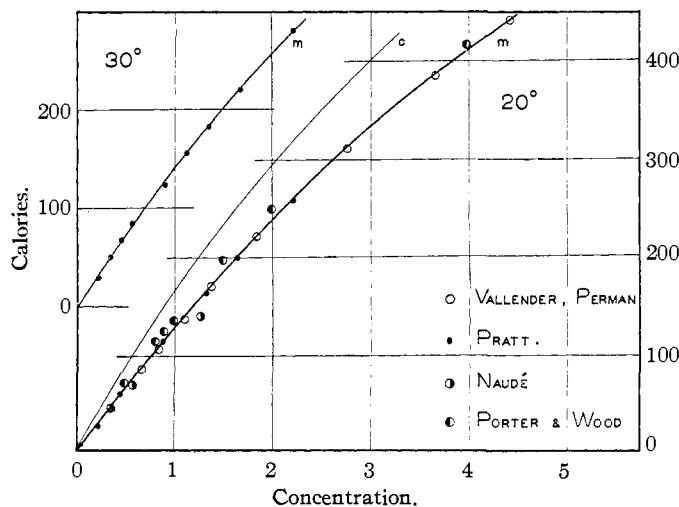


Fig. 9.—Apparent relative molal heat content of sucrose at 20 and 30°.

Apparent Relative Molal Heat Content at 25°.

—An equation for ΦL_2 at 25° was obtained by correcting the above equations for 20° and 30° using the apparent molal heat capacity at 25°. This gave two equations differing only in the coefficient of the squared term. Since twice as many experimental data were used at 20° as at 30°, the coefficient derived from the 20° equation was weighted twice that obtained from the 30° equation. This procedure resulted in the equation

$$\Phi L_2 = 134.6 m - 7.05 m^2 \quad (25^\circ)$$

which represents the best value now available for the apparent relative molal heat content curve at 25°, up to 2.2 *m*.

Apparent Molal Heat Capacity.—Since the apparent molal heat capacity and the apparent rela-

tive molal heat content are connected by the relationship

$$\frac{\partial}{\partial m} (\Phi C_{p_2}) = \frac{\partial}{\partial T} \left(\frac{\partial \Phi L_2}{\partial m} \right)$$

it is a simple matter to calculate from the data at hand a very accurate value of the limiting slope of the apparent molal heat capacity curve for 25°. Since the slopes of the ΦL_2 curves are 140.2 and 128.9 at 20 and 30°, respectively, $\frac{\partial}{\partial m} (\Phi C_{p_2}) = 1.13$.

This differs slightly from the value 1.325 which was obtained in this Laboratory⁵ by the direct measurement of specific heats at higher concentrations. We have evaluated the coefficients for a new second degree equation, making the limiting value of the slope 1.13. This new equation, covering the range up to 5.8 *m*, is

$$\Phi C_{p_2} = 151.50 + 1.130 m - 0.0466 m^2 \quad (25^\circ)$$

It predicts values of ΦC_{p_2} which agree with the experimental data slightly better than those obtained from the original equation. Our dilution results thus supplement the earlier heat capacity measurements and are in complete agreement with them. The new equations for the partial molal heat capacities of solute and solvent, respectively, are

$$\bar{C}_{p_2} = 151.50 + 2.260 m - 0.1398 m^2$$

$$\bar{C}_{p_1}^\circ - \bar{C}_{p_1} = 0.018016 (1.130 m^2 - 0.0932 m^3)$$

Discussion of Results.—Our experiments show that, within an experimental uncertainty of about ± 3 microdegrees, the heat of dilution of sucrose at 20 and 30° changes linearly with the first power of the concentration in very dilute solutions. This proves for the first time a distinct and clear-cut difference between the behavior of a typical non-electrolyte and electrolytes, for which the limiting slope is linear with the square root of the concentration. At higher concentrations the plot against the molality shows a downward curvature. Since the molarity is much less than the molality in concentrated solutions of sucrose, we calculated the heat of dilution curve at 20° for this abscissa (*c*) and plotted it in Fig. 9, omitting the individual points to avoid confusion. The slope of this curve is appreciably steeper than the other, but the curvature still persists to as low a concentration, showing there is no advantage in using the volume concentration as abscissa.

The linearity of the heat of dilution and ap-

parent molal heat capacity with the concentration in the dilute region parallels the apparent molal volume of sucrose which Redlich and Klinger⁴ found was linear with the concentration in this region. It also agrees with the theoretical predictions of Fuoss³⁰ for the behavior of a dipolar solute of small dipole moment, although we are not yet in a position to calculate the dipole moment from these measurements.

Acknowledgments.—It is a pleasure to acknowledge our indebtedness to the National Research Council for a Grant-in-Aid which helped materially to defray the expenses of the apparatus used in this work; to the Graduate School of Northwestern University for a Grant-in-Aid for laboratory assistance for the senior author; to Mr. K. H. Schminke for preliminary tests in designing the apparatus and for a considerable amount of its construction; to Professor R. G. Bigelow and the late Mr. M. L. West of the Northwestern Engineering School and to Mr. Howard S. Martin for advice and assistance in constructing the apparatus and to Dr. F. J. Bates of the Bureau of Standards for furnishing the sucrose used in these experiments.

Summary

We have described the construction and operation of a new micro-calorimeter, employing twin metal calorimeters and sensitive to 1 microdegree.

With this apparatus we have studied the heats of dilution of sucrose from 0.2 to 0.005 *m* at 20° and from 0.2 to 0.0001 *m* at 30°. The heat of dilution is a linear function of *m* over the whole range, within an average deviation of ± 3 microdegrees.

The apparent molal heat capacity, calculated from these data, is also a linear function of *m* over the same range, as indicated by previous work in this Laboratory at higher concentrations.

We have presented our results in tables and figures and combined them with the results of other workers on more concentrated solutions, to obtain equations for the apparent and partial molal relative heat contents and heat capacities of sucrose and the partial molal relative heat content and heat capacity of water in these solutions.

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(30) Fuoss, *This Journal*, **58**, 982 (1936).