The Journal of the American Chemical Society

VOL. 51 FEBRUARY, 1929 No. 2

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

HEAT CAPACITIES IN AQUEOUS SALT SOLUTIONS

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RECEIVED JUNE 22, 1928 PUBLISHED FEBRUARY 5, 1929

Whenever two substances, A and B, are mixed together the heat capacity of the mixture will be the sum of the heat capacities of the separate substances if the temperature function of the energy state of A, and of B, is the same in the mixture as for each substance separately. It is possible also for their heat capacities to be additive if the deviation of the heat capacity of A, in going from the pure state into the mixture, is exactly negative that of B. If, however, molecules B exert some special influence upon molecules A, then their heat capacities usually will not be additive.

It has been known for a long time that the heat capacity of a given amount of water is greater than that of the same amount of water plus a small amount of any substance which is a strong electrolyte.[1] This behavior can be explained in the following manner. Suppose we have a system consisting of 1000 g. of water, whose heat capacity is G calories. If we add to this water one single molecule of sodium chloride we shall have a system consisting of 1000 g. of water, one sodium ion, and one chloride ion. The heat capacity of this system we find to be $(G - a)$ calories. Then $(-a)$ calories is, apparently, the heat capacity of one sodium ion plus one chloride ion. Since we are dealing with an infinitely dilute solution,[2] Φ° and also $\bar{c}_{p_2}{}^\circ$ for one gram mole of sodium ion plus one

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[1] Thomsen, "Thermochemistry," Longmans Green and Co., London, **1908**, p. 165, says, "When an aqueous solution is diluted with water the molecular heat of the solution formed is less than the sum of that of the original solution together with that of the water." This is true in every case only if the solute is a strong electrolyte. It is possible also that it is not always true for very concentrated solutions.

[2] The symbols which are pertinent to the main discussion of this paper are defined as follows: m, the molality, the number of moles of solute per 1000 g. (or 55.508 moles) of water *in vacuo*. C_p, the heat capacity of that amount of solution, of molality m, which contains 1000 g. of water plus m moles of solute. $\bar{c}_{p_2}$, the partial molal heat capacity of the solute. This is dC_p/dm, and is the change in the heat capacity of a very large amount of solution on the addition of 1 mole of solute. (Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co.,

gram mole of chloride ion equals $-a \times 6.06 \times 10^{23}$ cal. The presence of the two ions has so affected the water molecules that their heat capacity has been decreased by an amount equal to a calories plus the intrinsic heat capacity of one sodium ion and one chloride ion.

Methods of Determining and Calculating the Apparent and Partial Molal Heat Capacities and the Specific Heat

The method employed in this work to determine these quantities is to measure the difference in the heat capacity of the two systems, (A) 1000 g. of water (heat capacity is 55.508 $\bar{c}_{p_1}^{\circ}$); (B) 1000 g. of water plus m moles of salt (heat capacity is C_p). Then ΔC_p, the apparent heat capacity of the added salt, is given by the equation

$$\Delta C_p = C_p - 55.508\ \bar{c}_{p_1}^{\circ} \tag{1}$$

The apparent heat capacity of the added salt per mole of the added salt is

$$\Phi = \Delta C_p/m \tag{2}$$

If Φ is plotted against $m^{1/2}$, as in Fig. 3, then

$$\bar{c}_{p_2} = \Phi + {}^1/_2 m^{1/2}(\mathrm{d}\Phi/\mathrm{d}m^{1/2}) \tag{3}$$

That this is true can be shown as follows. From Equations 1 and 2

$$\Phi = (C_p - 55.508\ \bar{c}_{p_1}^{\circ})/m \tag{4}$$

Differentiating Φ with respect to $m^{1/2}$, we find

$$\mathrm{d}\Phi/\mathrm{d}m^{1/2} = m(\mathrm{d}C_p/\mathrm{d}m^{1/2}) - (C_p - 55.508\ \bar{c}_{p_1}^{\circ})2m^{1/2}/m^2 \tag{5}$$

But $C_p - 55.508\ \bar{c}_{p_1}^{\circ} = m\Phi$, and $m(\mathrm{d}C_p/\mathrm{d}m^{1/2}) = 2m^{3/2}(\mathrm{d}C_p/\mathrm{d}m) = 2m^{3/2}\bar{c}_{p_2}$. Making these substitutions and multiplying by ${}^1/_2 m^{1/2}$, we have Equation 3. Or, the partial molal heat capacity of the solute is equal to the apparent molal heat capacity plus ${}^1/_2$ the product of $m^{1/2}$ times the slope of the curve of Fig. 3.

When Φ and $\bar{c}_{p_2}$ are known, $\bar{c}_{p_1}$ can be calculated as follows.[2] By definition

$$C_p = m\bar{c}_{p_2} + 55.508\ \bar{c}_{p_1} \tag{6}$$

then

$$\bar{c}_{p_1} = (C_p - m\bar{c}_{p_2})/55.508 \tag{7}$$

From Equations 1 and 2

$$C_p = m\Phi + 55.508\ \bar{c}_{p_1}^{\circ} \tag{8}$$

Hence

$$\bar{c}_{p_1} = (m\Phi + 55.508\ \bar{c}_{p_1}^{\circ} - m\bar{c}_{p_2})/55.508 = (m/55.508)(\Phi - \bar{c}_{p_2}) + \bar{c}_{p_1}^{\circ} \tag{9}$$

The specific heat of 1 gram of a solution of molality m is

$$\text{Specific heat} = (m\Phi + 55.508\ \bar{c}_{p_1}^{\circ})/W \tag{10}$$

New York, **1923**, p. 83.) $\bar{c}_{p_2}^{\circ}$, the value of $\bar{c}_{p_2}$ when m is zero. $\bar{c}_{p_1}$, the partial molal heat capacity of the water. This is the change in the heat capacity of a very large amount of solution on the addition of 1 mole of water. Specific heat, the heat capacity of one gram of solution. $\bar{c}_{p_1}^{\circ}$, the value of $\bar{c}_{p_1}$ when m is zero. Φ, the apparent molal heat capacity of the solute, is $(C_p - 55.508\ \bar{c}_{p_1}^{\circ})/m$. It is the change in heat capacity per mole of solute, caused by the addition of m moles of solute to 1000 g. of water. $\Phi^{\circ} = \bar{c}_{p_2}^{\circ}$, the value of the apparent molal heat capacity at $m = 0$.

where W is the weight of the amount of solution which contains 1000 g. of solution.

From the foregoing it is seen how all the four quantities, Φ, $\bar{c}_{p_2}$, $\bar{c}_{p_1}$ and specific heat can be calculated if the ΔC_p of Equation 1 is measured.

In this investigation, the method suggested by Randall and Bisson[3] and used by Randall and Ramage[4] is employed: given two calorimeter units identically alike, and containing like resistance heating units connected in series.

Charge both Units 1 and 2 with the same amount of water, say 1000 g. Pass a current in series through the two units for such a time as to cause a temperature rise in Unit 1 of Δt_1. If Unit 2 were identically the same as Unit 1 in every respect, its temperature rise would also be Δt_1, but there will be some small physical difference between the two units, so that actually the temperature rise in Unit 2 will be $\Delta t_1 + \Delta t_2$, where Δt_2 is the difference in temperature rise between Units 1 and 2 and is very small compared with Δt_1. Now m moles of salt are added to Unit 2 and again a current is passed through Units 1 and 2 in series until the temperature rise in 1 is again Δt_1. The temperature rise in Unit 2 will now be $\Delta t_1 + \Delta t_2'$. The heat capacity of Unit 1 is the same for both runs; the same amount of electrical energy must have gone into Unit 1 in both runs. Since the two units are in series and have like heating resistances, the energy that has gone into Unit 2 is the same in both runs. Hence for Unit 2

$$(C_p, \text{Unit } 2 + C_p, \text{H}_2\text{O})(\Delta t_1 + \Delta t_2) = (C_p, \text{Unit } 2 + C_p, \text{solution})\,(\Delta t_1 + \Delta t_2') \quad (11)$$

or

$$(\Delta t_1 + \Delta t_2)/(\Delta t_1 + \Delta t_2') = (C_p, \text{Unit } 2 + C_p, \text{solution})/(C_p, \text{Unit } 2 + C_p, \text{H}_2\text{O}) \quad (12)$$

Subtracting one from both sides, we have

$$(\Delta t_2 - \Delta t_2')/(\Delta t_1 + \Delta t_2') = (C_p, \text{solution} - C_p, \text{H}_2\text{O})/(C_p, \text{Unit } 2 + C_p, \text{H}_2\text{O}) \quad (13)$$

Hence

$$\Delta C_p = [(\Delta t_2 - \Delta t_2')/(\Delta t_1 + \Delta t_2')](C_p, \text{Unit } 2 + C_p\text{H}_2\text{O}) \quad (14)$$

The Calorimeter

The calorimeter of Randall and Ramage[4] was rebuilt. A nickel-plated brass plate fitted the guide frame on the vertical runways of the thermostat case of Randall and Bisson.[3,4] This plate was laid out so that three nickel-plated brass cylinders A, 15 cm. × 27 cm., could be bolted to it from the lower side, and so that the three leg multiple thermel case would fit from above, one leg into each cylinder. Above each cylinder were sets of holes with extension tubes to provide for the entry of stirrer, heating coil leads and cooling coil leads. The 20-junction and 50-junction thermel of Randall and Bisson[3,4] and their mechanism for propelling the stirrers in the three units were slightly altered and used in this assembly.

As recommended by Randall and Ramage,[4] the Dewar flasks containing the water or solution were placed within cylinders and the whole assembly was submerged in the

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[3] Randall and Bisson, This Journal, **42**, 347 (1920).

[4] Randall and Ramage, *ibid.*, **49**, 93 (1927).

oil-bath of the thermostat. In this manner the slight variation in the temperature of the oil-bath was ironed out before reaching the liquid in the Dewar flasks. The air in the enclosed space above the bath was always in temperature equilibrium with the oil.

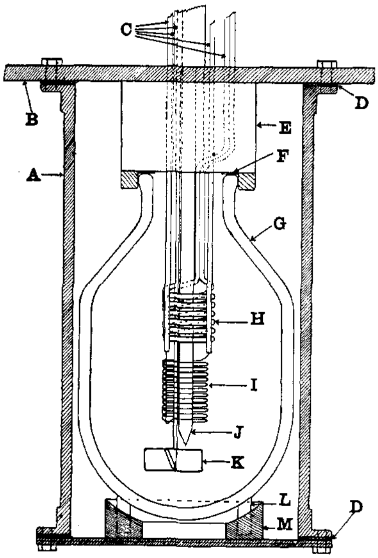

Fig. 1.—One unit of calorimeter.

A cross section of one of the three calorimeter units ($^2/_7$ of actual size) is shown in Fig. 1. The nickel-plated brass cylinder, A, was bolted to the nickel-plated brass main plate, B, with the various extension tubes, C, leading to above the surface of the oil in the bath. The gasket, D, made of Garlock sheet rubber packing was shellacked to the cylinder. The vacuum flask, G, was supported on the rubber pieces, L, which were held in the circular piece of balsa wood, M. The flask was tightly held against the rubber gasket, F, which was shellacked to the balsa wood block, E, through which run the stirrer, thermel, entry opening, heating coil leads and cooling coil leads. The protecting tube, J, of the copper-constantan thermel was of Pyrex glass. The cooling coil, H, was of 0.32 cm. copper tubing, joined to leads of thin-walled German silver tubing, and K was a three vane all glass stirrer with 0.3 cm. glass shaft, which was joined to the driving mechanism with rubber tubing.

The heating coil, I, was made by drawing fine silver tubing over double silk covered manganin resistance wire, having a thin coating of bakelite. This silver tubing was coiled and then joined to 0.32 cm. German silver tubing leading out of the unit. A cross section of one of the tubing junctions of the heating coil is shown in Fig. 2. The silver tubing P, whose outside diameter was about 0.064 cm., was tightly drawn over the No. 38 D.S.C. manganin resistance wire, Q. The double silk insulation, S,S,S, has a thin coating of bakelite. The small silver tubing, P, was soldered, R,E, to a larger piece of silver tubing, which in turn fitted snugly into a brass bushing, U, in the 0.32-cm. German silver tubing, V. The lead, T, was No. 28 copper, and the lead, W, was No. 24 copper wire.

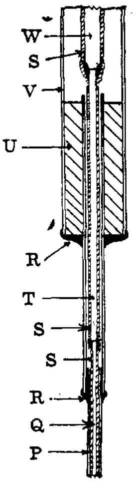

Fig. 2.—Detail of heating coil.

This type of heating coil has a very low heat capacity and the interchange of heat between the resistance wire and the solution is very rapid. About 120 cm. of wire was used in the coil and its resistance was about 70 ohms. The first coils used were of No. 30 D.S.C. manganin wire and had a resistance of about 10 ohms. The heating unit was silver plated and then gold plated; the cooling unit was heavily gold plated.

A 10-junction thermel gave the difference in temperature between the bath and Unit 3; the 20-junction thermel gave the temperature difference between Units 1 and 3; while the 50-junction thermel showed the difference in temperature between Units 1 and 2.

When the entire calorimeter assembly was submerged, the extension tubes, C, extended about 2.5 cm. above the surface of the oil. In this manner every part of the calorimeter proper, including the multiple thermel case, was completely immersed in the constant temperature oil-bath. The thermel case was screwed to the main plate of the calorimeter with rubber as gasket material and then shellacked to prevent dissolution of the rubber.

A Leeds and Northrup, White Double Potentiometer, with a range of 100,000 microvolts, and a Leeds and Northrup high sensitivity galvanometer were used to measure the potentials of the three thermels, the potential drop across and the current through the heating coils. These latter two were read only in the direct heat capacity runs.

To supply the working current in the potentiometer, two batteries of two each of Type B6H Edison alkaline cells were used. The entire electrical system was doubly shielded according to the recommendations of White.[5]

Calibration of the Apparatus

Two Meylan stop watches, for use in measuring the time in the direct heat capacity runs for determining the heat capacity of the flasks, were checked against the Observatory time signals and against the Howard Mean Time clock in the Observatory of the Astronomy Department. We thus found the factor (mean solar seconds) to be 1.0000 for the 0.2-sec. watch and 1.0002 for the 0.1-sec. watch.

Since the potential drop across the heating coils was much greater than the capacity of the potentiometer, a fraction $R_a/(R_a + R_b)$ was measured. The value of $(R_a + R_b)/R_a$, found by measuring the current through and the potential drop across known standard resistances, was 181.50, 181.50, 181.52, 181.50; mean 181.50.

The standard cell used for balancing the working current in the potentiometer was a saturated cell of the Weston type which was kept in the thermostat at 25.25°. The cell was placed in a metal can and the leads were brought out through a bakelite plate. The potential was checked against two new Weston and four new Eppley cells over the period of the investigation and was found to be 1.01808 ± 0.00002 v. at 25.25°. This agrees well with the value of 1.01807 v. calculated from the value 1.01830 v. for a saturated Weston cell at 20°, when corrected for the temperature difference.

The insulation resistances on all the thermels were checked and found to be greater than ten million ohms.

The energy current, furnished by lead storage batteries, was found to be nonfluctuating if the batteries were maintained at the proper charge.

The temperature of the oil in the thermostat was maintained at 25.25 ± 0.010°. The period of the fluctuations in the oil-bath temperature was from ten to eighteen minutes, depending upon the temperature of the room. The oil in the bath was kept well stirred with a four-vane, 8-cm. fan stirrer, running at about 600 r.p.m. Two special thermostat thermometers, which could be read to 0.005°, and which had been calibrated at the Bureau of Standards, were placed at different points in the oil-bath and indicated practically uniform temperature throughout the bath.

The high sensitivity galvanometer used was a Leeds and Northrup, Catalog No. 2285, with a period of six sec., an internal resistance of 37 ohms and an external critical damping resistance of 380 ohms. The galvanometer scale was placed 6.7 meters from the galvanometer, and with a telescope having a very high magnification one could estimate 0.2 mm. on the scale. Table I gives the approximate sensitivity of the galvanometer (in mm. on the scale) with the various thermels in the circuit.

TABLE I

SENSITIVITY OF GALVANOMETER

Thermel	10-Junction	20-Junction	50-Junction
Resistance of thermel, ohms	78.4	147	347
Sensitivity, mm. per mv.	40	30	18
Sensitivity, degrees per mm.	0.000057	0.000038	0.000025

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[5] White, THIS JOURNAL, **36,** 2011 (1914).

The 20-junction and the 50-junction thermel had been calibrated by Randall and Bisson[3] against a 4-junction thermel calibrated by the Bureau of Standards. Then the equation for the e.m.f. per junction was

$$\text{E.m.f.} = 40.875t + 0.05075t^2 - 0.0000613t^3 \qquad (15)$$

when one junction was at 0° and the other at a temperature of t°.

The e.m.f. produced on the thermel when one leg was at 0° and the other at the sodium sulfate triple point, 32.383°, was determined for all three thermels.

TABLE II

CALIBRATION OF THERMELS

Thermel	Measured e.m.f., microvolts	E.m.f. calcd. in microvolts	Ratio $\frac{\text{e.m.f. measured}}{\text{e.m.f. calcd.}}$
10-jc.	13,753.6	13,789.6	0.99738
20-jc.	27,504.3	27,579.1	.99729
50-jc.	68,759.9	68,947.8	.99727

The factors to be applied to the e.m.f.-temperature equation were 0.9973 for the 20- and the 50-junction thermels and 0.9974 for the 10-junction thermel. In this calibration the figures in the second column show the e.m.f. reading when it was constant to 0.3 microvolt for thirty minutes, with one leg in a mixture of clear cracked ice and conductivity water and the other in a solution of sodium sulfate in equilibrium with the two solid forms Na_2SO_4 and $Na_2SO_4 \cdot 10H_2O$, which has a temperature[6] of 32.383°. Conductivity water and thrice recrystallized sodium sulfate were used in making the solutions.

The optimum rate for the stirrers in the flasks was found to be 130 r.p.m. This produced good mixing of the water or the solution without developing an excessive amount of stirring energy. The stirring energy was found to be about 0.025 cal. per min. for the above rate with the stirrers used. This was determined by running the stirrers in Units 1 and 2 with the flasks containing water at the temperature of the bath. The only change in temperature occurring in the two flasks, 1 and 2, was then that due to evaporation and stirring. Readings on the 50-junction thermel joining these two flasks were taken for thirty minutes. Stirrer 2 was stopped for ten minutes and then again started. Then readings were again taken after equilibrium had been established. An extrapolation gave the reading which would have been found if Stirrer 2 had not been stopped. The difference in this and the actual observed reading was translated from microvolts to degrees to calories per minute by a simple calculation.

The heat leak from the bath into one of the vacuum flasks containing about 1200 g. of water was found to be about 10^{-5} cal. per sq. cm. per sec. per deg. This is an average for the entire surface of the Dewar flask, although actually most of this leak occurred through the thermel, stirrer, heating coil, and cooling coil leads. With the above amount of water in the vacuum flask, the heat flow into the flask (when its temperature was below that of the bath) from the bath was such as to cause a temperature rise in it of 0.00037 deg. per min. per deg. difference in temperature. Since at the start of an experiment the flask was 0.5° below the temperature of the bath, and was brought to the temperature of the bath in eight minutes, the total temperature rise due to the Newton flow of heat was $0.5 \times 8 \times 0.00037 = 0.00148$°, or about 0.003 of the total rise.

The stirring and evaporation difference between Flasks 1 and 2 as registered by the 50-junction thermel, and between Flasks 1 and 3, as registered by the 20-junction

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[6] (a) Richards, *Am. J. Sci.*, **6**, 201 (1898); (b) Richards and Wells, *Proc. Am. Acad. Sci.*, **38**, 431 (1902); (c) Dickinson and Mueller, THIS JOURNAL, **29**, 1381 (1907).

thermel, varied slightly from run to run but was practically constant for a given run. Great precision in the determination of the stirring and evaporation difference between Flasks 1 and 2 was necessary, and in most of the runs the stirring and evaporation difference was such as to cause a temperature difference in Units 1 and 2 of about 0.000010° per min. In some runs this was zero and in some as much as 0.000025° per min.

Most of the stirring and evaporation difference between Flasks 1 and 2, which is of great importance in a differential run, was due to a difference in evaporation from the two flasks. This evaporation was reduced by preventing gaseous connection between the inside of the flask and the air space between the flask and the cylinder. The only opening from the interior of the flask to the air space in the thermostat case was along the stirrer tube. This was reduced with some packing. All the other tubes were packed tightly. The 2.2 cm. cylindrical entry tube was neatly fitted with a removable cylinder of balsa wood.

The cooling of the calorimeters to the starting temperature, if they were above it, was accomplished by running compressed air, under a pressure of 0.5 atm. gage through coils of 0.6 cm. copper tubing immersed in liquid air and thence through rubber tubing to the cooling coil of a unit. The air from the exit tube of the cooling coil in each unit was discharged into the air above the bath. With this cooling system, each unit having a heat capacity when charged of about 1200 cal. could be cooled 0.5 deg. in about forty minutes. The moisture and carbon dioxide in the compressed air were removed with calcium chloride, soda lime and a liquid-air trap.

The lag of the rise in temperature of a solution, as registered by the e.m.f. of the thermel, behind the electrical energy input was found to be about twenty-two seconds for an energy input of 75 cal. per min.

Heat Capacity of a Unit

By the capacity of a unit we shall mean the heat capacity of the vacuum flask plus the thermel, stirrer, heating unit and cooling unit within the flask.

Before any differential runs were made, the heat capacity of Unit 2 was determined. A weighed amount of water was placed in Flask 2 and brought to 24.75°. Units 1 and 3 contained water at 25.25°, the temperature of the bath. An amount of energy was put into Unit 2 such that its temperature rise was 0.5 deg. From the energy input and the temperature rise the heat capacity of the unit plus the contained water was calculated. The heat capacity of the unit alone was found by subtracting the heat capacity of the water.

In these direct heat capacity runs the heating time was made about 1000 sec. as the time was measured with a tenth-second stop watch. The energy input was found by taking the average value of potential times current over the period of the run (not the average value of potential times the average value of current) from appropriate plots of the observed value. The method of operation and method of calculation is indicated in Table III, which gives a condensed log of Run 19.

A plot of the temperature (in microvolts) of Unit 2 against the time during the run shows that from the tenth minute to the thirtieth minute

TABLE III

CONDENSED LOG OF RUN 19

C_p Unit 2 (Flask 387). 1:18 P.M., 8/10/27. 1244.62 × 1.00106 g. of water in 2. 1250 cc. of water in 1 and in 3. Energy time, 16 minutes and 12.8 seconds. Stirring rate, 135 r.p.m. Room temp., 21.4°. Bath temp., 25.25°.

Time		Reading		Time		Reading	
		Dial	Scale			Dial	Scale
0	50-jc.	1160	86.80[a]	21	50-jc.	410	67
2			85.00	22	P. D.	27670	63.2
4			83.00	23	Current	57850	89.0
6			81.10	24		57860	78.4
8			79.10	25	50-jc.	120	81
10[b]		1160	77.10[c]	26		60	64
				27[d]		20	77
11		1110	72	28		10	93.30
12	Current	57880	83.0	30		10	93.00[e]
13			82.2				
14			80.6	32			92.70[f]
15	P. D.	27680	66.0	34			92.50
16		27670	73.5	36			92.25
17	Current	57870	78.0	38			92.00
18			83.2	40			91.70
19	P. D.	27670	81.0	42			91.30
20			68.0	44			91.00[g]

[a] Zero, 84.65. [b] Energy on. [c] Zero, 84.65; e.m.f., 1155.80. [d] Energy off. [e] Zero, 84.40; sensitivity, 18.00 (50); e.m.f., 14.80. [f] Sensitivity, 29.90 (20). [g] Zero, 84.20.

Fore period, 50-jc., 0.97 cm./min. at 1158 microvolts. After period, 50-jc., 0.15 cm./min. at 1158 microvolts. U is the constant stirring and evaporation difference between Units 1 and 2. K is the heat leak constant.

$$1158\,K - U = 0.97 \qquad U = 0.15 \text{ cm./min.}$$
$$10\,K - U = 0.15$$
$$1148\,K = 0.82 \qquad K = 0.00071 \text{ cm./min./microvolt}$$

of the run Unit 2 was 9760 microvolt-minutes below the bath. Therefore the rise in temperature of Unit 2 during the run, due to the heat leak, was 9760 × 0.00071 = 6.90 cm. (scale deflection). The rise in temperature of Unit 2 due to the stirring and evaporation difference between Units 1 and 2 was 20 × 0.15 = 3.00 cm.

The total temperature rise not due to the energy input is then 6.90 + 3.00 or 9.90 cm., which is 5.50 microvolts. From the tenth minute to the thirtieth minute the actual temperature rise was 1155.80 − 14.80 or 1141.00 microvolts. The temperature rise due to the energy input alone was 1141.00 − 5.50 or 1135.50 microvolts, or 1135.50/(2165.8 × 0.9973) deg. The average input for the heating period, obtained by plotting the current and potential drop, was 0.016011 × 181.50 watts. The potential drop across the heating unit was obtained by multiplying the reading (P. D. in Table III), in microvolts, by 181.50 and dividing by 10^6. The current is the reading (Current in Table III) of the potential drop in microvolts across a standard 0.1 ohm, multiplied by 10 and divided by 10^6. The time was 972.8 sec. The energy input = $(972.8)(0.016011 \times 181.50) - (0.9989)$ = 2823.10 joules. The factor correcting for the resistance of the leads to the heating unit is 0.9989. The total heat capacity is then $2823.10 \times (2165.8 \times 0.9973)/1135.50 = 5370.07$ joules per deg. The heat capacity of the water at 25° is $(1244.62)(1.00106) \times 4.1728 = 5199.06$ joules per deg., whence C_p for Unit 2 = 171.01 joules per deg., or 40.89 cal. per deg.

Runs 17, 18 and 19 gave 40.76, 40.96 and 40.89 cal. for the heat capacity of Unit 2, with Flask 387.

By making some differential runs, as explained in the next section, the change in the heat capacity of Unit 2 with volume of liquid was found to be as recorded in Table IV.

TABLE IV

CHANGE IN HEAT CAPACITY OF UNIT 2 (FLASK 387) WITH VOLUME OF SOLUTION

Vol. of liq., cc.	1180–1200	1200–1220	1220–1240	1240–1260	1260–1280	1280–1300
Change in C_p in cal./cc. (Unit 2)	0.005	0.006	0.007	0.008	0.009	0.010

These values were calculated from the results of eighteen runs.

The Differential Heat Capacity Run

The procedure followed in measuring ΔC_p was to charge Units 1 and 2 with water at 24.75° and Unit 3 at 25.25°, the temperature of the bath. An amount of energy sufficient to heat Units 1 and 2 to 25.25° was passed through the heating units in series. The temperature rise of Flask 2, $\Delta t_1 + \Delta t_2$, for a given temperature rise in Flask 1, Δt_1, was measured. Then Δn_2 moles of salt were added to Flask 2, and $\Delta t_1 + \Delta t_2$ was found for the rise of Δt_1 in Flask 1. In this way measurements of Δt_1 and Δt_2 were made after successive additions of salt and the ΔC_p between the original amount of water in Flask 2 and any given solution following it is

$$\Delta C_p(m) = (\Delta t_2(m = 0) - \Delta t_2(m))\,(C_p,\text{Unit }2 + C_p,\text{H}_2\text{O})(m = 0)/(\Delta t_1 + \Delta t_2(m)) \quad (16)$$

The method of operation and of calculation is shown in Table V, which gives a condensed log of Run 64.

Materials, Constants, Molecular Weights, etc.

The salts used in this work were anhydrous C. P. samples thoroughly dried in an oven at 105°—Kahlbaum's sodium and potassium chlorides, and sodium and potassium nitrates; Merck's potassium sulfate; Baker and Adamson's sodium sulfate and bromide, and potassium bromide and Mallinckrodt's "Reagent Quality" potassium iodide.

The molality of a given solution is calculated from the weight of the water and the weight of the salt added. The water in the flask is weighed to 0.01 g. and the added salt to 0.001 g. All weighings are reduced to vacuum. The molecular weights of the salts are calculated from the International Atomic Weights for 1927.

The unit calorie was taken as the amount of energy required to raise the temperature of 1 g. of water from 15 to 16°. The ratio of the heat capacity of water at 25° to that

TABLE V

CONDENSED LOG OF DIFFERENTIAL RUN NO. 64

9:00 A.M., 12/13/27. 1250 cc. of water in Flask 1 and in 3. 1238.25 g. of water and 0.1005 moles of sodium chloride in Unit 2. Stirring rate, 115 r.p.m. Room temp., 21.0°. Bath temp., 25.25°.

Time		Reading		Time		Reading			
		Dial	Scale			Dial	Scale	Zero	Sensitivity
0	20-jc.	430	51.50	1	50-jc.	0	52.55	51.25	
4			48.90	5			52.70	51.30	
8			46.40	9			52.90	51.35	
12			43.90	13			53.10	51.35	
16		430	41.35	15			53.15	51.38	
17		390	69	16		0	53.20	51.40	
18		340	72						
23		90	73						
24		40	78						
25		0	66						
				31		0	51.45	51.40	
32		0	45.30	35			51.50	51.40	
36			44.80	39		0	51.60	51.40	17.80 (50)
40		0	44.20	43			51.55	51.30	
44			43.60	47			51.70	51.30	29.90 (20)
48			43.05	51			51.90	51.40	
52			42.50	55			52.05	51.35	
56			41.90						

Unit 1—Unit 3, 20-jc.		Unit 1—Unit 2, 50-jc.	
Fore period	−0.650 cm./min.	Fore period	0.032 cm./min.
After period	−0.138 cm./min.	After period	0.031 cm./min.

Stirring and evaporation, 24 × −0.138 = −3.31 cm. Total difference, 23 × 0.032 = 0.74 cm. Heat leak, 1900[(−0.650 − 0.138)/430] = −2.25 cm. Stirring, evaporation and leak, −5.56 cm. or −0.185 microvolts.

16th min.......	426.50	16th min........	53.20 cm.
40th min.......	−2.40	39th min........	51.60 cm.
	428.90		1.60 cm.
	−1.85		0.74 cm.
	427.05		2.34 cm. or
Multiplying by 2.5000			
	1067.63		1.31 microvolts
Δt_1 =	1000.00 microvolts	Δt_2 =	1.23 microvolts

at 15.5° is taken from the data of Callendar and Barnes[7] to be 0.9979. The unit calorie is assumed to be equivalent to 4.182 joules.

Experimental Data

The experimental data are summarized in Table VI, in which Col. 1 gives the number of moles of salt added to the amount of water indicated

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[7] See résumé of Lewis and Randall, ref. 2.

in the sub-heading of each section of the table; Col. 2 gives the molality of the solution; Cols. 3 and 4 give Δt_2 (in duplicate experiments), the temperature rise in microvolts of Unit 2 above Unit 1 for a rise of 1000 microvolts in Unit 1; Col. 5 gives $\Delta t_2^\circ - \Delta t_2$ or the mean of the differences between Δt_2 for the runs when m is zero and the runs of the given molality; Col. 6 gives (ΔC_p) or the uncorrected change in heat capacity of the system due to the total added salt; Col. 7 the true ΔC_p of the system found by correcting the value of the previous column for the change in the heat capacity of the unit with the change of the volume of solution in the flask (see Table IV), and the last column the apparent molal heat capacity, Φ, which is found by dividing the value in Col. 7 by the molality. Two or more series of runs were made on each salt and the runs of different series are distinguished on the plots.

TABLE VI

APPARENT MOLAL HEAT CAPACITY OF SODIUM CHLORIDE[a]

1238.25 g. water. C_p (Unit 2) = 1275.8 cal.

Moles	m	Δt_2(I) Δt_2(II)	$\Delta t_2^\circ - \Delta t_2$	(ΔC_p)	ΔC_p	Φ
0.0	0.0	−0.20, −0.26	0.0	0.0	0.0	
.0502	.0405	0.74, 0.53	−0.86	− 1.10	− 1.11	−22.1
.1005	.0812	1.21, 1.23	−1.47	− 1.87	− 1.89	−18.8
.2009	.1622	2.53, 2.63	−2.81	− 3.57	− 3.61	−18.0
.3013	.2433	3.66, 3.71	−3.92	− 4.98	− 5.03	−16.7
.4266	.3445	4.82, 4.91	−5.10	− 6.47	− 6.55	−15.35
.5520	.4458	5.93, 5.85	−6.12	− 7.76	− 7.86	−14.25
.7023	.5671	6.82, 6.77	−7.03	− 8.91	− 9.04	−12.87
.8527	.6886	7.60, 7.70	−7.88	− 9.99	−10.15	−11.90
1.0030	.8100	8.32, 8.54	−8.66	−10.96	−11.15	−11.12
1.2036	.9720	8.84 ..	−9.07	−11.47	−11.69	− 9.71
1.4042	1.1340	9.08 ..	−9.31	−11.77	−12.03	− 8.57
1.6048	1.2958	9.27 ..	−9.48	−11.98	−12.28	− 7.65
1.8054	1.4580	8.91 ..	−9.14	−11.56	−11.90	− 6.59
2.0564	1.6607	8.17 ..	−8.41	−10.64	−11.04	− 5.37
2.3074	1.8634	7.22 ..	−7.45	− 9.44	− 9.89	− 4.29
2.5583	2.0660	5.71 ..	−5.94	− 7.54	− 8.04	− 3.14
2.8093	2.2687	4.27, 4.28	−4.50	− 5.72	− 6.27	− 2.23
1192.96 g. of water. C_p (Unit 2) = 1230.6 cal.						
0.0	0.0	0.87, 0.75	0.0	0.0	0.0	0.0
2.2205	1.8613	8.00, 8.13	−7.26	− 8.87	− 9.12	− 4.11
2.7393	2.2961	4.96, ..	−4.15	− 5.08	− 5.43	− 1.98

[a] Similar data for the other salts worked with may be found in a manuscript thesis by the Junior Author, filed in the University of California Library, May, 1928.

The rounded values of the apparent molal heat capacity for the usual rounded values of m are given in the third column of Table VII. The values of the partial molal heat capacity of the solute calculated by means of the plots of Figs. 3 and 4 and the method of Equation 3, are found in Col. 4. The values of the partial molal heat capacity of the water calculated by means of Equation 9 are given in Col. 5, and the specific heat of the solution referred to water as 0.9979 is calculated according to Equation 10 and is given in the last column.

Table VII

Rounded Values of Φ, $\bar{c}_{p2}$, $\bar{c}_{p1}$ and Specific Heat at 25° in Calories

m	Φ	$\bar{c}_{p2}$	$\bar{c}_{p1}$	Sp. ht.
		Sodium Chloride		
0.00	−23.30	−23.30	17.9776	0.9979
.01	−22.05	−21.40	17.9774	.9971
.02	−21.55	−20.60	17.9772	.9963
.05	−20.40	−18.90	17.9763	.9940
.10	−19.15	−17.00	17.9736	.9902
.20	−17.35	−14.20	17.966	.9829
.35	−15.30	−11.15	17.951	.9726
.50	−13.65	−8.65	17.933	.9629
.75	−11.35	−5.25	17.895	.9478
1.00	−9.50	−2.30	17.848	.9338
1.25	−7.80	0.25	17.796	.9209
1.50	−6.28	2.60	17.738	.9088
2.00	−3.50	6.90	17.603	.8872
2.50	−1.03	10.65	17.451	.8684
		Sodium Bromide		
0.00	−24.50	−24.50	17.9776	0.9979
.01	−23.25	−22.60	17.9774	.9966
.02	−22.75	−21.80	17.9772	.9954
.05	−21.65	−20.10	17.9763	.9917
.10	−20.40	−18.20	17.9736	.9857
.20	−18.60	−15.45	17.966	.9741
.35	−16.55	−12.30	17.951	.9576
.50	−14.90	−9.75	17.931	.9420
.75	−12.55	−6.10	17.891	.9177
1.00	−10.50	−3.00	17.843	.8953
		Sodium Iodide		
0.00	−24.80	−24.80	17.9776	0.9979
.01	−23.20	−22.45	17.9774	.9962
.02	−22.60	−21.55	17.9772	.9945
.05	−21.30	−19.55	17.9760	.9894
.10	−19.80	−17.35	17.9733	.9812
.20	−17.70	−14.10	17.965	.9654
.35	−15.40	−10.50	17.947	.9430
.50	−13.50	−7.60	17.924	.9220
.75	−10.85	−3.70	17.881	.8897
1.00	−8.65	−0.40	17.829	.8603
		Sodium Nitrate		
0.00	−12.00	−12.00	17.9776	0.9979
.01	−10.30	−9.45	17.9774	.9970
.02	−9.60	−8.35	17.9772	.9960
.05	−8.10	−6.10	17.9758	.9933
.10	−6.45	−3.45	17.9722	.9888
.20	−3.95	0.50	17.962	.9804
.35	−1.00	5.15	17.939	.9687
.50	1.45	9.10	17.909	.9579
.75	4.95	14.65	17.847	.9416
1.00	8.00	19.40	17.770	.9271
		Potassium Chloride		
0.00	−28.50	−28.50	17.9776	0.9979
.01	−27.50	−27.00	17.9774	.9969
.02	−27.10	−26.45	17.9772	.9959
.05	−26.25	−25.15	17.9767	.9929
.10	−25.35	−23.75	17.9747	.9880
.20	−24.00	−21.70	17.969	.9785
.35	−22.50	−19.40	17.958	.9649
.50	−21.30	−17.55	17.944	.9518
.75	−19.55	−14.90	17.915	.9312
1.00	−18.10	−12.65	17.879	.9118
1.25	−16.80	−10.55	17.837	.8936
1.50	−15.60	−8.70	17.791	.8765
2.00	−13.45	−5.35	17.668	.8441
2.50	−11.55	−2.45	17.568	.8168
		Potassium Bromide		
0.00	−29.70	−29.70	17.9776	0.9979
.01	−28.70	−28.15	17.9774	.9964
.02	−28.30	−27.50	17.9772	.9950
.05	−27.40	−26.30	17.9767	.9906
.10	−26.45	−24.75	17.9745	.9835
.20	−25.00	−22.60	17.969	.9698
.35	−23.45	−20.20	17.957	.9501
.50	−22.20	−18.20	17.942	.9314
.75	−20.35	−15.35	17.910	.9021
1.00	−18.80	−12.90	17.871	.8750
		Potassium Iodide		
0.00	−30.10	−30.10	17.9776	0.9979
.01	−29.00	−28.20	17.9774	.9960
.02	−28.50	−27.45	17.9772	.9940
.05	−27.50	−25.80	17.9760	.9883
.10	−26.40	−23.95	17.9733	.9790
.20	−24.60	−21.20	17.965	.9611
.35	−22.45	−18.00	17.950	.9357
.50	−20.70	−15.25	17.929	.9119
.75	−18.20	−11.50	17.887	.8753
1.00	−16.20	−8.35	17.836	.8419

TABLE VII (*Concluded*)

m	Φ	$\bar{c}_{p_2}$	$\bar{c}_{p_1}$	Sp. ht.
Potassium Nitrate				
0.00	−17.20	−17.20	17.9776	0.9979
.01	−15.60	−14.75	17.9774	.9967
.02	−14.95	−13.75	17.9772	.9956
.05	−13.55	−11.50	17.9758	.9922
.10	−11.95	−9.10	17.9724	.9867
.20	−9.55	−5.35	17.963	.9763
.35	−6.75	−0.90	17.941	.9615
.50	−4.45	2.60	17.914	.9478
.75	−1.25	7.60	17.858	.9267
1.00	1.55	12.05	17.788	.9077
Sodium Sulfate				
0.00	−50.0	−50.0	17.9776	0.9979
.01	−44.7	−42.2	17.9770	.9960
.02	−42.6	−38.8	17.9763	.9942
.05	−37.8	−31.6	17.9720	.9890
.10	−32.3	−22.6	17.9601	.9807
.20	−23.7	−8.5	17.923	.9657
.35	−14.0	5.8	17.852	.9460
.50	−6.40	15.80	17.778	.9287
.75	3.20	29.00	17.629	.9040
1.00	11.05	39.00	17.474	.8835
1.25	17.60	47.60	17.302	.8661
1.50	23.00	55.00	17.113	.8510
Potassium Sulfate				
0.00	−60.6	−60.6	17.9776	0.9979
.01	−56.7	−54.7	17.9772	.9956
.02	−55.1	−52.4	17.9767	.9933
.05	−51.7	−47.1	17.9734	.9867
.10	−47.9	−41.0	17.9652	.9761
.20	−42.1	−31.8	17.941	.9562
.35	−35.2	−21.4	17.890	.9289
.50	−29.90	−13.40	17.829	.9042
.65	−25.30	−6.40	17.756	.8816

Discussion

In Figs. 3 and 4 are shown plots of the experimentally determined values of the apparent molal heat capacity, Φ, for the ten salts. Since Φ is equal to $\Delta C_p/m$, a given error (in cal.) in the measurement of ΔC_p will appear as a larger or smaller error in Φ (in. cal.) on the plot, depending upon whether m is less than or greater than unity. For very small values of m this error becomes large and for the smallest measured concentration, $m = 0.043$, the error in Φ is about 23 times that in the actual measurement of ΔC_p. Nevertheless, the extrapolation of the data to $m = 0$ is fairly certain, as is shown in an examination of the plots. The average error in any given measurement of ΔC_p for all the runs is found to be 0.10 cal. For sodium chloride the average error in a given determination of ΔC_p is 0.06 cal.

The data for sodium and potassium chlorides, sodium sulfate, potassium sulfate, nitrate, bromide and iodide were obtained in the order named. The value of Φ when m is zero is identical with $\bar{c}_{p_2}°$. We find

$$\bar{c}_{p_2}°(\text{KCl}) - \bar{c}_{p_2}°(\text{NaCl}) = \bar{c}_p°(\text{K}^+) - \bar{c}_p°(\text{Na}^+) = -5.2 \text{ cal.} \tag{17}$$

and

$$\bar{c}_{p_2}°(\text{K}_2\text{SO}_4) - \bar{c}_p°(\text{Na}_2\text{SO}_4) = 2\bar{c}_p°(\text{K}^+) - 2\bar{c}_p°(\text{Na}^+) = -10.6 \text{ cal.} = 2 \times (-5.3 \text{ cal.}) \tag{18}$$

Within the limits of error of the extrapolation to zero concentration, these two results are identical and show that the partial heat capacities of ions at infinite dilution are additive.

Given the difference in $\bar{c}_p°$ for Na$^+$ and K$^+$, then, if $\bar{c}_{p_2}°$ is found for potassium bromide, iodide and nitrate, $\bar{c}_{p_2}°$ for sodium bromide, iodide and nitrate is known. This relation was utilized in extrapolating the curves for these latter salts on which relatively few measurements were made.

In Fig. 4 is plotted $\bar{c}_{p_2}$ against $m^{1/2}$ for sodium and potassium sulfates, while Fig. 5 gives $\bar{c}_{p_2}$ against $m^{1/2}$ for sodium and potassium chlorides, bromides, iodides and nitrates. The limiting values of the partial molal heat capacity of the various salts are given in Table VIII.

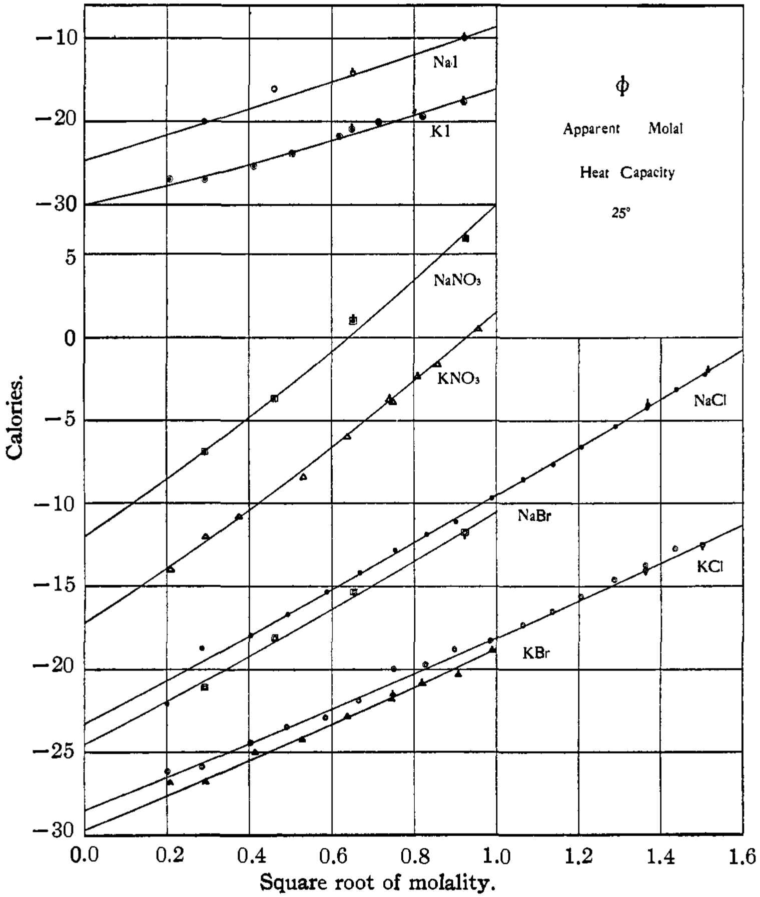

Fig. 3.

TABLE VIII

SUMMARY OF VALUES OF $\bar{C}_{p_2}^{\circ}$ (25°)

$NaNO_3$	−12.0 cal.	KNO_3	−17.2 cal.	K^+-Na^+	− 5.2 cal.
NaCl	−23.3 cal.	KCl	−28.5 cal.	$SO_4^{--}-I^-$	− 0.2 cal.
NaBr	−24.5 cal.	KBr	−29.7 cal.	I^--Br^-	− 0.3 cal.
NaI	−24.8 cal.	KI	−30.1 cal.	Br^--Cl^-	− 1.2 cal.
Na_2SO_4	−50.0 cal.	K_2SO_4	−60.6 cal.	$Cl^--NO_3^-$	−11.3 cal.

The values of the differences in the partial molal heat capacities of certain indicated ions at infinite dilution are given in the last column of Table VIII. They are found by subtracting the values for a pair of salts having a common ion.

$\bar{C}_{p_2}^{\circ}$ becomes increasingly negative for the positive ions in the order Na^+, K^+, and for the negative ions in the order NO_3^-, Cl^-, Br^-, I^-, SO_4^{--}. The value of $\bar{C}_{p_2}$ seems to increase to remarkably high values as the concentration is increased. For sodium sulfate at $m = 1.96$, $\bar{C}_{p_2}$ is 66.9 cal. This is more than twice the molal heat capacity of solid sodium sulfate, at the same temperature. At higher concentrations we should expect the value of $\bar{C}_{p_2}$ to become even larger.

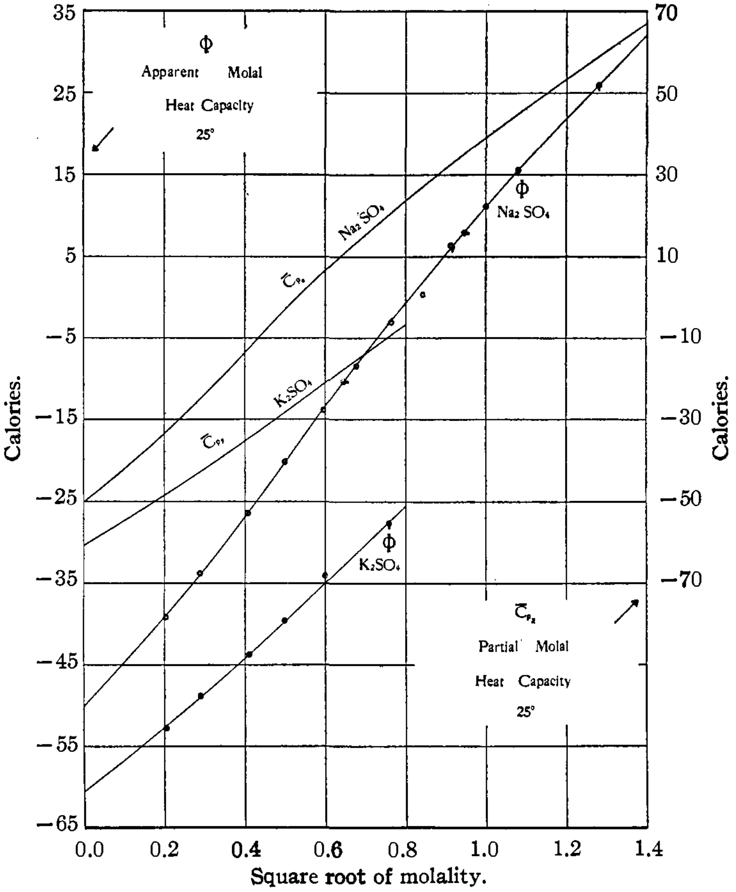

Fig. 4.

The Rate of Change of $\bar{C}_{p_2}$ with Molality

The introduction of a charged particle, as one sodium ion, into an atmosphere of electrical dipoles, as water molecules, changes the energy–temperature relations of all the water molecules within the sphere of influence of the ion in such a manner as to decrease the capacity of these water molecules to take up heat energy. The presence of the charged particle has restricted and damped the kinetic motion (and its temperature coefficient) of the dipoles. Then, too, there may be a direct attachment of a number of the dipoles to the charged body. These effects all make for a considerable decrease in the total number of degrees of freedom in the system, resulting in a diminution of the energy content and of the heat capacity. From these considerations it is easily seen why the apparent heat capacity of a strong electrolyte at infinite dilution is abnormally low, and in nearly every case negative.

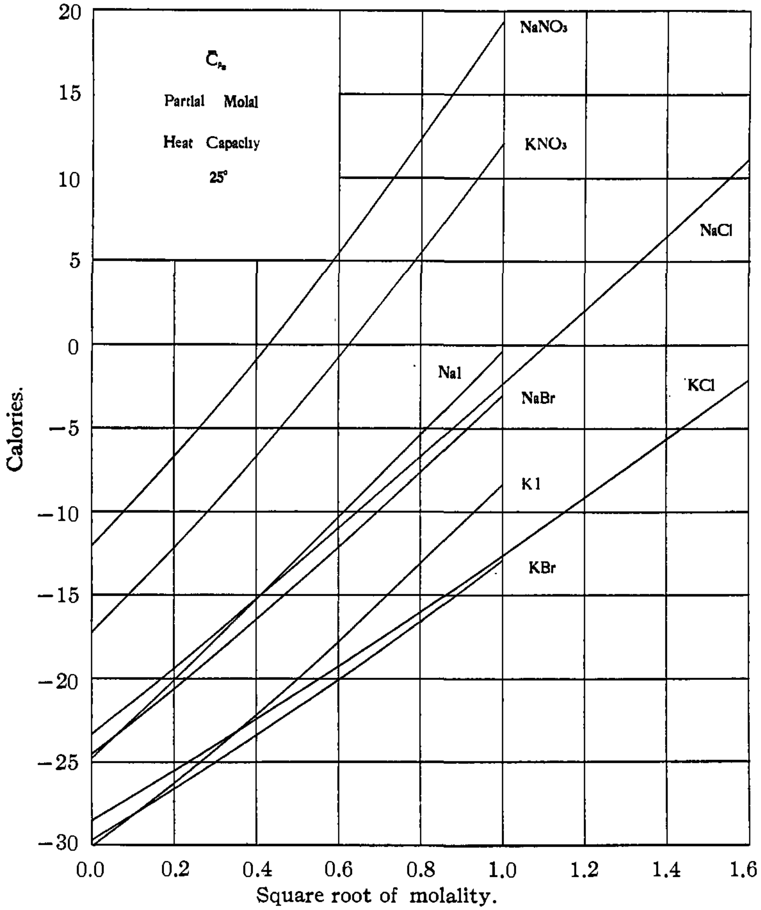

Fig. 5.

Zwicky[8] has attacked the problem of the heat capacity of electrolytic solutions by considering the electrolytic polarization of the water, the ionic atmosphere about a given ion, the compression of the solvent about the ion and the hydration of the ion. Bennewitz[9] considered the change in the intermolecular forces in seeking a theoretical solution of this problem.

Since at infinite dilution a given ion can have within its sphere of influence only a definite number of water molecules, the effect which a given ion has upon the heat capacity of the water molecules will be independent of the source of the ion. The apparent heat capacity of a sodium ion, at infinite dilution, will be the same whether we obtain it from sodium chloride or from sodium sulfate. In other words, the apparent or partial molal heat capacities of ions at infinite dilution will be additive.[10] The effect that a given ion will have upon the capacity of the neighboring water molecules to absorb heat energy will depend upon the charge of the ion, the size of the ion and the configuration of the ion, if it is a polyatomic ion, such as nitrate or sulfate ion.

Randall and Ramage[4] found $\bar{c}_{p_2}$ to rise linearly with the square root of the molality. Their result is verified in the present measurements. We shall consider how the presence of other ions will affect the influence which a given ion has upon the water molecules. On the basis of the Debye-Hückel[11] theory of strong electrolytes one predicts that, in the dilute region, where the theory has been shown to be applicable, $\bar{c}_{p_2}$ should vary linearly with the square root of the concentration.[12]

Consider two systems, A consisting of an infinitely dilute solution, and B consisting of a solution of molality m. In going from State A to State B the change in the free energy of one mole of solute is $\bar{F}_2 - \bar{F}_2{}^\circ$. Following Debye and Hückel,[11a] we may separate this free energy change into two parts, the first of which is that due to the particles considered as solute molecules of a perfect solution, in which case the activity of the solute is equal to the concentration, and the second of which is the free energy change due to the fact that the particles are charged ions.

$$\Delta F = [\bar{F}_2\ (\text{class.}) - \bar{F}_2{}^\circ\ (\text{class.})] - [\bar{F}_2(\text{elec.}) - \bar{F}_2{}^\circ(\text{elec.})] \qquad (19)$$

We can substitute for the second parenthesis the value given by Debye and Hückel,

$$\bar{F}_2(\text{elec.}) - \bar{F}_2{}^\circ(\text{elec.}) = -\frac{Ne^2\Sigma\nu_i z_i}{2\mathbf{D}}\,\frac{\xi}{1+\xi\alpha} \qquad (20)$$

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[8] Zwicky, *Physik. Z.*, **27**, 271 (1926).

[9] Bennewitz, *Z. Elektrochem.*, **33**, 540 (1927).

[10] A statement which leads to this result was made by Lewis, THIS JOURNAL, **35**, 15 (1913).

[11] (a) Debye and Hückel, *Physik. Z.*, **24**, 185 (1923); (b) Debye, *ibid.*, **25**. 97 (1924).

[12] Lange and Messner, *Z. Elektrochem.*, **33**, 431 (1927), applied the Debye-Hückel theory in deriving the variation of $\bar{c}_{p_1}$ in the dilute region.

where $\xi^2 = 4\pi Ne^2\Sigma c_i z_i^2/1000\mathbf{D}kT$, and e is the electronic charge, $\mathbf{D}$ the dielectric constant of the medium, N Avogadro's number, k Boltzmann's constant, T absolute temperature, c concentration of solute in moles per liter, c_i concentration of i^{th} kind of ions in moles per liter, z_i charge on the i^{th} kind of ions, ν_i the number of the i^{th} kind of ions per molecule, and α a constant of the order or magnitude of the radius of the ion.

For $\bar{\text{F}}_2$ (class.) $-$ $\bar{\text{F}}_2^\circ$ (class.) Debye and Hückel write $RT \ln c$, whence

$$\Delta F = -\frac{Ne^2\Sigma\nu_i z_i^2}{2\mathbf{D}}\frac{\xi}{1+\xi\alpha} + RT\ln c \tag{21}$$

But

$$T(\delta^2(\Delta F))/\delta T^2 = -\Delta C_p = -(\bar{\text{c}}_{p2} - \bar{\text{c}}_{p2}^\circ) \tag{22}$$

Substituting Equation 21 in Equation 22, we find

$$\bar{\text{c}}_{p2} - \bar{\text{c}}_{p2}^\circ = -T\frac{\delta^2}{\delta T^2}\left[-\frac{Ne^2\Sigma\nu_i z_i^2}{2\mathbf{D}}\frac{\xi}{1+\xi\alpha}\right] - T\frac{\delta^2\,(RT\ln c)}{\delta T^2} \tag{23}$$

Performing this differentiation and making the slight assumption that $\mathrm{d}c/\mathrm{d}T$ and $\mathrm{d}^2c/\mathrm{d}T^2$ are zero, we obtain

$$\bar{\text{c}}_{p2} - \bar{\text{c}}_{p2}^\circ = \frac{3}{4}\left(\frac{\pi N}{1000k}\right)^{1/2}\frac{Ne^3}{(\mathbf{D}T)^{3/2}}f(\mathbf{D},\ T)(\Sigma\nu_i z_i^2)^{3/2}\frac{c^{1/2}}{(1+\xi\alpha)^2} \tag{24}$$

where

$$f(\mathbf{D},\ T) = 1 + 2\frac{T}{\mathbf{D}}\frac{\mathrm{d}\mathbf{D}}{\mathrm{d}T} + 5\left(\frac{T}{\mathbf{D}}\frac{\mathrm{d}\mathbf{D}}{\mathrm{d}T}\right)^2 - 2\frac{T^2}{\mathbf{D}}\frac{\mathrm{d}^2\mathbf{D}}{\mathrm{d}T^2} \tag{25}$$

In evaluating $\mathbf{D}$, $\mathrm{d}\mathbf{D}/\mathrm{d}T$ and $\mathrm{d}^2\mathbf{D}/\mathrm{d}T^2$ we can take the values for pure water (which will not be very different from that of a very dilute solution) as taken from the equation of Adams[13] $\mathbf{D} = 400{,}000T^{-3/2}$ deduced from the measurements of Kockel.[14] For $T = 298.1°K$, $\mathbf{D} = 77.75$; $\mathrm{d}\mathbf{D}/\mathrm{d}T = -0.3914$; $\mathrm{d}^2\mathbf{D}/\mathrm{d}T^2 = 0.003283$; $(T/\mathbf{D})(\mathrm{d}\mathbf{D}/\mathrm{d}T) = (\mathrm{d}\ln\mathbf{D})/(\mathrm{d}\ln T) = -3/2$; $f(\mathbf{D},\ T) = 1.75$. Evaluating

$$\bar{\text{c}}_{p2} - \bar{\text{c}}_{p2}^\circ = 2.14(\Sigma\nu_i z_i^2)^{3/2}[c^{1/2}/(1+\xi\alpha)^2] \tag{26}$$

In the dilute region $(1+\xi\alpha)$ closely approaches the value of 1, and the concentration in moles per liter is very nearly the same as the concentration in moles per 1000 g. of water. Hence

$$\bar{\text{c}}_{p2} = 2.14(\Sigma\nu_i z_i^2)^{3/2}\,m^{1/2} + \bar{\text{c}}_{p2}^\circ \tag{27}$$

The values of the valence factor $(\Sigma\nu_i z_i^2)^{3/2}$ (and 2.14 times the valence factor) for various types of solute are given in Table IX.

TABLE IX

SLOPE OF PARTIAL MOLAL HEAT CAPACITY AGAINST SQUARE ROOT OF MOLALITY

Valence type	1-1	2-1	2-2	3-1	3-2
$(\Sigma\nu_i z_i^2)^{3/2}$	2.82	14.7	22.6	41.6	165
$2.14(\Sigma\nu_i z_i^2)^{3/2}$	6.0	31	48	89	353

Equation 27 shows that in the dilute region in which the Debye-Hückel theory of strong electrolytes is applicable, $\bar{\text{c}}_{p2}$, when plotted against the

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[13] Adams, THIS JOURNAL, **48**, 625 (1926).

[14] Kockel, *Ann. Physik*, [4] 77, 417 (1925).

square root of the concentration, should be a straight line whose slope will depend upon the charge and the number of the ions making up a solute molecule. This slope is the same for solutes of the same valence type and is greater for the higher valence types. It must be remembered that Equation 27 gives only the values of $\bar{C}_{p_2} - \bar{C}_{p_2}{}^\circ$. The value of $\bar{C}_{p_2}{}^\circ$ for any given pair of ions must be sought in some other manner.

The slopes of the curves of partial molal heat capacity against $m^{1/2}$ given in Figs. 4 and 5 at $m^{1/2} = 0$ are approximately as given in Table X.

TABLE X

APPROXIMATE LIMITING SLOPE OF PARTIAL MOLAL HEAT CAPACITY AGAINST SQUARE ROOT OF MOLALITY

Salt	NaCl	NaBr	NaI	Na_2SO_4	$NaNO_3$	KCl	KBr	KI	K_2SO_4	KNO_3
$\bar{C}_{p_2}/m^{1/2}$	19	18	23	76	25	15	15	18	62	25

In all the curves for the uni-univalent salts the slope is increasing somewhat with increase in $m^{1/2}$. For the sulfates there appears a point of inflection, at $m^{1/2} = 0.7$ for potassium sulfate and $m^{1/2} = 0.5$ for sodium sulfate.

According to Equation 27 and Table IX the value of the slope of $\bar{C}_{p_2}$ against $m^{1/2}$, in the dilute region, should be about 6 for a 1–1 and 31 for a 2–1 salt. The slopes given in Table X show an average of about 18 or 20 for the 1–1 and about 70 for the 2–1 salts. These values show the proper order of magnitude and about the right variation with change in the valence types of the salt. A closer agreement might possibly be obtained with a more precise knowledge of the true values of $d\mathbf{D}/dT$ and $d^2\mathbf{D}/dT^2$, which are used in Equation 27, and by the non-neglect of the terms dc/dT and d^2c/dT^2. These results seem further to emphasize the validity of the assumptions underlying the Debye-Hückel theory of strong electrolytes as applied to dilute aqueous solutions.

The slopes of these curves of $\bar{C}_{p_2}$ increase in the order of Cl^-, Br^-, I^-, NO_3^- for the negative ions with a common cation and K^+, Na^+, for the positive ions with a common anion.

Other Ions

A complete review of all the available data on the specific heats of aqueous solutions of electrolytes was made to see if some values of $\bar{C}_{p_2}$ could be obtained on salts other than those measured in this work. In order that the data may be used to calculate Φ and by extrapolation to $m = 0$ find $\bar{C}_{p_2}$, the specific heat measurements must not only be reported to 1 in 10,000, but they must be precise to that extent. In comparatively few cases was the first requirement satisfied, and in these few there was lack of precision except in one or two cases. This, coupled with the fact that where the measurements were satisfying there were not enough of them in the dilute region to permit certain extrapolation to zero concentration, resulted in the securing of qualitative instead of quantitative information on values of $\bar{c}_{p_2}^\circ$ for additional salts.[15]

Using the data of Richards and Rowe,[15c,16] together with those here obtained, we find that the univalent positive ions can be arranged in the following order of decreasing (more negative) $\bar{c}_p^\circ$: Li^+, Na^+, K^+, H^+, Rb^+, Cs^+.

Combining the data of this work with those of Jauch[17] on potassium fluoride, we find the univalent negative ions in the following order of decreasing $\bar{c}_p^\circ$: F^-, Cl^-, Br^-, I^-.

The Jauch data also furnish the following qualitative information. In order of decreasing $\bar{c}_p^\circ$ we find Na^+, Mg^{++}, Al^{+++}. We also find $\bar{c}_p^\circ$ for Mg^{++} more negative than that for Be^{++}.

From the data of Cohen, *et al.*,[18] we find that $\bar{c}_p^\circ$ for Cd^{++} is more negative than for Zn^{++}.

The above information tells us that in any given group of the elements $\bar{c}_p^\circ$ becomes more negative as the atomic number increases and, in any given period, $\bar{c}_p^\circ$ becomes more negative as the charge on the ion increases.

The fact that H^+ does not fall into the regular order of the univalent positive ions indicates that it has some unique effect on the water molecules.

An ion at infinite dilution in water can be pictured as having oriented about it a number of water molecules (considered as electrical dipoles), some of which will be directly attached to the ion.[19] On this picture the partial molal heat capacity of the ion at infinite dilution will be the sum of three effects: $\bar{c}_p^\circ = A + B + C$, where A is the intrinsic heat capacity of the ion and has a positive value; B is the effect due to the breaking up of the ion hydrate (ion plus the directly attached water molecules) on the absorption of heat in the reaction: ion hydrate = ion + water molecules (for this reaction heat is absorbed and ΔH is positive; B has a positive value) and C is the effect that the charged body has on the heat capacity

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[15] An example of the inadequacy of some of the specific heat data in giving proper values of $\bar{c}_{p_2}^\circ$ is the following: (a) Lewis and Randall (ref. 2, p. 86) give $\bar{c}_{p_2}^\circ$ for H_2SO_4 in aqueous solution as calculated from the specific heat data of (b) Biron, *J. Russ. Phys.-Chem. Soc.*, **31,** 190 (1899), as 10.4 cal. From the specific heat data of (c) Richards and Rowe, THIS JOURNAL, **42,** 1621 (1920), and of (d) Wrewsky and Kaigorodoff, *Z. physik. Chem.*, **112,** 83 (1924), and the heat of solution data at various temperatures of (e) Wrewsky and Sawaritzky, *ibid.*, **112,** 92 (1924), one finds that $\bar{c}_{p_2}^\circ$ for HCl is about −34 cal. But $\bar{c}_{p_2}^\circ$ for NaCl is −23.3 cal. Hence $2\bar{c}_p^\circ(H^+) - 2\bar{c}_p^\circ(Na^+) = -21$ cal. Since $\bar{c}_{p_2}^\circ(Na_2SO_4)$ is −50 cal., $\bar{c}_{p_2}^\circ(H_2SO_4)$ should be about −71 cal.

[16] Richards and Rowe, THIS JOURNAL, **43,** 770 (1921).

[17] Jauch, *Z. Physik*, **4,** 441 (1920).

[18] (a) Cohen and Moesveld, *Z. physik. Chem.*, **95,** 305 (1920); (b) Cohen, Helderman and Moesveld, *ibid.*, **112,** 135 (1924).

[19] Ghosh, *Trans. Faraday Soc.*, **15,** 159 (1919).

of the water dipoles due to the restriction it places upon their motion, decreasing their capacity to absorb heating energy. (C has a negative value.)

Since $\bar{c}_p{}^\circ$ for all the ions here investigated is negative, $A + B$ is less than C. Since $\bar{c}_p{}^\circ$ for K^+ is less than that for Na^+, and since A is very nearly the same for both Na^+ and K^+, then $B + C$ is algebraically less (more negative) for K^+ than for Na^+. Since we should expect C to be more negative for the ion exerting the greatest electrical force upon the water molecules, then for ions of like charge C will be more negative for the smaller ion. Hence B must be greater for Na^+ than for K^+. This means that the temperature coefficient for the heat absorbed in the reaction

$$Na^+(H_2O)_{n_1} = Na^+ + n_1H_2O \qquad (28)$$

is greater than that for the reaction

$$K^+(H_2O)_{n_2} = K^+ + n_2H_2O \qquad (29)$$

This may be explained by assuming that n_1 is greater than n_2. This is in qualitative agreement with the data on the hydration of ions as given by various investigators.

Reverting to the unique effect observed in the case of H^+, we may postulate the formation of hydronium ion, H_3O^+, for which there is very good evidence from other sources. Effect C for H^+ will be large since it is reasonable to suppose that the intrinsic heat capacity of H_3O^+ is less than the sum of the intrinsic heat capacity of H_2O and that of H^+. This need not be a necessary argument in proving why $\bar{c}_p{}^\circ$ (H^+) is more negative than that for K^+ or Na^+, because Effect B will be less in the case of H_3O^+ since it will be larger and hence less hydrated than K^+ or Na^+.

Any consideration of the existence of $(H_2O)_2$ and $(H_2O)_3$ molecules as the molecular state of the water will not invalidate the foregoing arguments.

In the case of polyatomic ions, such as NO_3^- and SO_4^{--}, the configuration, as well as the charge and size, will play a predominant part in determining the value of $\bar{c}_p{}^\circ$.

Let us now consider the cause of the rapid increase in $\bar{c}_{p_2}$ with the concentration. This is obviously due to the fact that Effect C is becoming less negative as the concentration is increased because each ion is affecting fewer water molecules, or the effect per ion is less.

Another point to be considered is the almost linear relationship between $\bar{c}_{p_2}$ and $m^{1/2}$ throughout all the concentrations measured. For an electrolyte the logarithm of the activity coefficient can be approximately expressed in terms of the first two powers of $m^{1/2}$

$$\ln \gamma = Am^{1/2} + Bm \qquad (30)$$

also

$$RT \ln \gamma = \bar{F}_2 - \bar{F}_2{}^\circ \qquad (31)$$

Since $-(\bar{c}_{p_2} - c_{p_2}{}^\circ)$ is $T\,\delta\,(\bar{F}_2 - \bar{F}_2{}^\circ)/\delta T^2$ and if $\bar{c}_{p_2} - \bar{c}_{p_2}{}^\circ$ very nearly varies as $m^{1/2}$, this means that probably d^2B/dT^2 is zero. In other words, the physical properties which determine the value of B in the above equation have a temperature coefficient which is itself independent of the temperature.

For the data of Wrewsky and Kaigorodoff,[15d] who measured the specific heat of hydrochloric acid at various temperatures, and comparing Richards and Rowe's[16] 18° data with our 25° data we find that approximately $d\bar{c}_{p_2}{}^\circ/dT$ is about 0.2 cal. per deg. around 25° for a uni-univalent electrolyte.

This agrees with the results of Randall and Ramage,[4] who found that in a dilute solution of sodium chloride, $\bar{c}_{p_2}$ increased with the temperature. This is in complete accord with the arguments presented here, since the polarizing and orienting effect of the ion upon the water molecules will decrease with increase in the kinetic energy of the dipoles.

From the values of $\bar{c}_{p_2}{}^\circ$ obtained in this research, it can be stated definitely that for the reaction of dissolving one mole of a substance which is a strong electrolyte in a very large amount of water, ΔH will decrease with increase in temperature.

Given the reaction

$$\mathrm{MX(s)} + n_1\mathrm{H_2O} = \mathrm{M^+}(m) + \mathrm{X^-}(m) + n_1\mathrm{H_2O} \qquad (32)$$

If n_1 is taken so large as to make the molality practically zero, we may write

$$\mathrm{MX(solid)} = \mathrm{M^+}(m = 0) + \mathrm{X^-}(m = 0) \qquad (33)$$

Now we have shown that $\bar{c}_p{}^\circ\ (\mathrm{M^+}) + \bar{c}_p{}^\circ\ (\mathrm{X^-})$ is negative. Then $\Delta C_p = d\Delta H/dT$ is negative. Of course ΔC_p will be negative even though $\bar{c}_p{}^\circ\ (\mathrm{M^+}) + \bar{c}_p{}^\circ\ (\mathrm{X^-})$ be positive, provided the latter sum be less than the heat capacity of the solid.

In the case of a substance giving polyatomic ions, $\bar{c}_{p_2}{}^\circ$ may be positive but will be less than the heat capacity of the pure substance. For very weak electrolytes, such as mercuric chloride and cadmium iodide, $\bar{c}_{p_2}{}^\circ$ has a positive value which may be greater than the heat capacity of the solid.

In conclusion, we wish to express our thanks to Messrs. Jack Sherman, Albert Sherman and Bernard Weidenbaum for their assistance in drawing Figs. 1 and 2, and in recalculating the specific heat data of other investigators; and to Mr. G. F. Nelson for building much of the apparatus.

Summary

The assembly of a calorimeter having a precision of greater than 0.1 per mille in measuring differentially the heat capacities of aqueous salt solutions is described, and a description of its calibration and method of operation for direct and for differential heat capacity measurements is given.

Methods of determining and calculating Φ, the apparent molal heat

capacity of the solute, $\bar{c}_{p_2}$, the partial molal heat capacity of the solute, $\bar{c}_{p_1}$, the partial molal heat capacity of the solvent and the specific heat of the solution are given.

Tables and plots of the experimental data and tables of rounded values of Φ, $\bar{c}_{p_2}$, $\bar{c}_{p_1}$ and specific heat are given for the nitrates, chlorides, bromides, iodides and sulfates of sodium and potassium in aqueous solution from infinite dilution to 1.0 molal, and in some cases to 2.5 molal.

A theoretical equation for $\bar{c}_{p_2} - \bar{c}_{p_2}^{\circ}$ is derived on the basis of the Debye-Hückel theory of strong electrolytes in aqueous solution, and is compared with the experimentally determined values. ($\bar{c}_{p_2}^{\circ}$ refers to infinite dilution.)

The partial molal heat capacity of a given ion is shown to depend upon the charge, the size and the configuration of the ion. The partial molal heat capacities of ions are shown to be additive at infinite dilution.

The relation of the results obtained to hydration of ions and the temperature coefficient of the heat of solution of a strong electrolyte in a large amount of water is discussed.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, NO. 585]

THE REDUCTION OF PERMANGANATE ION BY CHROMIC ION IN ACID SOLUTION

BY H. A. FALES AND P. S. ROLLER[1]

RECEIVED AUGUST 8, 1928 PUBLISHED FEBRUARY 5, 1929

The peculiar nature of the reduction of permanganate ion in acid solution has long interested chemists. As early as 1866 Harcourt and Esson[2] in their study of the reduction of permanganate by oxalic acid observed that the reaction was autocatalytic and catalyzed by manganous ion, and that in the presence of the latter excess of oxalic acid slowed down the rate of oxidation. They imputed the catalytic effect to the formation of manganese dioxide in solution.

In 1903 the study of the reduction by oxalic acid was again undertaken by Schilow,[3] who endeavored to show that the autocatalysis was due to the interaction between the permanganate and a trivalent manganic oxalate complex, the primary reduction product.

The same reaction was next studied by Skrabal,[4] who observed a period

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[1] This paper is constructed from a dissertation submitted by P. S. Roller in partial fulfilment of the requirements for the degree of Doctor of Philosophy at Columbia University.

[2] Harcourt and Esson, *Phil. Mag.*, 201 (1866).

[3] Schilow, *Ber.*, **36**, 2735 (1903).

[4] Skrabal, *Z. anorg. Chem.*, **42**, 1 (1905).