

tile organic substances has been developed. No catalytic agent is used. The material, volatilized with air, is drawn through a heated quartz tube; the combustion products are absorbed in alkaline sodium sulfite solution; the excess of sulfite is oxidized; and the halogen is determined by the Volhard volumetric method.

2. With some modification of the apparatus, and with the partial use of tank oxygen, the method is equally applicable to non-volatile organic materials.

3. The method is a general one for the determination of halogen in organic compounds; and, in our opinion, it yields to none in accuracy of results or in ease and convenience of execution.

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

THE HEAT OF SOLUTION AND THE PARTIAL MOLAL HEAT CONTENT OF THE CONSTITUENTS IN AQUEOUS SOLUTIONS OF SODIUM CHLORIDE.

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In order to calculate the free energy of a reaction at one temperature, when the free energy at another temperature is known, we must first obtain the value of ΔH , the increase in heat content accompanying the reaction.¹ This quantity, is defined as the difference between the heat contents of the substances formed and the heat contents of the substances disappearing. For pure substances, ΔH is identical with the negative of the heat of reaction as ordinarily measured. In case one or more of the substances involved in the reaction occurs in solution, we must use, obviously, not the molal heat content, H , of the pure substance, but the heat content of the substance when in solution at the given concentration. This quantity \bar{H} is the partial molal heat content, and is defined as the increase in the heat content of a large amount of the solution at the given concentration when one mol of the substance is added to it.

It is not possible to determine the absolute value of H or \bar{H} for any substance, for we can measure only the difference ΔH between the heat content of the substances appearing and those disappearing in a reaction. However, when no ambiguity will result, we have found it convenient, at a given temperature, to call the value of ΔH , when a substance is formed from the elements in their standard state at the same temperature, the molal heat content or the partial molal heat content of the substance. It is in this sense that these quantities are generally used in this paper, and when so used will always be symbolized by ΔH . The symbols H

¹ Lewis, "The Free Energy of Chemical Substances," THIS JOURNAL, 35, 1 (1913).

and \bar{h} will be reserved for the absolute molal heat content and the absolute partial molal heat content of the substance.

From the results of the present investigation we have been able to calculate ΔH for the constituents of aqueous solutions of sodium chloride.

Before proceeding further it will be convenient to define a number of quantities related to h and \bar{h} , and to consider which of these related quantities have been used by the various investigators who have measured heats of solution and of dilution.

If we consider the reaction, $\text{Na}(s) + \frac{1}{2}\text{Cl}_2(g) = \text{NaCl}(0.1 M)$ the partial molal heat content, ΔH (NaCl in $0.1 M$), is the heat absorbed when one mol of sodium chloride is formed from its elements and dissolved in such a large volume of solution that the concentration remains unchanged. The *partial molal heat of solution* of sodium chloride in $0.1 M$ solution, $\text{NaCl}(s) = \text{NaCl}(0.1 M)$, is $\bar{h}(\text{NaCl}$ in $0.1 M) - h(\text{NaCl})$. Similarly the *partial molal heat of solution* of sodium chloride in its saturated solution is $\bar{h}(\text{NaCl sat.}) - h(\text{NaCl})$. The *partial molal heat of dilution*, $\text{NaCl}(1 M) = \text{NaCl}(0.1 M)$, is $\bar{h}(\text{NaCl}$ in $0.1 M) - \bar{h}(1 M)$.

Of equal importance with the partial molal heat content of the solute is the partial molal heat content of the solvent. These quantities can be defined in terms of each other by the familiar equation,

$$d\bar{h}(\text{solute}) = -\frac{N(\text{solvent})}{N(\text{solute})} d\bar{h}(\text{solvent}) \quad (1)$$

where N represents the mol-fraction. The partial molal heat content of the water in $0.1 M$ NaCl , $\bar{h}(\text{H}_2\text{O}$ in $0.1 M$ NaCl), is the increase in heat content when one mol of water is added to such a large quantity of solution that the concentration remains unchanged. And, as above, we have the important quantity, $\bar{h}(\text{H}_2\text{O}$ in $0.1 M$ $\text{NaCl}) - h(\text{H}_2\text{O})$, the partial molal heat of solution of water in $0.1 M$ NaCl .

The molal heat content of the solution is defined in terms of the partial quantities,

$$h(\text{solution}) = N(\text{solute})\bar{h}(\text{solute}) + N(\text{solvent})\bar{h}(\text{solvent}). \quad (2)$$

For a given pure substance it is possible to determine directly the value of the heat content ΔH , but $\bar{h} - h$ has never been measured directly. Rümelin¹ obtained values which approximated $\bar{h} - h(\text{H}_2\text{O})$ for water in concentrated solutions of sodium and potassium chlorides by adding in a calorimeter small amounts of water to large amounts of solution. The partial molal heat content of sulfuric acid was determined by Brönsted,² who discussed the relation between this quantity and the heat of

¹ Rümelin, *Z. physik. Chem.*, 58, 449 (1907).

² Brönsted, *ibid.*, 56, 645 (1906); 64, 641 (1909); 68, 693 (1910). Brönsted calls the heat of solution and the partial molal heat content the integral and differential heats of solution. The temperature of his calorimeter was not stated. From the discussion we may infer that it was probably about 17°.

solution. He also determined the heat of solution of sodium chloride at several concentrations.

While this investigation was in progress MacInnes and Braham¹ determined the value for $\bar{H} - H$ for water in aqueous solutions of ethyl alcohol by adding varying small amounts of water to large amounts of the alcohol solution. The values of the heat obtained per mol of water added when plotted as ordinates and the quantity of water added as abscissas gave approximately a straight line. The true value of $\bar{H} - H$ is the intercept of this straight line upon the ordinate axis.

Berthelot and Thomsen and others have determined the *heat of solution* of a large number of substances by adding the substances to pure water. This quantity is of little use in thermodynamic calculations. In those cases in which the *heat of solution* of substances has been determined for a series of dilutions, $\bar{H} - H$ may be calculated by the method used by Lewis.²

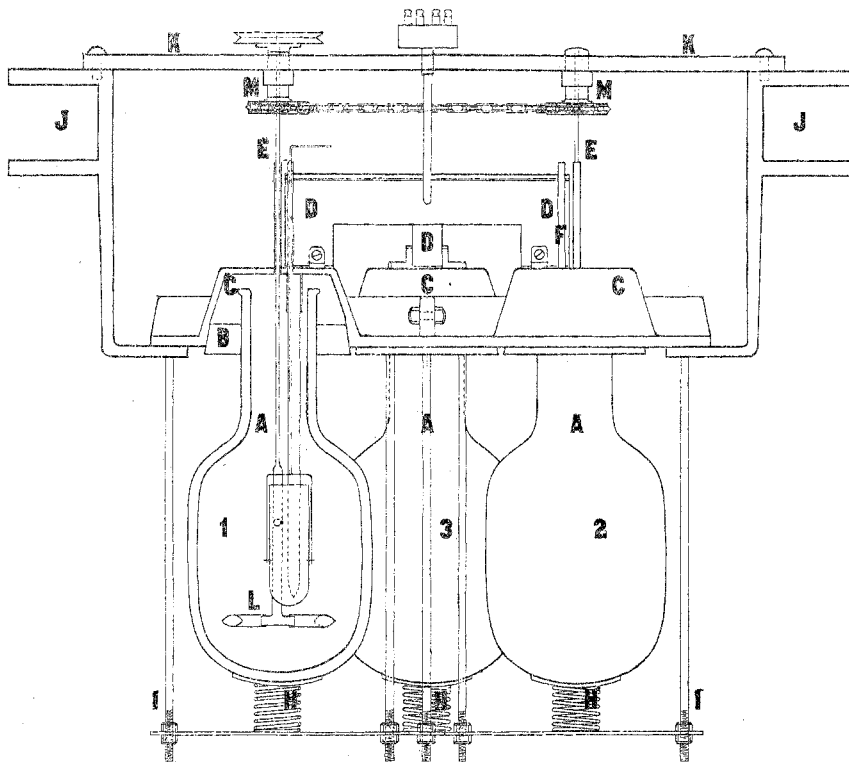


Fig. 1.—Twin vacuum jacketed calorimeters. Elevation.
Scale: 1 cm. = 5 cm.

¹ MacInnes and Braham, *THIS JOURNAL*, 39, 2110 (1917).

² Lewis, *ibid.*, 35, 1 (1913).

The Calorimeter.—Our apparatus consisted essentially of twin calorimeters (Fig. 1) completely enclosed in a constant temperature air jacket (Fig. 4), a 50-junction differential copper-constantan thermoelement, and a sensitive potentiometer. A third calorimeter and a 20-junction thermoelement also formed a part of the apparatus. These were intended primarily to be used in connection with another investigation. It will be desirable to describe the entire apparatus, as the auxiliary vessel and thermoelement were used in the calibration of the main thermoelement.

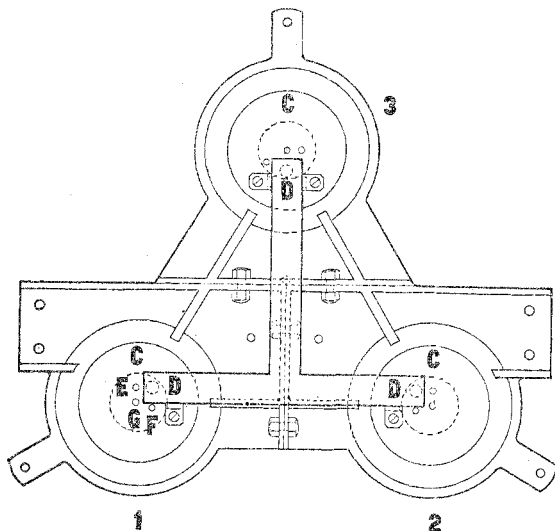


Fig. 2.—Twin vacuum jacketed calorimeters. Plan.
Scale: 1 cm. = 5 cm.

the approximate heat leak determined. Three flasks, A A A, (Figs. 1 and 2), with like heat leaks were selected. These were fitted by means of large rubber stoppers, B B B, into the caps, C C C. These caps were of cast brass and formed a part of the framework of the calorimeter unit. The interiors of the caps were highly polished, then silver plated and again polished. In the tops of the caps were openings for the thermocouple D, and tubes E F G for the passage of the stirrer, electric leads, upsetting device, etc. The joint between the thermocouple and the cap was made tight by means of rubber packing. The flasks were held in place by means of the supporting springs, H H H. These were in turn held in position by means of framework I I, which was attached to the castings C C C. The whole calorimeter unit was supported upon brackets J J. The rod K served as a brace and as a support for the stirrers M L. The stirrer L consisted of a glass T-tube fitted with tips of rubber tubing. A hole was blown in the stirrer shaft just below the level of the liquid in the calorimeter vessel, and just above this point the tube was sealed to the glass rod which was, in turn, joined to a steel shaft at E by means of a bit of rubber tubing. The three stirrers were driven at a uniform speed of about 150 R. P. M. by means of a chain and sprockets, M M M.

¹ No. 322 F, one quart Carafe Filler, Vacuum Specialty Co., Meriden, Conn. These vessels have the desired shape and are manufactured in a uniform size and with uniform opening.

The dilution cup N (Fig. 3) was constructed from a very thin-walled glass test-tube which was cut off to the proper length. Short platinum wires, about 0.5 mm. in diameter, were sealed in at A, and cut off about 3 mm. from the side of the tube. The stirrup was forged from No. 16 nichrome wire and then gold plated. A small piece of platinum wire C prevented the cup from tipping in that direction. The opposite side of the dilution cup rested against the thermoelement D. When it was desired to mix the contents of the dilution cup with those of the calorimeter, the handle F attached to the stirrup was turned through 90°, which allowed the tube N to upset, after which it was raised into the neck of the flask. In this manner it was possible to make the dilution with certainty

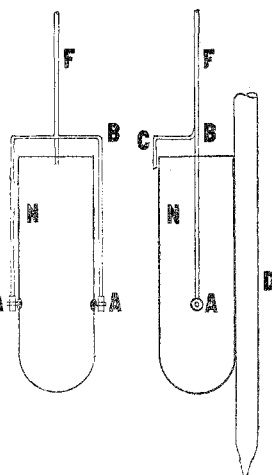


Fig. 3.—Dilution cup.
 Scale: 1 cm. = 2.5 cm.

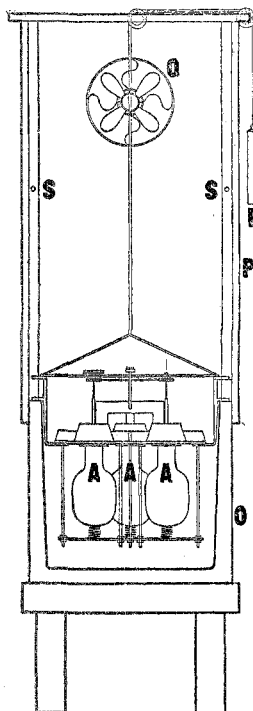


Fig. 4.—Twin calorimeters in constant temperature jacket.

Scale: 1 cm. = 20 cm.

and without stopping the stirrer L.

The calorimeter unit, consisting of the 3 calorimeters, their supporting framework and stirrers, were mounted in a constant temperature jacket, as shown in Fig. 4. This consisted essentially of one of the standard cast-iron water thermostats O 36" × 18" × 18", as used in this laboratory. This thermostat was well stirred, well lagged and kept constant to 0.01°. Above this was constructed a wooden thermostat, P, of 5/8" matched lumber. The air was stirred by means of an ordinary 8" desk fan, Q, was heated by means of lamps, and was regulated to 0.02° by means of a relay and a brass-rubber thermal regulator. The operation of the dilution cup was accomplished through small openings covered with canvas in larger doors which gave access to the calorimeter. The operating position of the calorimeter unit was as shown in Fig. 4. It was counterbalanced by means of the weight R and was raised vertically along the guides SS for convenience in assembling.

The main thermoelement D consisted of 50 junctions of No. 36 double silk covered copper wire soldered to No. 30 double silk covered constantan (Electrical Alloy Co. "Ideal") wire. The auxiliary consisted of 20 similar junctions. The

wire was carefully tested by the method of White.¹ The junctions were insulated by means of cellulose acetate, the couples bundled, and the wire held in place by wrapping the bundle with a single layer of silk binding tape. Seven No. 24 double, silk-covered, copper leads were brought out from the thermocouples and connected to non-thermo-electric binding posts² mounted on hard rubber. Four of the leads divided the main thermocouple into 2 independent 25-junction elements, a fifth divided one of the 25-junction elements into 10- and 15-junction elements, and the last 2 served the 20-junction auxiliary element. The

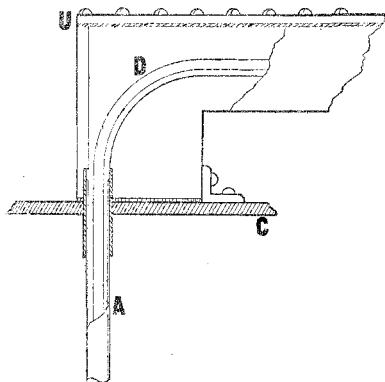


Fig. 5.—Detail of thermocouple mounting. Scale: 1 cm. = 2.5 cm.

thermoelements, after being bound and taped into shape, were placed in the brass trough-shaped mounting shown in Figs. 1 and 2, a detail of which is shown in Fig. 5. Thin glass protecting tubes partly filled with naphthalene at a temperature just above its melting point were put in position as shown. The trough and the remaining space in the glass tube were then completely filled with paraffin and the paper gasket and brass cover U put in place. The lead wires were then soldered to the copper binding posts, the copper tube and terminal box completely filled with paraffin, and the hard rubber block carrying the binding posts fastened in place. With a difference of temperature of 3° between Calorimeters 1 and 2 no observable electromotive force has ever been observed when the two 25-junction elements were opposed. In constructing the couple and in designing the mounting extreme care was taken to avoid making sharp bends in the wire or introducing strains due to bending the bundle. The use of silk tape in binding greatly facilitated the careful handling of the thermocouple. The satisfactory performance of our thermocouple is in large measure to be attributed to the careful observance of the above precautions and to the rigid mounting employed.

Our potentiometer has already been described.² The system was shielded as suggested by White.³ Parallel copper wires were supported on a wooden framework and soldered to the various units of the shield and to the main casting C C C of the calorimeter. Between these wires, glass tubes, the surfaces of which were heavily paraffined, were supported

¹ White, *THIS JOURNAL*, 36, 2292 (1914).

² Randall, Bichowsky and Rodebush, *ibid.*, 38, 1266 (1916).

³ White, *ibid.*, 36, 2011 (1914).

by means of wires running through the centers. The lead wires to the potentiometer from the thermocouples, standard cell, galvanometer, etc., were supported upon these paraffined glass rods. The shielding wire, ordinary No. 14 black, weatherproof, copper conductor, was not only an electrical shield, but also an effective mechanical guard and support.

Calibration of Thermocouples.—At the same time as our thermocouples were constructed, Dr. Rodebush, of this laboratory, made two 4-element thermocouples from the stock of wire which we had tested. One of these thermocouples was sent to the Bureau of Standards, where it was compared with their standard resistance thermometer. One end of the couple was placed in melting ice, and the other end in baths at various temperatures between -41° and 50° . Above 0° they found the relation between the electromotive force and the temperature to be given by the following equation with a probable accuracy of 0.005° to 0.01° :

$$E = 163.50t + 0.2030t^2 - 0.000245t^3 \quad (3)$$

Rodebush¹ found that his second 4-element thermocouple was identical with the first. Our 20-junction element was compared with the standardized 4-junction element and found to have an electromotive force exactly 5 times that of the 4-junction element within the limits of the Bureau of Standards equation. For this comparison large Dewar test-tubes were substituted for the Calorimeter Flasks 2 and 3 (Figs. 1 and 2).

The temperature of the water in a third Dewar test-tube which was substituted for Calorimeter No. 1, was kept at approximately 25° , the water in No. 2 was kept constant at approximately 24.5° and 26.5° , and No. 3 was filled with a mixture of ice and water. The temperature of the water in No. 1 was measured accurately by means of the 4-junction element, and that in No. 2 was measured by means of the 20-junction element. The e. m. f. readings of the 50-junction element were taken every minute, those of the 20- and 4-junction elements alternately on the half minute over a period of about 30 minutes, and these readings interpolated to common times.

The following table summarizes the averages of the results of the several series. The second column gives the average e. m. f.s of the 4-junction element, the third gives the averages of the temperatures of Tube 1 calculated from Equation 3, the fourth gives $1/5$ of the average e. m. f.s of the 20-junction element, the fifth the average temperatures of Tube 2, the sixth the average e. m. f.s of the 50-junction element divided by 12.5, the seventh the difference between the sum of the e. m. f.s in Cols. 4 and 6 and those in Col. 2, and the eighth the average value of $\Delta E/\Delta t$ for the 50-junction element as calculated from the individual values of E_{50} and the calculated temperatures of the two Dewar tubes.

¹ Rodebush, THIS JOURNAL, 40, 1204 (1918).

TABLE I.—MICROVOLTS PER DEGREE FOR THE 50-JUNCTION THERMOELEMENT.

Series.	E_4 M.m.v.	t	$E_{50} \times 0.2$ M.m.v.	t	$E_{50} \times 0.08$ M.m.v.	Difference. M.m.v.	$\Delta E_{50}/\Delta t$ M.m.v./deg
I.....	4182.1	24.84	3957.7	23.54	223.4	-1.0	2152
2.....	4187.7	24.97	4439.4	26.32	-250.2	+1.5	2152
3.....	4188.4	24.88	3942.8	23.46	244.9	-0.7	2152
4.....	4209.4	24.99	4480.4	26.55	-272.1	-1.1	2172
5.....	4208.2	24.99	4480.1	26.55	-272.6	-0.7	2174
6.....	4207.5	24.98	4478.9	26.55	-272.4	-1.0	2177
7.....	4188.5	24.86	4519.1	26.78	-331.5	-0.9	2155
8.....	4186.4	24.86	4520.3	26.79	-331.5	+2.4	2152
9.....	4188.8	24.88	4521.6	26.79	-331.2	+1.6	2160
10.....	4192.2	24.90	4526.3	26.82	-333.2	+0.9	2162
11.....	4203.8	24.96	4532.4	26.86	-328.8	-0.2	2171

It would have been very desirable to compare directly the 50-junction element with the standardized 4-element couple, but owing to its peculiar form of mounting we were unable to arrange it alongside the 50-junction element. The direct comparison of the 20-junction with the 4-junction thermoelement showed that these couples were identical. If the 50-junction thermoelement was also identical with the 4-junction thermoelement, the difference shown in Col. 7, Table I, should be zero, provided that the temperatures of the two sets of junctions in each vessel were identical. We will take as the final values for dE/dT those obtained by differentiating Equation 3, by which we obtain 2163 microvolts per degree at 24.5° , 2165 at 25° , and 2167 at 25.5° . These values agree, as would be expected, within the limits of experimental error, with those given in Col. 8 of Table I. Any small error in the value of dE/dT will affect the calorimetric determinations to a much smaller degree.

Heat Capacity of the Calorimeter.—The heat capacity of the calorimeter was determined in the following manner: A weighed amount of water was placed in the calorimeter flask and a constant current passed through a known resistance. The resistance consisted of a coil, of manganin¹ (Therlo) wire, whose resistance was determined by means of a Wheatstone bridge. The current was measured by means of the usual standard ohm coil and potentiometer, and the time (about 10 minutes) by means of a stopwatch. The quantity of water used was varied so that the level of the water corresponded with that used in the dilution experiments. The temperature of the jacket and twin calorimeters was 25° . The change of the e. m. f. of the 50-junction differential element was measured by means of the combination potentiometer. The usual initial and final periods were taken at half minute intervals. The rate of change

¹ This coil had a resistance of 1.951 ohms. It consisted of a coil of No. 26 Therlo wire wound upon mica and enclosed in a flat, copper case which was afterwards silver-plated. The specific heat of the mica (0.388 g.) was taken as 0.208, of the copper (5.75 g.) as 0.0917, and of the Therlo wire 0.098. The total heat capacity was 0.67 cal. per degree.

during these periods reached a very constant value which was not greater than $dE/dt = 1.1$ m.m.v. per minute. The results of these experiments are given in Table II. The first column gives the number of the vacuum bulb used, the second the weight of water used, the third the electrical energy added expressed in calories, the fourth the observed change in e. m. f., the fifth the temperature rise, the sixth the total heat capacity of the system, the seventh the heat capacity of the water and the heating coil, and the last the heat capacity of the calorimeter. All weights are reduced to vacuum, one calorie equals 4.182 joules, and the specific heat of the water at 25° was taken as 0.9978.

TABLE II.—HEAT CAPACITY OF VACUUM FLASK CALORIMETERS.

	Wt. of H ₂ O. G.	Energy added. Cal.	ΔE . M.m.v.	Δt .	C _p . System. Cal./deg.	C _p . Water + coil. Cal./deg.	C _p . Calorim- eter. Cal./deg.
L 1.....	800.8	522.0	1345.6	0.6209	840.6	799.2	41.4
L 1.....	800.8	487.5	1261.0	0.5819	837.8	799.2	38.6
L 1.....	800.8	540.4	1400.9	0.6465	835.9	799.2	36.7
L 2.....	800.8	593.9	1518.9	0.7009	847.3	799.2	48.1
L 2.....	800.8	704.2	1799.3	0.8303	848.2	799.2	49.0
L 2.....	600.6	677.9	2273.0	1.0489	646.3	600.0	46.3
L 2.....	600.6	650.8	2183.9	1.0078	645.7	600.0	45.7
L 2.....	900.9	682.7	1566.2	0.7229	944.6	899.7	44.9
L 2.....	900.9	653.0	1496.1	0.6904	945.9	899.7	46.2
L 2.....	900.9	668.8	1533.4	0.7076	945.2	899.7	45.5
L 2.....	800.8	42.86	109.66	0.05068	847.8	799.8	48.0
L 2.....	800.8	44.57	114.26	0.05272	846.6	799.8	46.8

The value for the heat capacity of flask L 1, together with that of the stirrer and thermocouple was taken as 38.9 calories per degree, that for L 2, etc., as 46.0 calories per degree. In the last two measurements only a very small current was passed through the heating resistance, and the temperature rise was very much smaller than in the preceding experiments. It was found that the heat capacity of the flask was, within the limits of experimental error, the same as that obtained in Expts. 3 to 10, in which the temperature rise was nearly one degree.

Specific Heat of Solutions of Sodium and Potassium Chlorides at 25°.—The experimental procedure used in determining the specific heats of these solutions was the same as that employed in determining the heat capacity of the calorimeter flasks, except that the solution was substituted for the pure water. The results are given in Tables III and IV. In each experiment 800.8 g. of solution was placed in calorimeter flask L 2. The first column gives the concentration, the second the energy added expressed in calories, the third the observed change in e. m. f. of the thermocouple, the fourth the temperature change, the fifth the total heat capacity of the system, the sixth the heat capacity of the solution, and the last the calculated specific heat of the solutions.

TABLE III.—SPECIFIC HEAT OF SOLUTIONS OF SODIUM CHLORIDE AT 25°.

M.	Energy added. Cal.	ΔE . M.m.v.	Δt .	C_p . System. Cal./deg.	C_p . Solution. Cal./deg.	Specific Heat. Cal./g./deg.
6.20	361.9	1169.6	0.5397	670.5	623.8	0.779
6.17	446.2	1433.8	0.6616	674.4	627.7	0.784
6.20	735.9	2372.5	1.0947	672.2	625.5	0.781
6.20	736.3	2366.5	1.0925	673.9	627.2	0.784
4.04	688.0	2112.1	0.9746	705.9	659.2	0.824
4.03	585.0	1800.9	0.8311	704.0	657.3	0.821

TABLE IV.—SPECIFIC HEAT OF SOLUTIONS OF POTASSIUM CHLORIDE AT 25°.

M.	Energy added. Cal.	ΔE . M.m.v.	Δt .	C_p . System. Cal./deg.	C_p . Solution. Cal./deg.	Specific Heat. Cal./g./deg.
4.85	655.3	2308.4	1.0655	615.1	568.4	0.710
4.84	618.4	2180.0	1.0060	614.7	568.0	0.710
4.84	715.2	2514.1	1.1602	616.5	569.8	0.712
2.72	723.0	2279.4	1.0517	687.4	640.7	0.801
2.73	724.3	2277.2	1.0508	689.2	642.5	0.803
2.73	703.5	2212.6	1.0210	689.0	642.3	0.803

The mean value of the specific heat in the above tables, together with the data obtained by Thomsen,¹ are given in Tables V and VI. The first column gives the observer, the second the concentrations, and the third the specific heat in terms of the 15° calorie.

TABLE V.—SPECIFIC HEAT OF SODIUM CHLORIDE SOLUTIONS AT 25°.

	Mols/1000 g. H ₂ O.	Sp. H.
R and B.....	6.20	0.782
T.....	5.55	0.791
R and B.....	4.04	0.822
T.....	2.78	0.863
T.....	1.85	0.895
T.....	1.11	0.931
T.....	0.555	0.962
T.....	0.278	0.978
	0.000	0.9978

TABLE VI.—SPECIFIC HEAT OF POTASSIUM CHLORIDE SOLUTIONS AT 25°.

	Mols/1000 g. H ₂ O.	Sp. H.
R and B.....	4.84	0.711
T.....	3.70	0.761
R and B.....	2.73	0.802
T.....	1.85	0.850
T.....	1.11	0.904
T.....	0.555	0.948
T.....	0.278	0.970

¹ Thomsen, "Thermochemistry," trans. by Burke, p. 162. Longmans, Green and Co., 1908. Thomsen's measurements were made between 18° and 20° and were expressed in 18° calories. His calorie was, therefore, smaller than the 15° calorie which we have used, and his results were 0.1% high. If we assume, however, that the specific heats of sodium and potassium chloride solutions decrease with an increase in temperature at the same rate as that at which water varies, then we must decrease Thomsen's values by 0.1%. The values given in his book are then approximately correct at 25°.

The measurements given in Tables V and VI have been plotted in Fig. 6. All the values fall upon smooth curves except the one for sodium chloride (2.78 M), at which concentration the value 0.860 appears to be the best value.

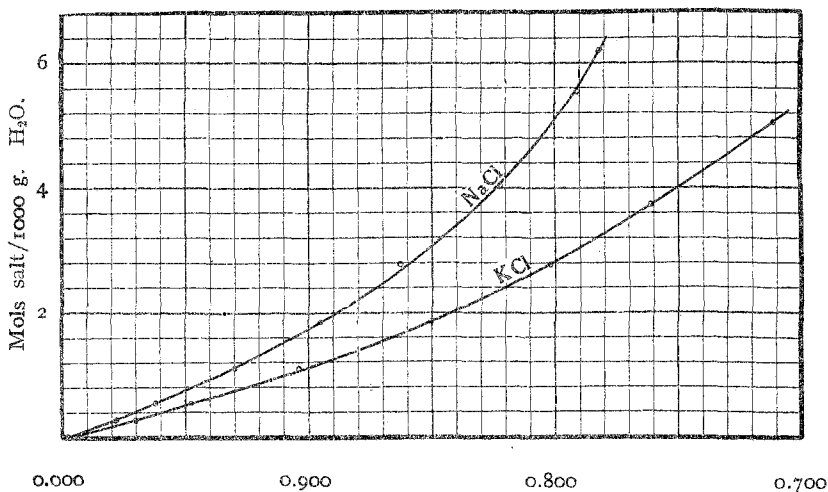


Fig. 6.—Specific heat of solution.

If, in calculating the change of the free energy of a reaction with the temperature, ΔH is not constant but is a function of the temperature, then we must know the difference between the heat capacities of the substances appearing in the reaction and those disappearing.¹ If one or more of the substances taking part in a reaction occur in solution, we must use not the heat capacity of the solution, or the heat capacity of the pure substances, but the heat capacity of the substance when in the solution at the given concentration. This quantity, \bar{c}_p , the partial molal heat capacity, is the increase in the heat capacity of a large amount of the solution at the given concentration when one mol of one of the constituents is added to it. If we attempt to evaluate the partial molal heat capacity of the constituents, using the values given in Tables V and VI, and using the method suggested by Lewis,² we find that the value of \bar{c}_p for sodium chloride and for potassium chloride in their dilute solutions is negative. It is zero near 1.5 M for sodium chloride and 2.5 M for potassium chloride, and is positive at greater concentrations. The above data are sufficiently accurate for the calculation of the results of our calorimetric measurements and for an approximate calculation of \bar{c}_p , especially in the more concentrated solutions.³

¹ See Lewis, *THIS JOURNAL*, 35, 1 (1913).

² Lewis, *loc. cit.*, p. 7.

³ The apparatus which we have described is, however, very well suited for the very accurate determination of the ratio of the specific heats of water and that of

The Partial Molal Heat of Solution of Water, $\bar{H} - H(H_2O)$, in Solutions of Sodium Chloride.—The measurement of the heat absorbed when water was added to solutions of sodium chloride was carried out as follows: The temperature of the room was adjusted to $24^\circ \pm 1^\circ$, and that of the air thermostat to $25^\circ \pm 0.02^\circ$. The solution and distilled water were brought to 25° in a water thermostat. The Calorimeter Flask 1 was removed from the air thermostat and the required amount of solution quickly weighed into it, and the flask replaced in the air thermostat. Water at 25° was likewise transferred to Calorimeter Flask 2. In some cases it proved convenient to introduce the water into Flask 2 at a temperature slightly less than 25° and to adjust it by means of a small heating coil which was left in the flask during the experiment. Distilled water at 25° was then transferred to the dilution cup (Fig. 3) by means of a calibrated pipet, delivering 24.92 g. of water in Expts. 1 to 52, and 24.96 g. of water in the remaining experiments. When not in use the pipet was kept in the air thermostat. The calorimeter was then assembled, lowered to its operating position, and the stirrers set in operation. The stirrers were allowed to operate for about 4 hours, at the end of which time, if the above precautions were properly observed, the e. m. f. of the 50-junction element would be between 0 and 10 microvolts, and its rate of change would not be greater than 0.5 mm. on the galvanometer scale, which corresponded to 0.05 m.m.v. per minute. In some cases this rate was as small as 0.001 m.m.v. per minute.

If the rate of change of e. m. f. was uniform, the rest point of the galvanometer was taken, then the usual initial period of about 8 minutes, after which the dilution was made as previously described. The rest point of the galvanometer was again determined, the readings of the e. m. f. continued at minute intervals until a constant rate of change of the e. m. f. was again reached, usually between 40 and 60 minutes, when the rest point of the galvanometer was again determined. The curve of the galvanometer deflection against time was then extrapolated to the time at which the dilution was made and the extrapolated value reduced to microvolts. As the greater part of the temperature change occurred during dilute solutions. For this purpose two heating coils of like resistance are connected in series and one of them placed in Calorimeter 1 and the other in Calorimeter 2. The difference in the heat capacities of the two calorimeters can be accurately measured by placing equal amounts of water in the two calorimeters, passing a known current for a given time through the heating coils, and measuring, by means of the 20-junction element, the total rise in temperature of Calorimeter 1, and, by means of the 50-junction thermoelement, the difference in the temperature changes of Calorimeters 1 and 2. In the measurement of the specific heats of the solutions, the water in one of the calorimeters is replaced by solution. From the data obtained in such measurements it should be possible to calculate the values which \bar{c}_p for NaCl and for KCl approach in dilute solutions.

the first 2 or 3 minutes, no large uncertainty in the method of extrapolation can exist.

The results of the experiments are given in Table VII. Col. 1 gives the number of the experiment, the second column gives the initial weight of the solution, the third the initial concentration, the fourth the final concentration, the fifth the specific heat of the final solution taken from the curve given in Fig. 6, the sixth the difference in the initial and final values of the e. m. f., extrapolated to the time of dilution, the seventh the corresponding change in temperature, the eighth the heat absorbed, and the ninth the heat absorbed per mol. of water added. Calorimeter flask L 1 was used in Expts. 1 to 11, and L 2 in Expts. 12 to 59.

TABLE VII.— $\bar{H}(\text{H}_2\text{O IN NaCl}) - \bar{H}(\text{H}_2\text{O})$ AT 25°.

No.	Wt. of solution. G.	M. Initial.	M. Final.	Sp. H. Final solution.	-- ΔE . M.m.v.	-- Δt . $\times 10^3$.	Heat absorbed. Cal.	Heat per mol. H_2O . Cal.	$\bar{H} - \bar{H}$. Cal.
1	790.7	6.12	5.97	0.784	53.62	24.76	16.81	12.15	11.5
2	790.7	5.97	5.74	0.788	59.90	28.39	19.35	13.98	12.9
3	790.7	5.74	5.54	0.791	76.44	35.30	24.15	17.46	...
4	790.7	4.63	4.47	0.811	99.66	46.01	32.22 ^a	22.20	21.8
5	790.7	4.47	4.31	0.815	99.94	46.12	32.43	23.43	23.1
6	790.7	4.31	4.12	0.820	102.43	47.28	33.46	24.18	...
7	790.7	3.99	3.84	0.827	89.98	41.56	29.63	21.42	21.5
8	790.7	3.84	3.69	0.831	97.30	44.94	32.20	23.27	...
9	790.7	3.69	3.54	0.836	91.33	42.18	30.40	21.99	...
10	790.7	3.46	3.35	0.842	78.09	36.80	26.18	18.94	19.4
11	790.7	3.35	3.24	0.845	74.52	34.41	25.05	18.13	...
12	780.7	3.24	3.13	0.848	77.45	35.77	26.08	18.86	19.3
13	780.7	3.13	3.01	0.852	72.91	33.67	24.66	17.84	18.2
14	780.7	3.01	2.90	0.855	69.23	31.99	23.50	16.99	17.3
15	780.7	2.90	2.80	0.858	66.21	30.58	22.54	16.30	16.5
16	780.7	2.80	2.70	0.862	63.88	29.51	21.84	15.80	16.0
17	780.7	2.70	2.60	0.866	61.88	28.60	21.26	15.39	15.5
18	780.7	2.60	2.51	0.869	60.22	27.82	20.76	15.02	...
19	780.7	2.06	1.99	0.889	41.08	18.97	14.45	10.46	10.6
20	780.7	1.50	1.45	0.913	22.83	10.54	8.24	5.96	6.0
21	780.7	1.45	1.40	0.916	22.75	10.50	8.24	5.96	...
22	780.7	0.944	0.912	0.942	10.41	4.81	3.86	2.79	2.8
23	780.7	0.882	0.858	0.944	11.29	5.21	4.20	3.03	3.0
24	780.7	0.425	0.412	0.970	2.00	0.92	0.76	0.55	0.55
25	780.7	3.09	3.00	0.836	72.28	33.38	24.00	17.34	17.7
26	780.7	3.00	2.91	0.838	69.54	32.13	23.15	16.78	...
27	780.7	1.95	1.87	0.891	37.07	17.12	13.07	9.45	9.6
28	780.7	1.87	1.82	0.897	35.68	16.47	12.66	9.16	9.3
29	950.8	6.25	6.00	0.784	42.04	19.43	15.76	11.40	10.9
30	950.8	6.01	5.79	0.785	46.49	21.47	17.44	12.82	12.0
31	950.8	5.99	5.79	0.786	47.93	22.15	18.00
32	950.8	5.79	5.60	0.789	54.36	25.10	20.49	14.82	13.9
33	950.8	5.60	5.40	0.793	61.48	28.40	23.29	16.85	16.3

^a A plot of Expts. 1 to 9 gave a value of 30.53 cal. for Expt. 4. This value was used in calculating heat/mol and $\bar{H} - \bar{H}$.

TABLE VII (continued).

No.	Wt. of solution. G.	M. Initial.	M. Final.	Sp. H. Final solution.	$-\Delta E$ M.m.v.	$-\Delta t \times 10^3$	Heat absorbed. Cal.	Heat per mol H ₂ O. Cal.	$\bar{H} - H$. Cal.
34	950.8	5.40	5.21	0.796	65.23	30.14	24.80	17.94	17.5
35	950.8	5.21	5.02	0.800	63.23	29.31	24.15 ^b	18.60	17.9
36	950.8	5.02	4.89	0.802	71.26	32.90	27.36	19.71	19.4
37	950.8	4.89	4.73	0.806	73.35	33.86	28.20	20.40	20.1
38	950.8	4.73	4.60	0.808	76.44	35.30	29.48	21.32	21.2
39	950.8	4.60	4.45	0.812	77.07	35.59	29.82	21.57	21.7
40	950.8	4.46	4.29	0.816	78.45	36.23	30.42	22.01	22.1
41	950.8	4.29	4.15	0.819	76.33	35.24	29.75 ^c	21.78	21.9
42	950.8	4.15	4.00	0.823	76.56	35.35	29.88	21.62	21.6
43	941.8	3.39	3.29	0.843	65.81	30.39	26.39	19.24	19.6
44	950.8	3.29	3.19	0.846	63.66	29.40	25.62	18.88	19.2
45	950.8	3.19	3.09	0.850	61.34	28.33	24.78	18.56	...
46	950.8	2.43	2.37	0.874	44.79	20.77	18.67	13.50	13.8
47	950.8	2.37	2.30	0.877	42.69	19.70	17.78	12.86	13.2
48	950.8	1.89	1.84	0.896	28.73	13.26	12.19	18.83	9.0
49	950.8	1.84	1.80	0.897	33.04	15.25	14.04
50	950.8	1.80	1.76	0.899	26.77	12.34	11.41	8.26	8.4
51	950.8	1.13	1.10	0.931	13.61	6.28	5.99	4.33	4.4
52	950.8	1.10	1.07	0.933	12.94	5.97	5.71	4.13	4.2
53	1000.9	4.31	4.18	0.818	71.06	32.83	28.45	20.40	21.1
54	1000.9	4.18	4.07	0.821	72.16	33.31	28.91	20.87	21.0
55	1000.9	4.07	3.94	0.825	71.63	33.08	28.81	20.80	21.0
56	950.8	3.94	3.82	0.828	73.54	33.97	28.25	20.40	20.6
57	950.8	3.82	3.70	0.831	72.33	33.39	27.93	20.16	...
58	950.8	3.70	3.57	0.835	72.00	33.23	27.90	20.15	...
59	950.8	3.57	3.44	0.839	65.39	30.20	25.47	18.38	...

^b From a plot 25.72 appears to be a more likely value.

^c From a plot 30.10 appears to be a more likely value.

The heat absorbed per mol of water added, given in Col. 9, is very nearly $\bar{H} - H$. However, the amount of water added is not infinitesimal as compared with the amount of solution. In most cases the final solution of an experiment was the initial solution of the succeeding one. In these cases, by combining the results of one experiment with those of the succeeding experiments and making corrections for the additional quantity of water needed to dilute the 25 g. of solution which was removed for analysis, etc., and the additional heat which would accompany this dilution, we obtain the amount of heat which would be absorbed when the original amount of solution was diluted with a little more than 50 g. of water. By combining these results once again with those of the next succeeding experiment, we obtain the quantity of heat absorbed when a little more than 75 g. of water is added to the original amount of the solution. If, then, the amount of heat per mol of water added is plotted as a function of the amount of water added,¹ we may extrapolate and find the

¹ MacInnes and Braham, THIS JOURNAL, 39, 2110 (1917).

value of $\bar{H} - H$ at the initial concentration of the first solution. If the variation of \bar{H} with the concentration is nearly linear over the concentration change considered, the extrapolation is quite satisfactory, otherwise the result is somewhat uncertain. The values of $\bar{H} - H$ are given in the last column of Table VII and are plotted in Fig. 7.

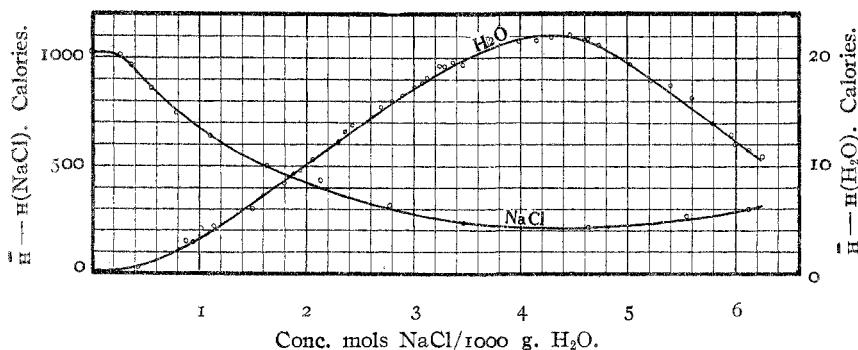


Fig. 7.—Partial molal heat of solution of the constituents in aqueous solutions of sodium chloride:

Besides the values given in this table, we also know that the partial molal heat content of the water will approach a constant value in dilute solutions, namely, the heat content of water. Thus $\bar{H} - H = 0$ at infinite dilution. The values gradually increase, reaching a maximum of about 21 calories at 4.2 *M*, and then decrease to a value of about 11 calories in a saturated solution. The shape of the curve will be discussed further in a later section.

Partial Molal Heat Content of Water in Solutions of Sodium Chloride.

—For liquid water Lewis and Randall¹ have used the value $\Delta H_{273^\circ} =$

TABLE VIII.—PARTIAL MOLAL HEAT CONTENT OF WATER IN AQUEOUS SOLUTIONS OF SODIUM CHLORIDE.

Conc. mol. per 1000 g. H ₂ O.	$\Delta H(\text{H}_2\text{O in NaCl aq.}),$ Cal.
0.00	—68,272
0.55	—68,271
0.8	—68,270
1.0	—68,269
1.4	—68,266
2.0	—68,262
2.5	—68,268
3.0	—68,255
3.5	—68,252
4.2	—68,250
4.8	—68,251
5.2	—68,254
5.8	—68,258
6.12	—68,261

¹ Lewis and Randall, *THIS JOURNAL*, 36, 1969 (1914).

—68470 cal. This corresponds at 25° to —68272 cal. Combining this value of ΔH_{298} with the values for $\bar{H} - H(H_2O)$ given in the last column of Table VII, we obtain the following values for the partial molal heat content of water in solutions of sodium chloride. The first column gives the concentration and the second the values of $\Delta H(H_2O \text{ in NaCl aq.})$.

Heat of Dilution of Solutions of Sodium Chloride.—The measurements of the heat absorbed when a small amount of saturated solution (6.12 *M*) of sodium chloride at 25° was added to 790.8 g. of water, contained in flask L 1, were made in the same manner as those described in the previous section. In Table IX the first column gives the final concentration of the solution as determined by analysis, the second the specific heat, the third the weight of saturated solution added, as calculated from the final analysis, the fourth $-\Delta E$, the fifth $-\Delta t$, the sixth the heat absorbed in calories, and the seventh the heat absorbed when a solution 6.12 *M*, containing one mol of sodium chloride is diluted to the final concentration, given in Col. 1. The mean of the last 4 measurements gives 606 calories.

TABLE IX.—HEAT OF DILUTION OF 6.12 *M* NaCl.

<i>M.</i> Final.	Sp. Heat. Cal./g./deg.	Wt. of solution added. G.	$-\Delta E$. M.m.v.	$-\Delta t$. $\times 10^3$.	Heat absorbed. Cal.	Heat/mol NaCl. Cal.
0.1792	0.986	29.47	212.14	97.90	82.50	621.3
0.1761	0.987	28.95	202.51	93.41	79.15	606.4
0.1856	0.9855	30.51	214.12	98.80	83.78	609.0
0.1844	0.985	30.31	210.94	96.93	82.10	600.8
0.1758	0.9865	28.92	202.46	93.40	79.10	607.0

The value obtained above may be compared with that derived by the following method from the values given in Table VII. The values of ΔH are plotted as ordinates and the concentrations, expressed as mols of water per mol of salt, as abscissas in Fig. 8. The heat Q absorbed when

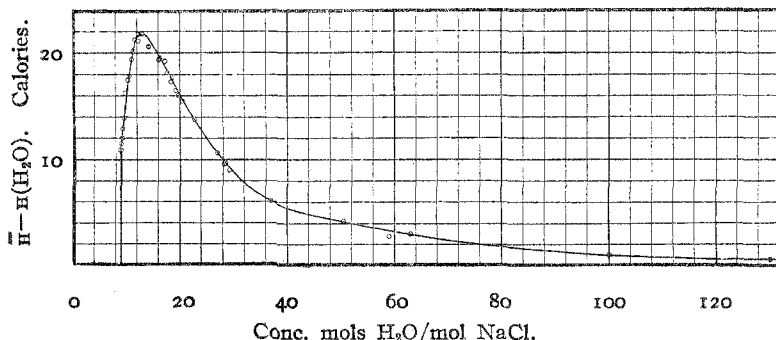


Fig. 8.—Partial molal heat of solution of water in aqueous solutions of sodium chloride.

$x_2 - x_1$ mols of water is added to a solution containing x_1 mols of water per mol of solute is given by the equation

$$Q = \int_{x_1}^{x_2} \bar{H} dx. \quad (4)$$

Now the value of this integral is the area under the curve (Fig. 8) between the concentration limits x_1 and x_2 , and the heat of dilution may be found directly by counting squares. The first column in Table X gives the upper concentration limit, mols H_2O /mol NaCl, the second the lower concentration limit, mols H_2O /mol NaCl, the third the same concentration expressed in mols NaCl per 1000 g. H_2O , the fourth the heat absorbed on the dilution of a solution containing one mol of sodium chloride from the upper to the lower concentration, and the fifth the heat absorbed when a solution, 6.12 M NaCl, containing one mol of sodium chloride is diluted to the concentration given in Col. 3.

TABLE X.—HEAT OF DILUTION OF SODIUM CHLORIDE SOLUTION.

x_2 Mols H_2O . Mols NaCl.	x_1 Mols H_2O . Mols NaCl.	M . Mols NaCl. 1000 g. H_2O .	Q . x_1 to x_2 . Cal./mol NaCl.	Q . 6.12 M to M . Cal./mol NaCl.
9.04	10.0	5.55	13.0	13.0
10.0	12.0	4.63	38.2	51.2
12.0	14.0	3.96	43.8	95.0
14.0	16.0	3.47	41.0	136.0
16.0	18.0	3.08	37.6	173.6
18.0	20.0	2.78	34.1	207.7
20.0	22.0	2.52	30.4	238.1
22.0	26.0	2.13	51.2	289.3
26.0	28.0	1.982	20.0	309.3
28.0	30.0	1.850	18.5	327.8
30.0	34.0	1.632	31.4	359.2
34.0	38.0	1.461	26.0	385.2
38.0	50.0	1.110	60.6	445.8
50.0	60.0	0.925	36.5	482.3
60.0	100.0	0.555	80.0	562.3
100.0	150.0	0.370	35.0	597.3
150.0	200.0	0.278	10.0	607.3
200.0	2.0	609.3

The further dilution of a 0.278 M solution of sodium chloride produces only a small heat effect. From a consideration of the probable value of $\bar{H} - \bar{H}$ for water in solution, as indicated by the curve in Fig. 7, we have estimated approximately 2 calories for the heat of dilution from 0.278 M to infinite dilution. The value for the heat of dilution of one mol of sodium chloride from 6.12 M to infinite dilution, namely 609 calories, agrees well within the limits of experimental error with 606 calories, the value given by Table VIII. For convenience in using Table X we will make two small adjustments, calling the heat of dilution from 60.0 to 100.0 mols equal to 77.7 cal., and that from 100.0 to 150.0 mols equal to 34.0 cal. We then have for the values for the heat of dilution of 6.12 M NaCl to 0.555 M , 560.0 cal.; to 0.370 M , 594 cal.; to 0.278 M , 604 cal.; and to infinite dilution, 606 cal.

Heat of Solution of Sodium Chloride.—The heat of solution of sodium chloride was determined by placing small amounts of pure dry sodium chloride in the dilution cup and adding it, as in the previous experiments, to 790.8 g. of pure water. Calorimeter Flask L 1 was used. The first column of Table XI gives the concentration of the final solution, the second the specific heat of the final solution, the third $-\Delta E$, the fourth $-\Delta t$, the fifth the heat absorbed in calories, the sixth the heat absorbed per mol of sodium chloride dissolved, and the last column the sum of the values in the sixth column and the heat absorbed when the solution is further diluted to infinite dilution.

TABLE XI.—HEAT OF SOLUTION OF SODIUM CHLORIDE AT 25°.

<i>M.</i> Final.	Sp. H. Cal./g./deg.	$-\Delta E$. M.m.v.	$-\Delta t$. $\times 10^3$.	Heat absorbed. Cal.	<i>Q</i> . Cal./mol NaCl.	<i>Q</i> in large amount of H ₂ O.
0.1266	0.9895	266.46	123.0	101.9	1018	1018
0.1297	0.9895	274.74	127.0	105.0	1024	1024
0.1277	0.9895	266.44	123.2	100.9	1009	1009
0.2667	0.9795	562.28	260.1	214.7	1018	1020
0.2597	0.9805	545.31	262.1	208.2	1014	1016
0.4601	0.9680	949.35	439.0	362.2	995	1021
0.5400	0.9630	1096.6	507.0	418.0	979	1023

The mean heat of solution of sodium chloride in a very large amount of water is 1019 calories per mol. Several attempts were made to dissolve larger amounts of solid sodium chloride in water in the calorimeter, and also to dissolve it in varying concentrations, but the temperature equilibrium was established very slowly. The results were erratic and of no value. The same results can, moreover, be directly obtained from the results already given in Table X and XI. The values for the heat of solution when one mol of sodium chloride is dissolved in enough pure water to form solutions of the various concentrations are given in Table XII and plotted in Fig. 9. The ordinates above the line $Q = 413$ cal.,

TABLE XII.—THE HEAT OF SOLUTION OF SODIUM CHLORIDE AT 25°.

<i>M.</i>	Mols H ₂ O/mol NaCl.	Heat of Solution. Cal./mols NaCl.	Heat of Solution. Cal./1000 g. H ₂ O.
6.12	9.04	413	2528
5.55	10.0	426	2364
4.63	12.0	464	2149
3.47	16.0	549	1905
2.78	20.0	621	1726
2.13	26.0	702	1495
1.632	34.0	772	1260
1.110	50.0	859	954
0.793	70.0	915	724
0.555	100.0	973	540
0.370	150.0	1007	372
0.278	200.0	1017	283
0.0	..	1019	0

which is the heat of solution to form 6.12 M solution (saturated solution 25°) represent the values of the heat of dilution given in Col. 5 of Table X. The first column of Table XII gives the concentration in mols of NaCl/1000 g. H₂O, the second the concentration in mols H₂O/mol NaCl, and the third the heat of solution per mol NaCl. The fourth column gives the heat absorbed when M mols of salt are dissolved in 1000 g. of water.

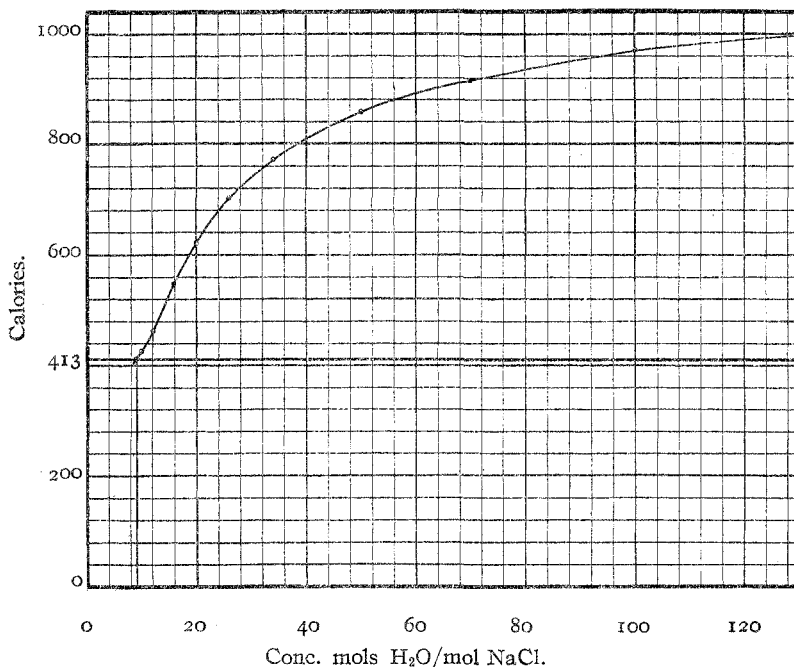


Fig. 9.—Heat of solution of sodium chloride in aqueous sodium chloride solution.

Partial Molal Heat of Solution and the Partial Molal Heat Content of Sodium Chloride in its Aqueous Solution.—The values given in the last column of the preceding table were plotted against the concentration expressed in mols NaCl per 1000 g. H₂O, and values dH/dM , or the partial molal heat content of the sodium chloride in the solution, were obtained by reading off the tangents of the curve at the various concentrations given in the first column of Table XIII. The second column gives the partial molal heat content of sodium chloride. Thomsen found for the heat content of sodium chloride at room temperature, -97690 cal., while Berthelot found -97900 cal. We will use the value $\Delta H(\text{NaCl}(s)) = -97800$ cal. The values of $\Delta H(\text{NaCl}, x \text{ mols})$ are given in the last column of Table XIII.

TABLE XIII.—THE PARTIAL MOLAL HEAT CONTENT OF NaCl IN ITS SOLUTION AT 25°.

$M.$	$\bar{H} - H(\text{NaCl}).$	$\Delta H(\text{NaCl}xM).$
6.12	300	-97,500
5.55	268	-97,532
4.63	216	-97,584
3.47	232	-97,578
2.78	314	-97,486
2.13	433	-97,367
1.632	503	-97,297
1.110	638	-97,162
0.793	746	-97,054
0.555	855	-96,945
0.370	965	-96,835
0.278	1010	-96,790
0.0	1019	-96,781

The Functional Relation between the Values of the Partial Molal Heat Content of the Water and of the Sodium Chloride in the Solutions.

—Having obtained the values of ΔH or $\bar{H} - H$ for both the solvent and the solute, we may now apply Equation 1 to these values. By the application of this equation we can make a careful scrutiny of the experimental results. It must be emphasized, however, that in applying the equation as has been done in this case, we have made use of not the individual values, but the average, which results in drawing a curve, more or less smooth, through these points.

In Table XIV the first column gives the concentration, the second the ratio of the mol fraction of solvent and solute, the third the rate of change of $\bar{H}(\text{H}_2\text{O})$ with the concentration, determined by reading the tangents to the curve in Fig. 7, the fourth the rate of change of $\bar{H}(\text{NaCl})$ with the concentration as calculated by means of Equation 1, and the last the value of this quantity as given by the tangents of the $\bar{H}(\text{NaCl})$ curve in Fig. 7.

TABLE XIV.—THE CHANGE OF THE PARTIAL MOLAL HEAT CONTENT OF THE CONSTITUENTS WITH THE CONCENTRATION.

$M.$	$\frac{N_1}{N_2}.$	$\frac{d\bar{H}(\text{H}_2\text{O}).}{dM}.$	$\frac{d\bar{H}(\text{NaCl}).}{dM}.$	
			Calculated.	Observed.
6.12	9.04	-8.6	78	56
5.55	10.0	-8.4	84	60
4.63	12.0	-3.5	42	50
3.47	16.0	4.6	-74	-36
2.78	20.0	6.7	-134	-160
2.13	26.0	7.8	-203	-175
1.632	34.0	6.9	-235	-200
1.110	50.0	6.0	-300	-305
0.793	70.0	6.0	-420	-450
0.555	100.0	4.6	-460	-560
0.370	150.0	2.5	-375	-475
0.270	200.0	1.4	-280	-230
0.0	..	0	0	0

An inspection of the curves in Fig. 7 will show that if the slope of one of the curves is negative, that of the other is positive. The agreement of the calculated and observed values of the rate of change of $\bar{H}(\text{NaCl})$ with concentration is probably within the limits of error of plotting. In a sense the two sets of experimental data used in calculating $\bar{H}(\text{H}_2\text{O})$ and $\bar{H}(\text{NaCl})$ are not entirely independent, for we integrated the values of $\bar{H}(\text{H}_2\text{O})$ and thus obtained values which were used, together with some independent data, to establish the curve which was differentiated graphically to obtain $\bar{H}(\text{NaCl})$. Several conclusions as to the shape of the $\bar{H}(\text{H}_2\text{O})$ concentration curve (Fig. 7) are, however, on the basis of Table XIV, probably justifiable. While the points upon this curve are the results of direct measurements, these experiments are exceedingly difficult and tedious, and despite the observance of very considerable precaution a sort of systematic error is likely to appear and not be found out for some time. The value of $\bar{H}(\text{H}_2\text{O})$, 0.55 cal., at approximately 0.4 M is probably too high. The slight bulge upward in the curve at approximately 3 M , which from the experiments appears to have experimental significance, probably should not exist. The shape near the maximum is rather uncertain, and the values interpolated from a curve in a region of this sort will depend upon the function of the concentration and upon the scale which has been chosen for the plot. In this connection the two curves shown in Figs. 7 and 8 are interesting.

We have not been able to compare our results with those of other investigators. Thomsen's experiments were made at about 18°. Brönsted's experiments were probably at about the same temperature. The temperature coefficient for these reactions is rather large and has not been determined with sufficient accuracy to make the results comparable. Thomsen made one or two experiments on the heat of dilution of sodium chloride at 25°, which agree roughly with ours. Rumelin, who added small amounts of water to concentrated sodium chloride solutions, made a few measurements at various temperatures near 14°.

It is hoped to continue the present investigation to include potassium chloride, hydrogen chloride and other simple substances, as well as substances which do not dissociate and those which dissociate into polyvalent ions. The investigation would include not only the determination of the partial molal heat content over the entire range of solubility, but also the partial molal heat capacities, the partial molal free energies, and a comparison of the free energy of dilution, as determined from freezing point and thermal measurements, with those obtained by means of e. m. f. measurements.