$SCSN_3$; rubidium azido-dithiocarbonate, $RbSCSN_3$; and cesium azido-dithiocarbonate, $CsSCSN_3$.

An outstanding characteristic of the rubidium and cesium salts is their extraordinary photosensitivity, in consequence of which they assume, respectively, on exposure to ordinary light, a light red or a violet-red tint, which gradually fades in the dark. It is suggested that this phenomenon may be attributed to the discharge of certain metallic and azido-dithiocarbonate ions, *in situ*, in the crystal lattice as a result of photolysis. Further work, looking toward the extension of this hypothesis to other cases of photosensitivity and radiosensitivity, is now in progress.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF MCGILL UNIVERSITY]

THE SURFACE ENERGY AND THE HEAT OF SOLUTION OF SOLID SODIUM CHLORIDE. I

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In this paper is described a new type of calorimeter which can be used with small quantities of material to determine directly the heat of solution from high to very low concentrations, with a high degree of accuracy in all cases. The calorimeter was applied to the determination of the heats of solution of sodium chloride over a wide range of concentrations. From determinations made with finely divided sodium chloride, the surface energy of solid sodium chloride was found.

The surface energy of solids is not susceptible of direct measurement, as in the case of liquids. A few investigators, by the use of indirect methods, have arrived at a partial solution of the problem and since an excellent summary of their work will be found in Freundlich's "Colloid and Capillary Chemistry"[1] it will not be repeated here.

In the present investigation, an attempt is made to determine the surface energy of solid sodium chloride by measurement of the difference between the heat of solution of ordinary crystalline sodium chloride and that of finely divided salt at the same concentration.

If sodium chloride be subdivided into cubes 1μ in diameter, an area of 1.6×10^6 sq. cm. per mole is produced. On solution, the energy associated with this surface should appear as heat and thereby produce a larger positive heat of solution than the coarsely ground solid. Since the heat of solution of ordinary sodium chloride is negative, this means that the heat of solution of the finely divided material should be numerically smaller. The experimental procedure adopted in this investigation is detailed in the following pages, but the result may be briefly indicated here.

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[1] Methuen and Co., Ltd., London, **1926**, pp. 102, 155.

The finely divided salt prepared was found to have a surface of about 1.25×10^6 sq. cm. per mole. Its heat of solution was found to be 12.3 cal. per mole less than that of the coarsely ground sodium chloride, from which the surface energy of solid sodium chloride is found to be about 400 ergs per sq. cm. The errors involved in these measurements are of necessity rather large, and this figure can be regarded as only approximate. It will serve to show, however, the practical applicability of this method to the determination of the surface energy of solids, for which experimental data, so far, are sadly lacking.

I

Description of Calorimeter. The Heat of Solution of Ordinary Sodium Chloride

Calorimetric Design.—A preliminary calculation had shown that the calorimeter to be used should be capable of giving results agreeing within 0.1%. The absolute accuracy was not so much in question, as the necessity of securing good comparative agreement. Owing to the difficulty in preparing large quantities of finely divided salt, it was found advantageous to construct a calorimeter of small capacity, so that determinations could be made using only 1 or 2 g. of salt and from 20 to 50 cc. of water.

A large source of error in calorimetric determinations is often due to heat transference to the environment and to heat losses due to evaporation. These effects, depending on the calorimeter surface, become correspondingly larger, the smaller the calorimeter; therefore, special attention was directed to their elimination.

Heat transference to the environment was rendered negligible by using an adiabatic method. For this purpose, the adiabatic control was not approximate but as exact as possible, so that the temperature of the calorimeter before and after solution of the salt could be kept absolutely constant for a fair length of time.

Since the temperature change in the experiments to be described was usually about 1°, it necessitated reading the temperature to 0.0001° if the desired accuracy were to be obtained. For this purpose, a platinum-resistance thermometer was used. Owing to its bulk and its uncertain heat capacity, this was placed, not in the calorimeter, but in the outer bath

A closed calorimeter was found to be the only type suitable for this work.[2] In a small calorimeter, a slight amount of evaporation produces a large temperature change, and if the calorimeter be open, evaporation does not cease when the surrounding air space is saturated with water vapor, even under close adiabatic control. The water vapor is continuously adsorbed on the walls of the surrounding jacket, forming thereon a layer of water possibly over 100 molecules thick.[2,3] This adsorption takes place

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

[3] McHaffie and Lenher, *J. Chem. Soc.*, **127**, 1559 (1925).

slowly, and in some preliminary experiments carried out by the authors it was found by no means complete after six hours. The temperature of the calorimeter, meanwhile, continued to fall, and with a small calorimeter containing 40 cc. of water the lowering experienced was about 0.001° per minute. This lowering of temperature, moreover, does not continue unchanged when the solution of the salt is caused to take place, since the temperature of the calorimeter and the jacket then suddenly drops about 1°, and a partial condensation of the saturated water vapor in the air gap between the calorimeter and jacket takes place. This condensation is accompanied by an evolution of heat, some of which is taken up by the calorimeter. Such erratic behavior may not be of serious consequence when using a large calorimeter, but when using a small one it leads to a fairly large error which cannot be accurately corrected for and can only be avoided by having the calorimeter hermetically sealed and the air in the air gap far from being saturated with water vapor.

In the mixing of the salt and water, it was deemed necessary to avoid any mechanism which might result in the admittance or escape of air from the calorimeter with a consequent possibility of the evaporation of a slight amount of water. In a calorimeter such as described here, having a heat capacity, when filled, of about 56 cal., the evaporation of even 1 mg. of water would cause a lowering of 0.01°. The same precaution was necessary in stirring the solution. At the same time, the stirring had to produce thorough mixing in a short space of time without the development of much heat due to friction. With this in mind a rotating calorimeter was devised. The salt and water were placed in separate compartments and mixed at the proper moment by rotating the calorimeter. The interior of the calorimeter was so designed that even with concentrations as high as 24%, only 15 minutes' rotation was required to effect complete solution and mixing, the heat developed by friction during this time causing a rise in temperature of about 0.0002° per minute.

In maintaining adiabatic control, some device is necessary to ascertain when the calorimeter and outer bath are at the same temperature. This is usually done by inserting one arm of a thermocouple into the calorimeter and the other into the outer bath. This is inconvenient when an hermetically sealed calorimeter is desired, and when the calorimeter is to be rotated the difficulties are multiplied. The method finally used is described in detail later, and consisted of a thermel placed *outside* of the calorimeter and not touching it. One of each pair of junctions was affixed to the outer jacket while the other faced the calorimeter at a distance of about 1 mm. and received its heat by radiation. This type of "radiation" thermocouple[4] was found to be very convenient and exceedingly sensitive.

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[4] Coblenz, *U. S. Bur. Standards Bull.*, **11**, 132 (1914).

The optimum size of the air gap between the calorimeter and jacket has been discussed by many investigators.[5] Barry,[2] from a series of experiments, concludes that the air gap should be from 10 to 40 mm. in width, the 40mm. gap being the most efficient. Owing to the relatively large heat capacity of the air in the gap, we were forced to cut down the size of the air gap as much as possible, consistent with the establishment of good thermal insulation. The gap finally used was 20 mm. The efficiency of the insulation was tested by rotating the calorimeter containing 50 cc. of water, with the outer bath 0.01° hotter than the calorimeter. The calorimeter was then found to heat at the rate of 0.0002° per minute after deducting the heat generated due to friction; since the surface of the calorimeter was 100 sq. cm., this amounted to an absorption of 0.01 cal. per minute per sq. cm. per 1° thermal head.[5a]

Description of Apparatus

The Calorimeter and Jacket.—The calorimeter constructed is shown in Fig. 1. It consisted of a cylinder of sterling silver 7.5 cm. in length and 4.2 cm. in diameter, having an internal capacity of 98 cc. The compartment (AA) in which the salt was placed had a capacity of about 35 cc. and ran almost the whole length of the calorimeter, with one edge B soldered with silver solder to the wall of the calorimeter, down its whole length. A piece of silver sheet C served to hold this inner box securely in position. The calorimeter had only one opening, so arranged with relation to the edge D of the inside box that both salt and water could be introduced into their respective compartments through the one opening. The salt compartment was thus surrounded on all sides (except the top) by water, which ensured having the salt and water at the same temperature. The opening was closed by a silver plug E, slightly tapered, which, coated with a thin film of vaseline and inserted with the help of pliers, gave a tight-fitting seal.

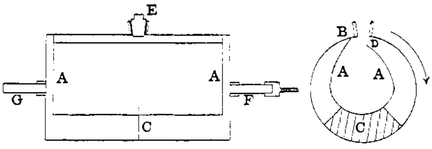

Fig. 1.—Calorimeter.

The arrow in Fig. 1 shows the direction of rotation. On each revolution, the salt was first thrown out of the inner box and then washed back again, thus producing thorough mixing. The rate of rotation was 13 r.p.m. This speed was found to cause only a slight heating and effected complete solution in about three or four minutes. In actual practice rotation was continued for a period of eight to 15 minutes depending on the amount of salt used.

F and G are small pieces of glass rod cemented with de Khotinsky cement into small silver tubes at each end of the calorimeter. Rod F was cemented into a piece of brass threaded at the end onto which the axle could be screwed, while Rod G was supported in a slot cut in a copper projection (A, Fig. 2) from the outer casing.

The outer jacket (B, Fig. 2) was of copper, 1 mm. thick, cylindrical in shape and coaxial with the calorimeter. Its length was 11.5 cm. and its diameter 8 cm. This jacket was made in two portions separating in a horizontal plane. Both halves were provided with a flange, which was vaselined and by which they could be clamped to-

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[5] (a) Richards and Tamaru, THIS JOURNAL, **44**, 1060 (1922). (b) White, *Phys. Rev.*, **7**, 682 (1916).

gether. Tube C leads from the jacket to the outside and through it was passed the axle, a copper rod, 4 mm. in diameter, which fitted snugly. To prevent heat conduction along the axle from the outside, a piece of bakelite 1 cm. long was inserted in the axle, 1 cm. from the inside end. The axle passed through a rigid support D, and was rotated by a pulley wheel E.

In assembling the apparatus, the calorimeter was inserted from above, the axle pushed in and screwed on, and then the upper half of the jacket was placed on and clamped down.

The Thermel (Multiple Thermo-elements).—The radiation thermel was constructed of copper and constantan wires about 0.02 mm. diameter. The wires were rolled out flat until they were about 0.8 mm. wide and 0.03 mm. thick and the junctions were soldered together using the smallest amount of solder possible. To increase the sensitivity, 11 pairs of junctions, in series, were employed. The junctions were soldered together in a straight line so that the 11 pairs of thermo-elements, before installation in the calorimeter, formed a straight length of wire made up of alternate copper and constantan segments. This length was arranged spirally inside the jacket (F, Fig. 2), one set of alternate junctions being in contact with the wall of the jacket, while the other set faced the calorimeter at a distance of about 1 mm. The upper junctions were held in place by passing over two very fine, parallel glass rods (not shown in diagram), about 1 cm. apart, which extended the length of the jacket. The upper part of each couple where it faced the calorimeter was thus horizontal, with the copper-constantan joint midway between the two glass rods, the length of this horizontal portion, of course, being 1 cm. The top of this 1 cm. length was coated with a mixture of platinum black and lampblack[4] to aid in its absorption of heat from the calorimeter. The junctions in contact with the jacket were electrically insulated from it with the thinnest plates of mica, and secured in place by means of shellac. The wires were also coated with shellac to avoid corrosion.

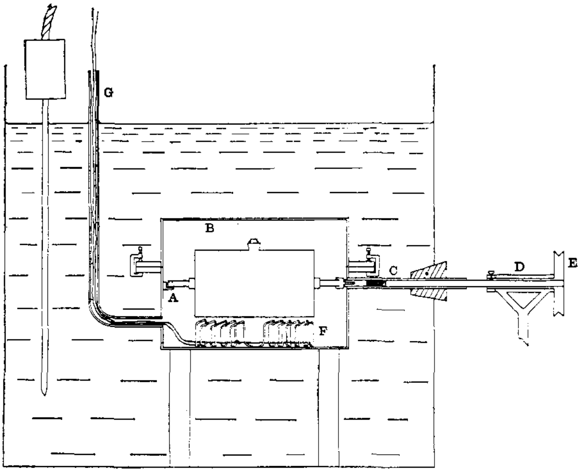

Fig. 2.—Adiabatic calorimeter.

The lead wires from the galvanometer entered through the brass tube G, and were soldered to the two ends of the spiral thermel. The lead wires were encased in rubber tubes in their passage down Tube G, and were insulated with mica from the walls of the inner part of the jacket. Any space remaining in Tube G was filled with paraffin.

When the calorimeter and jacket were at the same temperature, no deflection was given by the galvanometer, but the slightest change in the temperature of the calorimeter was immediately shown by change in temperature of the blackened junctions, and a deflection occurred. Lag on the part of the thermel was reduced to a minimum by the use of very thin wires whereby the amount of heat conducted away from the blackened junctions along the wires was much less than the amount of radiant heat absorbed by them, and in addition, this reduced the heat capacity of the junctions so that a small absorption of heat resulted in a large change in temperature. This, of course, was aided by flattening the wires so that as large a surface as possible was exposed to the radiating body. The use of very thin wires also ensured keeping the temperature of the blackened junctions as near as possible to that of the calorimeter.

The sensitivity of the 11-junction radiation thermel, so constructed, was such that a temperature difference of 0.0001° between the calorimeter and jacket produced a deflection of 1 mm. on the scale.

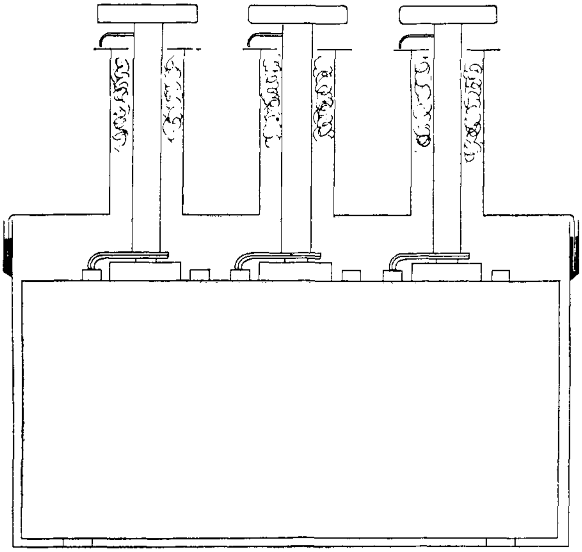

Fig. 3.—Bridge enclosed in box for immersion.

The Outer Bath.—The calorimeter and jacket were situated in a large porcelain crock holding about 15 liters of water, which was stirred effectively by four double-bladed stirrers. The temperature of the water was varied by running in hot or cold water, as required, from reservoirs. A fine drip of either hot or cold water was also provided, which could be adjusted to counterbalance the natural radiation to the room. The temperature of the calorimeter was found by adjusting the outer bath to the same temperature as the calorimeter and then obtaining the temperature of the outer bath by means of a platinum-resistance thermometer inserted in it. With care it was found possible to bring the outer bath to within 0.0001° of the temperature of the calorimeter and to keep it there long enough to read its temperature to 0.0001°.

Resistance Thermometer and Bridge.—The platinum-resistance thermometer and bridge were obtained from the Leeds and Northrup Company. The thermometer is described by Dickinson and Mueller.[6] Its resistance at 25° was about 27 ohms and the change in resistance was approximately 0.1 ohm per 1°. Its resistance was measured

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[6] Dickinson and Mueller, *U. S. Bur. Standards Bull.*, 3, 641 (1907).

by use of a five-dial bridge of the Mueller type,[7] reading directly to 0.0001 ohm and capable of being estimated to 0.00001 ohm. A deflection of 1 mm. on the scale corresponded to 0.00001 ohm. This bridge was placed in a specially constructed copper box (Fig. 3), the lid of which fitted into a mercury seal and was immersed in a thermostat kept at 25°. The copper box was previously painted and varnished. The dials of the box were operated by means of long handles projecting up through chimneys as shown.

The Galvanometer and Wiring.—The galvanometer was a Leeds and Northrup instrument Type 2285A, having a sensitivity of 10 mm. per microvolt at a distance of 1 meter, and a coil resistance of 12 ohms. The scale used was situated at a distance of 2 meters from the galvanometer. The galvanometer was enclosed in a metal case which was in turn enclosed in a wooden box, the space between being packed with wool to prevent thermo-electric effects. The connecting wires (double silk covered), in their passage overhead, were supported on glass rods heavily coated with paraffin, and to protect them still further from electrical leaks they were passed through paraffined glass tubes, about 10 cm. in length, each time they crossed a supporting rod. All switches used were of the clothes-pin "anti-thermo-electric" type.[8] Drift of zero point and erratic movements of the galvanometer were eliminated by insulation of the wiring, by insulation of batteries, switches, etc., by grounding of all stirrers and motors, and by shielding the different portions of the system with an equipotential shield according to White.[9]

Calibration of Resistance Thermometer.—Since the resistance thermometer was used only over a range of one or two degrees, it was calibrated over a range from 22° to 29° by direct comparison with a Beckmann thermometer standardized by the U. S. Bureau of Standards.

The determinations of the heat of solution of sodium chloride were carried out at 25° and, owing to the large temperature coefficient of the heat of reaction, it was thought desirable to establish this point within 0.01°. This was conveniently done by using the solubility of sodium sulfate as a thermometric standard.[10] We have taken as 25.00°, the temperature at which the solubility of $Na_2SO_4.10H_2O$ is 27.795 g. of anhydrous sodium sulfate per 100 g. of water. At this temperature, the resistance of the platinum-resistance thermometer was 27.8586 ohms.

Purification of Sodium Chloride

The sodium chloride used was Merck's C. P. and was recrystallized four times from water and finally dried by heating in quantities of about 100 g. in porcelain dishes, over a strong Bunsen flame. The salt was not fused since it was noticed that pure sodium chloride fused in open dishes became alkaline.[11] The salt heated as described gave no alkaline reaction towards phenolphthalein and was found to contain no moisture.

Procedure

The calorimeter was carefully dried and weighed. The salt and water were introduced successively and their weights found. All weighings were corrected to the vacuum standard. The calorimeter was sealed and placed

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[7] Mueller, *U. S. Bur. Standards. Bull.*, **13**, 547 (1916).

[8] White, THIS JOURNAL, **36**, 1856 (1914).

[9] Ref. 8, p. 2011.

[10] Richards and Yngve, *ibid.*, **40**, 164 (1918).

[11] (a) English and Turner, *Proc. Chem. Soc.*, **30**, 162 (1914). (b) Lange and Dürr, *Z. Elektrochem.*, **32**, 85 (1926).

in position inside the jacket, the top of the jacket was clamped on and the outer bath filled with water. The temperature difference between the calorimeter and the outer bath was now ascertained by means of the radiation thermel. Since a difference of several degrees often occurred, a resistance of 10,000 ohms was placed in the thermel circuit. The radiation thermel was thus found to give a fairly accurate estimate of temperature differences even as large as 5°. The calorimeter and contents had now to be brought to a temperature of 25°. If the temperature of the calorimeter originally was, say 23°, the outer bath was raised to about 28° and kept at that temperature. The calorimeter then slowly warmed up, and its rise in temperature was followed continuously by means of the thermel until, after about 45 minutes, it had reached 25°. The outer bath was now brought back to the same temperature as the calorimeter and the resistance removed from the thermel circuit. In this manner, the calorimeter and contents were brought to within 0.1° of 25°. A deviation from 25° larger than 0.1° would have introduced an unnecessarily large correction and was therefore avoided.

The fine drip of hot or cold water into the outer bath was now adjusted to maintain the temperature of the outer bath as close as possible to that of the calorimeter. Additional regulation was accomplished by adding a drop of hot or cold water, by means of a stopcock, as required. Since the temperature difference between the calorimeter and the outer bath was then kept usually less than 0.0001° and was never allowed to exceed 0.0005°, the control was truly adiabatic, and in several experiments the calorimeter and contents were kept for a period of an hour without undergoing a change in temperature greater than 0.0001°. This enabled the initial (and the final) temperature of the calorimeter to be measured with great certainty, since an almost indefinite length of time could be spent in the readings with the knowledge that no change in temperature was occurring. As a rule, readings were continued until four consecutive observations checked to 0.0001°.

After obtaining the initial temperature, the calorimeter was rotated for a definite length of time, usually ten minutes. The salt then dissolved and a rapid fall in temperature took place. The adiabatic control was maintained as closely as possible during this drop. At the right time, the rotation was stopped and the temperature of the calorimeter determined.

To determine the heat generated by friction during the rotation, the calorimeter was rotated again for an equal length of time and the rise in temperature found.

The Specific Heats of Sodium Chloride Solutions, Etc.

The values used for the specific heats of the sodium chloride solutions (Table I) were obtained by comparison of results by Bousfield and Bousfield,[12] and by Richards and Rowe.[13] The calorie used throughout this work is the 18° calorie. Its value as given by the "International Critical Tables,"[14] that is, 1 cal. at 18° = 4.1825 joules, has been used in converting Bousfield's results, which were expressed in joules, into calories. Bousfield gave the specific heats at 7°, 20° and 33°. From these results the temperature coefficients of the specific heats were estimated and the specific heats calculated for 25°. Richards and Rowe's values were given for an average temperature of 18° and were also recalculated to 25°.

The specific heat of the sterling silver constituting the calorimeter was taken as 0.0581. The reason for choosing this value will be shown later.

The specific heat of water at 25° was taken as 0.9989, accepting the value for the 25° calorie as 4.178 joules as given by the "International Critical Tables."

Corrections

In using a calorimeter as small as the one described here, several factors which ordinarily are too small to be of any account, come into prominence. The heat capacity of the thermel and its supports was too small to be taken into account, but the several other corrections which were found necessary are listed below.

1. **Heat Capacity of the Air in the Air Gap.**[15]—The quantity of air in the gap between the calorimeter and jacket was large enough to necessitate taking its heat capacity into account. When the calorimeter and outer jacket cooled down simultaneously, heat from the air was given to both. As an approximation, it was assumed that each absorbed an amount of heat proportional to the surface exposed. The volume of air in this air gap was 470 cc. The surface of the calorimeter was 99 sq. cm. and that of the jacket was 390 sq. cm. The heat capacity of the air which was effective in heating the calorimeter was thus found to be 0.029 cal.

2. **Heat Capacity of the Glass Parts.**—The total weight of the glass parts was 0.54 g. Taking the specific heat of glass as 0.18 and assuming that one half of the glass gave its heat to the calorimeter and the other half to the jacket, the effective heat capacity resulted as 0.049 cal.

3. **Heat Capacity of the Air Inside the Calorimeter.**—The amount of air inside the calorimeter differed in the various determinations, amounting to from 40 to 70 cc. Its heat capacity was found to range from 0.010 to 0.014 cal.

4. **Condensation of Water Vapor Inside the Calorimeter.**—The air

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[12] Bousfield and Bousfield, *Phil. Trans. Roy. Soc. (London)*, **218**, 119 (1919).

[13] Richards and Rowe, This Journal, **43**, 770 (1921).

[14] Compiled by the National Research Council of U. S. A., **1926**, p. 18.

[15] The heat capacity of the air in the air gap, plus that of the glass parts, was actually determined experimentally as is shown later, but the corrections are given here for the sake of completeness.

inside the calorimeter was saturated with water vapor. After the solution of the salt, the water vapor diminished in quantity, due to the lowering of the vapor pressure, first because of the diminution in temperature, and second because of the solution of the salt in the water. This correction was surprisingly large, amounting to from 0.1 to 0.4% of the total heat change in the different experiments. The correction for this was calculated, however, with a fair degree of accuracy.

5. **Heat Developed by Rotation.**—This correction was determined for each experiment as described previously. The correction was usually about 0.2% of the total heat change and any error in its determination was negligible.

6. **Correction for Initial Temperature.**—The initial temperature of the calorimeter and contents differed slightly from 25°, though by never more than 0.1°. The temperature coefficient of the reaction was calculated in the well-known manner from the difference in the heat capacities of the product and the reactants, and the experimental results were then corrected to an initial temperature of 25°. For this purpose the specific heat of solid sodium chloride was taken as 0.208.[16]

7. **Correction for Concentration.**—In carrying out duplicate experiments, it was impossible to obtain exactly the same concentration in each case. For purposes of comparison, therefore, a correction was applied to the second determination to bring it to the same concentration as the first. This correction was always small and was easily found from the slope of the curve obtained by plotting heat of solution against concentration.

Experimental Results

The values obtained are given in Table I.

In Col. 2 of Table I is given the volume of water in which the salt was dissolved, and in Col. 3 the average specific heat of the solution over the temperature range concerned, which in the most concentrated solution was only 1.9°. The values for the specific heats and the heats of solution are expressed in the 18° calorie.

When the heat of solution is plotted against the concentration (Fig. 4), the curve in the dilute region is not found to follow the direction of the main portion of the curve, as assumed by many other investigators,[17] but exhibits a maximum at a concentration of about 1%. This was noticed by Thomsen,[18] who obtained a positive heat of dilution of 3 cal. per mole, when a 1.59% solution of sodium chloride was diluted to 0.80% at a temperature of 25°.

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[16] Russell, *Physik. Z.*, **13**, 59 (1912).

[17] (a) Randall and Bisson, THIS JOURNAL, **42**, 347 (1920). (b) Wüst and Lange, *Z. physik. Chem.*, **116**, 161 (1925).

[18] Thomsen, "Thermochemistry," Longmans, Green and Co., London, **1908**, p. 178.

TABLE I

HEATS OF SOLUTION OF SODIUM CHLORIDE AT 25°

Concn., g. of NaCl per 100 g. of soln.	Volume of H_2O used, cc.	Spec. ht. of soln., cal.	Heat of soln. per mole NaCl, cal.
0.3984	50	0.9939	1005
.3984	50	...	1002
.9953	50	.9867	1015
1.3831	50	.9820	1006
1.9631	50	.9751	998
1.9631	50	...	1002
3.0892	50	.9619	970.6
5.6700	50	.9338	895.8
5.6700	25	...	895.9
5.6700	25	...	896.6
5.6700	25	...	894.8
8.0855	25	.9104	819.4
10.732	50	.8862	736.5
10.732	50	...	737.9
10.732	25	...	737.5
13.799	25	.8596	651.5
16.431	25	.8391	586.3
19.372	25	.8192	524.3
19.372	25	...	524.9
24.321	25	.7910	457.5

The accuracy of these results varies with the concentration of the solution. For the range of concentrations from 3 to 24%, divergence from a mean value was rarely greater than 0.1%, while for more dilute solutions the deviation was necessarily larger.

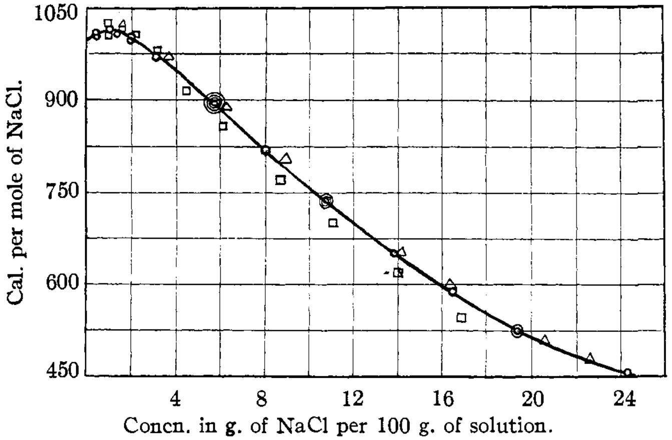

Fig. 4.—Heat of solution of sodium chloride. The circles represent values obtained by the authors; two or more concentric circles indicate points too close together to be individually distinguishable; the squares are values obtained by Randall and Bisson; the triangles are values due to Wüst and Lange.

The absolute accuracy of the results is limited, not by the various corrections which were applied, since these were all of small magnitude, but by the values used for the specific heats of the solutions and of the calorimeter. The possible error due to these factors might be estimated as 0.3%. The manner in which the heat capacity of the calorimeter was derived will now be shown.

Heat Capacity of the Calorimeter

Several determinations of the heat of solution of a 5.67% solution were carried out. In some of these 3 g. of salt was dissolved in 25 cc. of water and in others, 6 g. of salt in 50 cc. of water. The heat of solution per mole of sodium chloride should be the same in both cases. Assuming this, and knowing the specific heat of the solution, it was possible to calculate the heat capacity of the calorimeter plus all its adjuncts. This heat capacity can be calculated to an accuracy of 1%, if the determinations themselves are accurate to 0.1%. Using the values obtained for the 5.67% solutions, the heat capacity of the calorimeter plus its glass parts, plus the heat capacity of the air in the air gap was, by this means, found to be 6.296 cal., and this value was used, subsequently, in calculating the molal heats of solution for the other concentrations. It will be noticed that the results obtained for a 10.732% solution, using either 25 or 50 cc. of water, are in close agreement. The heat capacity of the glass parts, as shown before, was 0.049 cal., while the effective heat capacity of the air in the air gap was found to be 0.029 cal. Deducting these from 6.296, the heat capacity of the calorimeter itself (which weighed 107.17 g.) was found to be 6.218 cal., and from this, its specific heat results as 0.0581. The calorimeter was constructed of British sterling silver, whose composition approximates very closely 924 parts of silver to 76 parts of copper. Taking the specific heat of pure silver to be 0.0561,[19] and that of copper to be 0.0917[20] at 25°, and assuming that the heat capacities of both are unchanged in the alloy, the specific heat of sterling silver, thus calculated, amounts to 0.0588. This value differs by 1.2% from the value we obtained above. The law of mixtures, however, is not perfect, and the results obtained by arithmetical calculation may differ from the specific heats obtained practically by as much as 2%.[21] Hence, it is justifiable to use the value 0.0581, obtained experimentally.

Comparison of Results with Those of Other Observers

For a 3.147% solution Thomsen[22] obtained 1177 cal. per mole as the heat of solution at 17.75°. The temperature coefficient of the heat of solution

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[19] Griffiths and Griffiths, *Phil. Trans. Roy. Soc. (London)*, **214**, 319 (1914).

[20] Harper, *U. S. Bur. Standards Bull.*, **11**, 260 (1914).

[21] Giua, "Chemical Combination Among Metals," J. and A. Churchill, London, **1918.** Schimpff, *Z. physik. Chem.*, **71**, 257 (1910).

[22] Thomsen, *J. prakt. Chem.*, **16**, 323 (1877).

for this particular concentration was found experimentally by Berthelot and Ilosvay[23] to be 29.5 cal. per mole per degree. Thomsen's value recalculated to 25° then gives 964 cal.; Berthelot and Ilosvay gave 1080 cal. as the heat of solution for the same concentration at 21°, which gives 962 cal. at 25°. The value found by us was 968 cal. In extrapolating over several degrees, in calculations such as these, large errors may be introduced owing to the uncertain values of the temperature coefficient.

Randall and Bisson,[17a] working at 25°, obtained results which are, in the main, from 3 to 4% lower than our values, except in the dilute region, where there is better agreement, while Wüst and Lange,[17b] also at 25°, obtained values about 1% higher than ours (Fig. 4). A later paper by Lange and Dürr,[11b] indicates that their first results should be reduced by 3 cal. per mole.

The heats of dilution of an 11.5% solution have been determined accurately by Richards and Rowe[13] at 20°. In Table II these heats of dilution have been recalculated to 25°, using the temperature coefficient of the reaction as determined by Richards, corrected by a small amount for variation of this temperature coefficient with temperature. This correction was deduced from a knowledge of the variation of the specific heats of water and of sodium chloride solutions with temperature.[12]

Table II

Heats of Dilution of 11.5% Solution of NaCl at 25°

Concn. of soln. after dilution, g. of NaCl per 100 g. of soln.	Heat of dilution in cal. per mole of NaCl Richards and Rowe	Wüst and Lange[a]	The authors[c]
6.099	169	167	167
3.147	254	254	254
1.60	296	298	293
0.89	300	320[b]	298

[a] Ref. 17 b.

[b] This large value is due to these authors assuming the curve in the dilute region to be a simple continuation of the curve in the more concentrated region.

[c] The values in the fourth column are simply the differences between the heats of solution at the two concentrations concerned.

II

The Heat of Solution of Finely Divided Sodium Chloride

Preparation of the Finely Divided Salt.—The salt was prepared by subliming pure, dry sodium chloride in a platinum retort of about 200 cc. capacity (Fig. 5). Air, dried by passing successively through calcium chloride, potassium hydroxide, sulfuric acid, phosphorus pentoxide and glass wool, was blown into the retort through a Pyrex tube, and carried the salt vapors along a platinum tube and through two large bottles, the first of 1 liter and the second of 3 liters' capacity. The larger particles

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[23] Berthelot and Ilosvay, *Ann. chim. phys.*, **29**, 301 (1883).

settled out in the tube and in the bottles when the current of air, regulated to a constant pressure, was adjusted so as just to carry over the finest particles into the settling box. This box was about 75 cm. long, 20 cm. wide and 20 cm. high and its top was detachable. After about eight hours the salt was scraped from the glass bottom of the settling box, yielding about 1.5 g.

Some preliminary experiments were made by blowing air over sodium chloride heated in a platinum boat in a long silica tube. The salt so obtained was found not to be pure and the silica tube was noticeably attacked by the sodium chloride vapors.[24]

Before being used, the finely divided salt was heated at 120° for several hours to remove possible traces of absorbed water.

Purity of the Salt.—The finely divided salt, on solution in water, gave a neutral reaction to both methyl orange and phenolphthalein. Analysis showed the salt to be quite dry as collected. The best test of the absence of chemical impurity was furnished by taking the solution obtained after a determination of the heat of solution had been made with the fine salt, evaporating this solution to dryness, drying the residue by heating over a low Bunsen flame (but not to the melting point) and determining the heat of solution of this salt in the usual manner. The results agreed with those ordinarily obtained with coarsely ground sodium chloride.

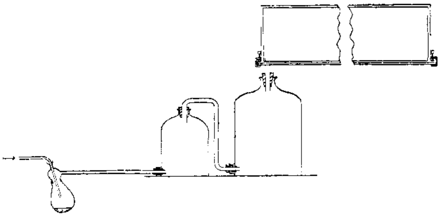

Fig. 5.—Apparatus for the preparation of finely divided sodium chloride.

Measurement of Size.—Microscope slides were introduced from time to time into the settling chamber and removed after a slight deposit of salt had fallen on them. The particles were at first measured directly under the microscope at 1000 magnification, using a micrometer eyepiece. Later a photomicrographical method, as described by Green,[25] was used. α-Bromonaphthalene, dried over sodium, was found to be a suitable immersion medium for the salt.

These measurements showed the finely divided salt to have a total area of about 1.25×10^6 sq. cm. per mole, which corresponds to an average diameter per particle of approximately 1.3μ.

With particles as small as these, the error in measurement may be relatively large. This is indeed the most uncertain factor in this investigation in the determination of the surface energy of solid sodium chloride.

Heat of Solution of Finely Divided Salt.—The heat of solution of

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[24] Clews and Thompson, *J. Chem. Soc.*, **121**, 1442 (1922).

[25] Green, *J. Franklin Inst.*, **192**, 638 (1921).

finely divided salt was determined in the same manner as that of the coarse salt. About 1.5 g. of salt and 25 cc. of water were used, giving in all cases a 5.67% solution. The results obtained in different experiments were 893.5, 892, 892.5, 892.5 cal. per mole compared with 895.8 cal. per mole found as the mean value for coarsely ground salt. The difference, although distinct, was not very large.

The question then arose as to the effect of water vapor on the salt while it was in the calorimeter during the period preceding its solution. An interval of one and a half to two hours usually elapsed between the introduction of water into the calorimeter and the measurement of the initial temperature of the calorimeter and contents. After that length of time, the temperature of the calorimeter was found to remain practically constant, but the possibility still remained that some heat effect had occurred within the first two hours.

Effect of Water Vapor on the Finely Divided Salt.—About 1 g. of the salt, in a weighing bottle, was placed in a space saturated with water vapor at room temperature (about 20°). The salt absorbed 0.0010 g. of water in 20 minutes. In 40 minutes it had absorbed 0.0014 g.; in one hour, 0.0019 g.; in two hours, 0.0030 g.; in five hours, 0.0069 g. The finely divided salt was at the commencement very bulky, 1 g. occupying a volume of about 8 cc. This volume is indicated by the top horizontal line in Fig. 6. The absorption of water vapor was marked by a striking contraction in volume, the mass gradually shrinking away from the walls of the vessel. Its appearance at various times is indicated by the outlines in the diagram.

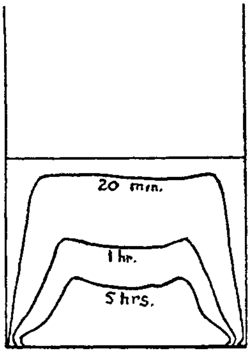

Fig. 6.

The salt was examined microscopically at various intervals during this absorption of water, and it was found that marked increase in the size of the particles took place. Whereas, originally, the salt consisted of innumerable small particles of diameter approximately 1μ, with an occasional large particle, after 30 minutes the number of small particles was greatly reduced and the main bulk of the salt seemed to be made up of particles from 4 to 10μ in diameter. At the end of two hours, the effect was still more pronounced, although the greatest change took place in the first half hour. This may be ascribed to the greater solubility of the small particles, which dissolved in the water absorbed, and recrystallized as larger particles. A few milligrams of water will thus act catalytically in transforming a large mass of finely divided salt into salt of much coarser subdivision.

The nature of the container was found not to influence the speed of agglomeration to any noticeable extent since the same effect was found to result whether the salt was placed in vessels of paraffin, beeswax, silver, platinum or in a dish coated with fused sodium chloride.

Absorption of water vapor is not restricted to finely divided salt since coarsely ground sodium chloride was found to absorb water almost at the same rate per gram, when placed in a space saturated with water vapor. This is not to be unexpected, for a film of water would condense on any solid placed in saturated water vapor.[26] If, as in the case of sodium chloride, the solid were soluble in water, the saturated solution so formed would continuously absorb water vapor, since its water vapor pressure would be less than that of pure water. Theoretically, the absorption of water would then keep on indefinitely.

In exposure to the air in the room, neither the finely divided salt nor the coarse salt was found to absorb any weighable amount of water in an hour, and no change in the appearance of the former was seen. Clearly, then, this absorption takes place only when the humidity is very close to saturation.

The effect of this absorption on the previous results must now be considered. In the case of the coarse salt, practically no error is introduced thereby. In the one or two hours preceding its solution, the salt would absorb only a few milligrams of water per g. Even assuming as an extreme case that the salt absorbed 1% of its weight of water, this would form a saturated solution, thereby dissolving 0.35% of the salt. The saturated solution so formed would still give a cooling effect on dilution equal to half of that normally given by the dry salt, so that the final error would be 0.17%. In practice, however, the error might be estimated as one-third of this.

In the case of the finely divided salt, water absorption introduces a serious error. It means that when the salt is placed in the calorimeter over the water, it immediately starts to agglomerate, and by the time the temperature control has been properly adjusted and the initial temperature taken, the specific surface of the salt has been enormously reduced. The salt, however, appears at this point to be finely divided enough to give a heat of solution 3.3 cal. per mole less than that of coarse salt.

Heat Effect on Absorption of Water Vapor.—The following experiments were carried out to determine whether the coalescence of the fine salt under the influence of moisture was accompanied by any heat change. The method used was not precise, but it indicated the magnitude of the effect.

An adiabatic calorimeter was again used (Fig. 7). A silver calorimeter A was closed by a lid which fitted into a vaseline seal. It rested on three glass points inside a copper jacket B whose lid was fastened by clamps in the usual manner to a flange at the top of the jacket. A single junction

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[26] Lenher, *J. Chem. Soc.*, **129,** 1785 (1926).

radiation thermocouple C, similar in construction to the thermel described before, enabled the adiabatic control to be kept within 0.001°.

The finely divided salt was placed in a small copper container D provided with a lid which was also fitted into a vaseline seal. This seal was perfectly air tight. Before being placed in the calorimeter, vessel D, containing 1.2 g. of the salt, was allowed to stand overnight in a desiccator over phosphorus pentoxide with its lid off. The lid was then pressed on while it was still in the desiccator, so that the vessel was filled with dry air. It was then placed in the calorimeter and fastened down securely. Five cc. of water was then run into the calorimeter. By means of a wire E, the lid of the salt vessel could be opened at any time and the water vapor allowed to come in contact with the salt. The wire passed through a small hole in the lid of the calorimeter and then through a layer of vaseline F, which served as a seal.

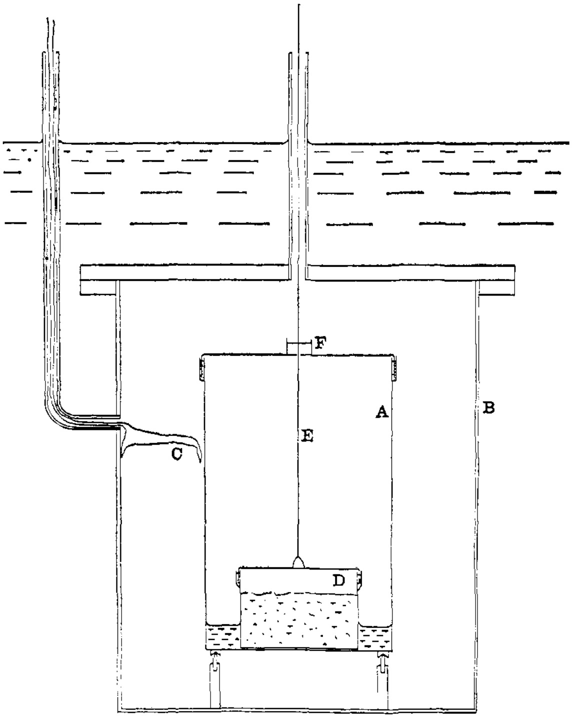

Fig. 7.—Adiabatic calorimeter.

The calorimeter was first brought to 25°, the adiabatic control adjusted, the temperature of the calorimeter read by means of a Beckmann thermometer placed in the outer bath, and then the lid of the salt vessel was pulled up. At first, there was a fall in temperature due to evaporation of water vapor into the dry air of the inner vessel. This reached its maximum at the end of one and a half minutes, when the temperature had fallen 0.004°. The temperature then began to rise suddenly and continued rising for 11 minutes, after which it remained constant for 70 minutes. At this point the experiment was terminated. It is a rather surprising fact that the entire heat change took place within 11 minutes with no observable change after that time. The difference between the initial and final temperatures was 0.0085°. To find the lowering of temperature due to the evaporation a blank experiment was carried out following the same procedure but without using any salt. The temperature dropped 0.0055°. The total heat change due to the 1.2 g. of salt was, therefore, $0.0085 + 0.0055° = 0.014°$. The calorimeter and contents had a heat capacity of approximately 14 cal. Calculation then showed that the evolution of heat occurring when the finely divided salt was placed in a space saturated with water vapor amounted to 9 cal. per mole.

If this had been included in the heat of solution as previously determined, then the negative heat of solution of fine salt would have been 883.5 cal. instead of 892.5. The difference between the heat of solution of the fine and the coarse salt is thus seen to be approximately 12.3 cal., of which the main portion is not found in the measurements of the heat of solution, over which much time was spent, but in these final experiments. The first experiments serve to give us, however, the value of the heat of solution of the finely divided salt after it has been in contact with water vapor and has changed its structure. By a combination of both series of experiments we are thus able to trace the heat changes produced by the salt from the moment it first meets the water vapor to the time it has gone completely into solution.

Surface Energy of Solid Sodium Chloride.—A mole of sodium chloride, having a total surface of 1.25×10^6 sq. cm., thus has an amount of energy equivalent to 12.3 cal. bound up in its surface, from which the surface energy of solid sodium chloride at 25° is found to be 400 ergs per sq. cm. Owing to the large errors involved in the determination, this value can be only approximate.

It is hoped, in future work, to construct a calorimeter of a similar type in which the salt will not be exposed to the water vapor, and to improve the method of preparing and measuring the salt particles so that greater accuracy will result.

Acknowledgment is made to the National Research Council of Canada for a grant to aid in this research and also for a studentship held by one of us, during the tenure of which the work was carried out.

Summary

1. Factors influencing precision in calorimetric work are discussed briefly.

2. A new type of adiabatic calorimeter is described which can be used with small quantities of material in determining directly the heat of solution from large to very small concentrations, with high accuracy in all cases. In its construction a new type of thermel is used, which does not touch the calorimeter but receives its heat by radiation.

3. Heats of solution of coarsely crystalline sodium chloride are determined at 25° over a range of concentrations from 0.4 to 24.3%. A maximum value is found at 1% concentration.

4. Preparation and measurement of finely divided sodium chloride are described. The heat of solution of this material is determined and, from the results, the surface energy of solid sodium chloride is calculated.

5. The effect of saturated water vapor on the finely divided salt is described and measured.

MONTREAL, CANADA

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

THE SOLUBILITIES OF SOME RARE-EARTH OXALATES[1]

BY LANDON A. SARVER AND PAUL H. M.-P. BRINTON

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Introduction

Perhaps the most characteristic reaction of the rare-earth elements is the precipitability of their oxalates in faintly acid solution. However, a survey of the existing literature on the subject showed that it was scattered, fragmentary and somewhat contradictory, so it was decided to determine the solubilities of as many of the rare-earth oxalates as could be obtained in a sufficiently pure condition.

Early references[2] to the insolubility of the rare-earth oxalates were of a qualitative nature, the first really quantitative contribution being by Brauner,[3] who determined the solubilities of lanthanum, cerium, praseodymium, neodymium and yttrium oxalates at 20° in ammonium oxalate solution of one concentration, and in normal sulfuric acid. Schéele[4] determined the solubilities of praseodymium and lanthanum oxalates in two concentrations of nitric acid. Benedicks[5] found values for gadolinium oxalate in ammonium oxalate and in sulfuric acid of the same concentra-

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[1] From a thesis submitted to the Graduate Faculty of the University of Minnesota, by Landon A. Sarver, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Vauquelin, *Ann. chim.*, **50**, 140 (1804). Berzelius and D'Hisinger, *ibid.*, **50**, 245 (1804). Mosander, *Ann. chim. phys.*, [3] **11**, 464 (1844). Marignac, *Ann.*, **88**, 232 (1853). Clève and Hoeglund, *Bull. soc. chim.*, **18**, 289 (1872).

[3] Brauner, *J. Chem. Soc.*, **73**, 951 (1898).

[4] Schéele, *Ber.*, **32**, 409 (1899).

[5] Benedicks, *Z. anorg. Chem.*, **22**, 393 (1900).