[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MCGILL UNIVERSITY]

A NEW TYPE OF ROTATING ADIABATIC CALORIMETER. THE SURFACE ENERGY AND HEAT OF SOLUTION OF SODIUM CHLORIDE. II

BY S. G. LIPSETT, F. M. G. JOHNSON, AND O. MAASS

RECEIVED MAY 6, 1927 PUBLISHED AUGUST 5, 1927

In a previous paper[1] a method was described for determining the surface energy of a solid by measurement of the difference between the heat of solution of the solid in a coarsely crystalline and in a finely divided condition. The calorimeter used for this purpose had a rather serious defect in that the salt was exposed to the action of water vapor before solution was effected. A modified form of this calorimeter was therefore constructed, in which this defect was remedied; and in this paper an account of the work done with this calorimeter will be described. The heat of solution of finely divided sodium chloride has been again determined, this time directly; the results substantiate those obtained before. The area of the finely divided salt has been measured with more precision by the use of two different methods, and a more accurate value for the surface energy of solid sodium chloride thereby attained. With this calorimeter the heat of solution of the coarsely crystalline sodium chloride has been determined at 20° over the whole range of concentrations. Comparative agreement between duplicate experiments was obtained to better than 0.05% for concentrations above 10%. The heats of solution at 25° determined in the previous paper were corroborated, and from the temperature coefficient of the heats of solution the specific heats of sodium chloride solutions were calculated with high accuracy.

The main features of the former calorimetric apparatus are embodied in the present form and their description will not be repeated here. For a complete description of the apparatus, method of procedure, the precautions and corrections necessary, etc., the reader is referred to the first paper. The silver calorimeter vessel was, however, completely remodeled, and its description follows.

Description of Calorimeter

The calorimeter (Fig. 1) was a rotating type, cylindrical in shape and of the same exterior dimensions as the previously used calorimeter, so that it could be substituted in place of the old calorimeter and used with the same copper jacket, radiation thermel and axle as before. It differed in this respect, that the salt was placed in a separate receptacle which was covered by a lid so that the salt was protected from water vapor. For proper manipulation it was found necessary to be able to remove

---

[1] Lipsett, Johnson and Maass, THIS JOURNAL, 49, 925 (1927).

this receptacle from the calorimeter and for this purpose one end of the calorimeter was made removable.

As before, the calorimeter was constructed of sterling silver sheet. The open end of the calorimeter was flanged with a rim A of silver 3 mm. thick. This was closed by a disk of silver sheet B, which carried the supporting axle. A stout ring of brass C was made to press the silver disk tightly against the flange by means of ten brass screws running into the flange. The flange was previously coated with a thin film of vaseline. This gave a water-tight seal which was never found to give trouble and which allowed the easy introduction and removal of the box, D, which contained the salt. This box is shown separately in Fig. 1, c and d as it appears when removed from the body of the calorimeter. To enable it to be inserted into the calorimeter without jarring, and to hold it in position once inserted, a "runway" was constructed inside the calorimeter. This was made of the same material as the rest of the calorimeter but is shaded in the diagram to differentiate it from the box. It consisted of two silver bars, E, soldered at each end to vertical pieces of silver sheet, which were in turn soldered to the wall of the calorimeter. The vertical sheet near the closed end of the calorimeter contained a slot into which fitted a projection F from one end of the box, while the other vertical sheet bore a small threaded rod which fitted into a hole in a projection G at the other end of the box. A small nut on the threaded rod served to hold the box in position. The top of the box was flanged and ground plane. A single piece of silver, 62 × 11 × 1.7 mm., ground plane on one side, served as a lid. On rotating the calorimeter, the lid fell off and solution of the salt took place as before. To give an air-tight seal between the lid and the box, the flange of the box was coated with Glycoline. A film of vaseline, although preferable as a seal, caused the lid to adhere so strongly that it did not fall off on rotation. Even with glycoline, a lighter lid did not fall off on rotation.

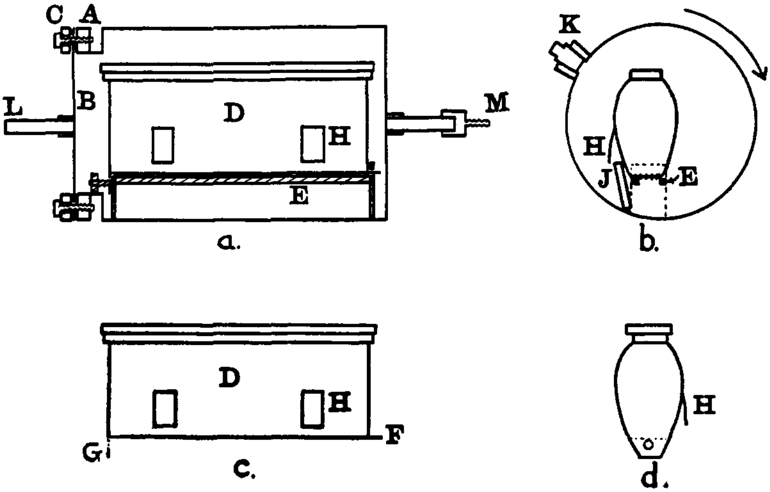

Fig. 1.

It was found that if the lid were left free to slide about at random in the box during rotation, a rather large amount of heat was generated by friction, enough to cause a rise in the temperature of the calorimeter, containing 50 cc. of water, of about 0.0005° per minute. Small projections H were, therefore, soldered to the box, which trapped the lid after the first revolution of the calorimeter and prevented it from moving about subsequently. The direction of rotation is indicated by the arrow in the diagram and the position of the trapped lid is shown at J. The lid, when so caught, acted as a baffle plate and caused more efficient mixing during the rotation, with the development by friction of only one-third of the heat generated when the lid was free to move about.

It will be noticed that the box is situated a little to one side in the calorimeter. This enabled a large quantity of water to wash in and out of the box on each revolution, thus increasing the speed of mixing.

The opening, K, for the water was so placed that there was no risk of wetting the lid of the box when the water was introduced. A silver plug closed this opening, as before.[1] The supporting axles, L and M, were constructed similarly to those in the previous calorimeter.

Other Parts of the Apparatus

Only one change was made in the remainder of the apparatus. This consisted in the addition of a small tube from the copper jacket to the atmosphere, which enabled the air in the space between the calorimeter and the surrounding jacket to be kept at atmospheric pressure. Previously, the only tubes leading from the jacket to the outside were the tube containing the thermel lead wires and the tube through which the axle passed. The former was impervious to the passage of air since it had been filled with paraffin wax. The latter was found to be air-tight when the calorimeter was at rest, the vaseline used as lubricant acting as a seal, but on rotation the movement of the axle apparently offered means for the slow passage of air. This affected the calorimetric determinations in the following way. The temperature of the room might be, say 15° when the calorimeter was put in position and the outer jacket clamped on. If the calorimeter were later warmed to 25°, the air enclosed in the air gap would exert a pressure slightly higher than atmospheric but would not be able to expand. When the calorimeter was rotated, however, it would be able to escape and its expansion would produce a cooling effect. To prevent this, the air in the air gap was, therefore, opened to the atmosphere after the calorimeter had been brought to the temperature at which the run was to be made.

Procedure

A weighed quantity of salt was put into the box, the flange of the box was covered with a film of glycoline, and the box and contents were then allowed to stand in a desiccator over phosphorus pentoxide for two hours. The lid was put on the box while it was still enclosed in the desiccator, so that the box was filled with perfectly dry air. The box was then slipped into the calorimeter, the flange of the calorimeter was coated with vaseline, the end screwed on and a weighed amount of water run in. The procedure then followed the same course as described for the previous calorimeter.

Corrections

The corrections applied were the same as those used previously, with two additions. A correction was made for the heat capacity of the glycoline and the vaseline. The amounts of these substances used were practically the same in all the experiments, namely, 0.016 g. of glycoline and 0.035 g. of vaseline for which a total heat capacity was estimated of 0.02 cal.

The other correction necessary was due to the evaporation of water vapor into the dry air of the box when the lid fell off on rotation. This correction became large when only a small amount of salt was present in the box and was one of the chief reasons for making the box as small as possible. As a check on this correction, a blank run was carried out without using any salt, but filling the box with dry air as in the regular procedure and using 50 cc. of water in the calorimeter. On rotation a cooling effect was observed which, after allowing for heat generated by friction, amounted to 0.0030°. The theoretical lowering, as calculated, was 0.0029°.

The specific heat of the brass (64% copper, 36% zinc) used for parts of the calorimeter was taken as 0.0907 at 25°.[2] The weight of the brass parts was 20.39 g. The total weight of the sterling silver which made up the calorimeter was 133.94 g. Its specific heat was taken as 0.0581, as before.

Heats of Dilution.—It is obvious that this type of calorimeter can be used in determining heats of dilution as well as heats of solution. To illustrate this, some determinations were carried out with very dilute solutions of sodium chloride.

At 25°, 8.2 cc. of a 1.0% solution was placed in the small box and 41.3 cc. of water outside. On dilution, a rise in temperature of 0.0016° was obtained, of which 0.0011° was due to heat generated by friction during the rotation, leaving 0.0005° as the rise in temperature due to the reaction itself. To show the accuracy possible in measuring such small changes in temperature, the rise in temperature due to rotation was determined three times in this experiment, giving the values 0.0012, 0.0010 and 0.0011°.

Other heats of dilution were determined at 20°.

Comparison with Previous Results.—As a check on the apparatus and the previous work, some of the former determinations were repeated. Two runs were made with coarse salt at 25°. For a final concentration of 5.670%, the heat of solution was found to be —896.3 cal. per mole, as compared with —895.8 cal. found before. For a 4.620% solution, —928.1 cal. per mole was obtained as compared with —927.6 obtained previously. To substantiate the maximum in the heat of solution curve at 1%, a 1% solution was diluted to 0.166% and as was expected heat was evolved on dilution, giving +23 cal. per mole as the heat of dilution. As was just shown, the change in temperature on this dilution is very small and the

---

[2] Doerinckel and Werner, *Z. anorg. allgem. Chem.*, **115**, 1 (1921).

error in this heat of dilution may be 8 cal. per mole. In the previous work the heat of solution for a 1% solution was found to be —1015 cal. per mole, which gives —992 cal. per mole as the heat of solution for a 0.166% solution.

A determination was also made with some of the finely divided sublimed salt which had been used in the previous work. Its heat of solution was found to be 12.1 cal. per mole less than that of the coarse salt. The indirect measurements used previously gave a difference of 12.3 cal.

Heats of Solution of Sodium Chloride at 20°.—The results obtained for the heats of solution of sodium chloride at 20° are given in Table I.

TABLE I

HEATS OF SOLUTION OF SODIUM CHLORIDE AT 20°

Concn., g. of NaCl per 100 g. of soln.	Sp. ht. of soln. at 20°, cal.	Wt. of H_2O used, g.	Approx. drop in temp., °C.	Heat of soln. per mole of NaCl, cal.
0.22	0.996			—1162
1.200	.9842	50	0.20	1158
1.200		50	.20	1152
4.620	.9438	41	.70	1042.8
4.620		41	.70	1043.6
8.085	.9092	50	1.17	915.5
8.085		50	1.17	914.6
10.732	.8850	50	1.41	819.3
10.732		50	1.41	818.9
13.946	.8572	50	1.65	710.7
13.946		50	1.65	710.9
19.540	.8173	50	1.90	560.2
19.540		50	1.90	560.0
25.791	.7838	32	2.00	460.8
25.791		32	2.00	460.6

The specific heats in Col. 2 were obtained from the same sources as in the previous paper. The calorie used throughout this paper is the 18° calorie and is taken equivalent to 4.1825 joules. Col. 3 gives the weight of water in which the salt was dissolved. The value for the 0.22% solution was obtained by diluting a 1.20% solution to 0.22%. For concentrations above 10%, the agreement between duplicate experiments is better than 0.05%, while for more dilute solutions, the agreement is of necessity not so exact.

The Specific Heats of Sodium Chloride Solutions.—The specific heat of a solution can be calculated very accurately from a knowledge of the temperature coefficient of the heat of solution, provided the specific heats of the pure solute and solvent are known. This is a direct application of the well-known Kirchhoff's Law, namely,

$$C - C^1 = (U^1 - U)/\Delta\theta \qquad (1)$$

In this equation U represents the heat of reaction at $\theta°$, U^1, the heat of reaction at $(\theta + \Delta\theta°)$, and C and C^1 represent the mean molal heat capacities, respectively, of the reacting substances and of the products between the temperatures Θ and $(\Theta + \Delta\Theta)$.

In the present case, this equation may be written in the following form.

$$C_A + C_B - C_S = \Delta U/5 \tag{2}$$

C_A is the heat capacity of one mole of sodium chloride solid at 22.5°; C_B is the heat capacity at 22.5° of the water in which it is dissolved, and C_S is the total heat capacity of the resulting solution, also at 22.5°. ΔU is the difference between the molal heats of solution at 25 and 20°.

The value for ΔU (disregarding all previous values used for the specific heats of sodium chloride solutions) may be expressed in terms of C_S and the actual experimental data obtained in determining the heats of solution at the two temperatures concerned. Knowing the values of C_A and C_B, the equation may be solved for C_S and the specific heat of solution thereby obtained. The details of such a calculation will not be given here since this method of obtaining specific heats has been described in detail by Richards and Rowe,[3] who determined the specific heats of solutions from the temperature coefficient of the heats of dilution.

This calculation, although quite straightforward, is somewhat tedious in execution and the procedure, in the present case, was considerably simplified by obtaining the values for ΔU directly by difference from the heats of solution at 25 and 20° as already determined in this work. Although the calculation of these heats of solution involved the use of specific heats of the solutions as available in the literature, yet it will be seen that a fairly large error (say 0.3%) in these specific heats, although leading to an equal error (0.3%) in the heats of solution at 25 and 20° and thereby producing the same error in the value of ΔU, will finally lead to a much smaller error (less than 0.01%) in the specific heat of the solution then calculated according to Equation 2. If the calculated specific heat, thus found, differs by more than 0.3% from the value in the literature, the former may then be used to recalculate ΔU, and this, in turn, will give a more accurate value for the specific heat. In the present case, the values for the specific heats of sodium chloride solutions in the literature were found to be sufficiently accurate for the purpose, and the values of ΔU obtained by their use were used to calculate C_S. The mode of calculation is illustrated by the following example.

The specific heat of a 4.62% solution was taken as 0.9444 at 22.5°.[3b] The molal heat of solution of sodium chloride at this concentration was found to be —928.1 cal. at 25°, and —1043.2 cal. at 20°. Substituting in Equation 2, the following result is obtained.

$$(0.208)(58.45) + (0.9993)(1206.7) - C_S = (1043.2 - 928.1)/5$$

or

$$12.16 + 1205.86 - C_S = 23.02$$

whence

$$C_S = 1195.0$$

---

[3] (a) Richards and Rowe, THIS JOURNAL, **42**, 1621 (1920); (b) **43**, 770 (1921).

The first term represents the specific heat of solid sodium chloride at 22.5° multiplied by its molecular weight. It will be seen that an error of 1% in this heat capacity would lead, in this instance, to an error of only 0.01% in the value of C_S. The second term represents the specific heat of water at 22.5° multiplied by the weight of water in which the mole of salt was dissolved. This term is by far the largest of the three which result in the value of C_S and it is the most accurately known. The accuracy with which C_S may be determined is, therefore, limited by the accuracy with which the specific heat of water is known. The term on the right-hand side of the equation is $\Delta U/5$, and it is evident that an error of 1% in the evaluation of ΔU will result in an error of only 0.02% in the value for C_S. The weight of solution formed on solution of one mole of salt is 1265.2 g. which gives 0.9445 as the specific heat of the solution at 22.5°. The above analysis is given in detail to show that this method of determining specific heats, although indirect, is yet capable of yielding results of high accuracy.

The specific heats of sodium chloride solutions were then calculated according to the following procedure. The heats of solution at 25°[1] and at 20°, obtained previously, were used, and values for ΔU were obtained by difference. Following the method suggested by Richards and Rowe, the values for ΔU were plotted against concentration and a smooth curve was drawn through the points. From the curve the values of ΔU at round concentrations were obtained and from these the specific heats of solutions at 22.5° were calculated, using Equation 2. The change in the specific heats with temperature was estimated from results given by Bousfield and Bousfield[4] and the specific heats at 20 and at 25° thereby calculated. The specific heats so obtained are possibly accurate to 0.05%. The previous values for the heats of solution have all been recalculated, using these specific heats, since it was thought that more reliance could be placed on the newer values than on some of the older ones. In view of the increased accuracy afforded by these results, a more careful calibration of the platinum-resistance thermometer was made and showed that the previous results were 0.06% too low. The results were, therefore, increased by this amount. The heats of solution so obtained were plotted against concentration and the values at round concentrations found from the curve. These values, together with the values for the specific heats of the solution, as calculated from the temperature coefficient of the reaction, are given in Table II.

Among the most accurate determinations previously made of the specific heats of sodium chloride solutions are those by Richards and Gucker,[5] and Richards and Rowe[3b] at 18°. In Table III, their results

---

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

[5] Richards and Gucker, THIS JOURNAL, **47,** 1876 (1925).

TABLE II

HEATS OF SOLUTION OF SODIUM CHLORIDE AND SPECIFIC HEATS OF SODIUM CHLORIDE SOLUTIONS AT 20 AND 25°

Concn. g. of NaCl per 100 g. of soln.	Heat of soln. cal. per mole of NaCl		Specific heat, cal.	
	20°	25°	20°	25°
0.200	—1163	— 993	0.9969	0.9963
.400	1168	1005	.9941	.9937
.600	1168	1010	.9915	.9911
.800	1166	1014	.9889	.9887
1.000	1162	1015	.9864	.9864
1.200	1156	1013	.9839	.9839
1.400	1150	1011	.9815	.9815
2.000	1133	1001	.9740	.9744
3.000	1100	974	.9625	.9629
4.000	1064.8	945.6	.9508	.9516
6.000	993.2	886.0	.9292	.9304
8.000	918.4	822.8	.9093	.9105
10.000	844.7	760.2	.8907	.8921
12.000	774.6	700.8	.8734	.8748
14.000	709.6	646.4	.8573	.8587
16.000	651.0	596.6	.8422	.8434
18.000	598.0	552.5	.8283	.8293
20.000	550.1	513.7	.8159	.8167
22.000	511.4	483.7	.8041	.8047
24.000	479.7	460.2	.7932	.7936
26.000	459.6	447.8	.7832	.7834

have been recalculated to 20° and compared with the values obtained in this work.

TABLE III

COMPARISON OF RESULTS WITH THOSE OF RICHARDS AND CO-WORKERS

Concn., g. of NaCl per 100 g. of soln.	Specific heat at 20°, cal.	
	Richards and co-workers	The authors
0.8046	0.9889	0.9888
1.5964	.9794	.9792
3.1426	.9607	.9607
6.0939	.9285	.9283
11.488	.8782	.8777

The Heat of Solution of Finely Divided Sodium Chloride

Preparation of the Finely Divided Salt.—The salt was prepared by sublimation as before, but a new settling box was used (Fig. 2).

The dimensions of this box were 20 × 20 × 210 cm. It was divided into eleven compartments by baffle plates, as shown. These compartments gradually increased in size. The first, where the salt entered, was 5 cm. and the last 35.5 cm. long. The salt was sublimed from the platinum retort and the vapors were blown through this box. The coarser particles settled out in the first compartments and only the finest reached the last compartments. Glass plates on the bottom of each chamber received the salt as it fell, very little adhering to the walls. The front of the box, a glass plate, was removable. Strips of rubber (shaded in the diagram) were glued around the open side of the box and down the edge of each baffle plate, and the glass was pressed against this by means of a wooden framework which was bolted to the box as shown.

Measurement of Size.—The size of the salt particles was obtained by two methods. In the first, the diameter of the particles was measured directly by the use of photomicrographs.[6] In the second, the number of particles in a given weight of salt was found by direct count using a hemacytometer.[7] In the latter procedure redistilled turpentine was used as a dispersion medium. Since the particles were not all of the same size, the relative distribution of the particles with regard to size was obtained from the photomicrographic measurements, and this, combined with the number of particles in a given weight, gave the average diameter per particle. The two methods gave results agreeing to within 0.1μ in the diameter of the average particle.

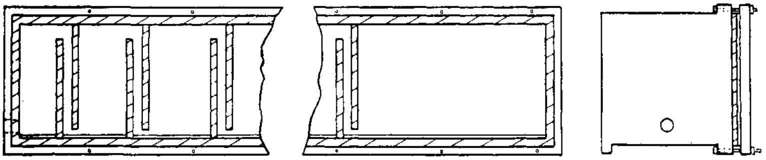

Fig. 2.

The Surface Energy of Solid Sodium Chloride

The heat of solution of the finely divided salt was measured at a concentration of 4.62% at 25°. The area of the salt was measured in the manner just indicated and the surface energy then calculated. The results are given in Table IV.

TABLE IV

SURFACE ENERGY OF SOLID SODIUM CHLORIDE AT 25°

Diameter of av. particle,[a] μ	Area per mole, sq. cm. × 10^{-6}	Surface energy per mole, cal.	Surface energy per sq. cm., ergs.
1.00	1.62	15.3	395
1.16	1.40	13.6	406
1.14	1.42	12.1	356

[a] This is not the arithmetical mean of the measured diameters but is a diameter such that, if the salt were composed of particles equal in size, which had this diameter, the area per mole would be the same as that actually occurring.

The figures in Col. 3 are the experimentally determined differences between the heat of solution of the coarse salt and the finely divided salt. The mean value for the surface energy of solid sodium chloride, as given above, is 386 ergs per sq. cm. at 25°.

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

---

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

[7] Kühn, *Z. angew. Chem.*, [1] **28**, 126 (1915).

Summary

1. An improved type of rotating adiabatic calorimeter is described with which heats of solution or heats of dilution may be determined with high accuracy using only small quantities of material. The apparatus is constructed so that the solute, before solution, is not exposed to the vapor of the solvent.

2. Heats of solution of sodium chloride were determined at 20° over the whole range of concentrations.

3. An indirect but accurate method of determining specific heats of solutions is described, in which the specific heats are calculated from the temperature coefficient of the heats of solution.

4. From the heats of solution of sodium chloride at 20°, and those determined previously at 25°, the specific heats of sodium chloride solutions were calculated with an accuracy perhaps of 0.05% over the whole range of concentrations.

5. The heat of solution of finely divided sodium chloride was determined directly and from the difference between its heat of solution and that of the coarse salt, the surface energy of solid sodium chloride was calculated.

MONTREAL, CANADA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE ADSORPTION OF MERCURY VAPOR BY CHARCOAL

BY ALBERT SPRAGUE COOLIDGE

RECEIVED MAY 25, 1927 PUBLISHED AUGUST 5, 1927

In most arrangements for measuring gas adsorption, the adsorbent is constantly exposed to the vapor of mercury in pumps, manometers, etc., but it is tacitly assumed that no mercury is adsorbed. Sufficient grounds for this assumption are not evident. In general, vapors are more copiously adsorbed, the smaller the vapor pressures and molecular volumes of their liquids, the latter influence being particularly strong when the vapor is nearly saturated. On this basis, one would predict that mercury vapor would be more readily adsorbed than any other vapor or gas usually present, and that in the presence of liquid mercury at the same temperature, a sample of ordinary activated charcoal would take up several times its own weight. It is true that the pressure of mercury vapor in the system is generally very low; but this would merely delay, not prevent, adsorption, and in the course of a prolonged experiment there would be opportunity for considerable quantities of mercury to reach the adsorbent.

Certainly no such great adsorption occurs, and this is intimately connected with the fact that mercury does not wet charcoal. This means not that there is no attraction of the carbon surface for mercury atoms, but that this attraction is less than that of the free mercury surface, so that