The measurements of Table III were made on prisms, from a few grams of glass cooled in air from fusion. The boric oxide prisms were protected from filming by oil and cover glasses.

Summary

A study of the phase equilibrium relationships in the system Na_2O–B_2O_3 has shown the existence of the compounds: sodium orthoborate, $2Na_2O \cdot B_2O_3$, with a congruent melting point at 625°; sodium metaborate, $Na_2O \cdot B_2O_3$, with a congruent melting point at 966°; sodium diborate, $Na_2O \cdot 2B_2O_3$, with a congruent melting point at 742°; sodium triborate, $Na_2O \cdot 3B_2O_3$, with an incongruent melting point at 766°, 76 weight per cent. B_2O_3; and sodium tetraborate, $Na_2O \cdot 4B_2O_3$, with a congruent melting point at 816°. The orthoborate, which is a newly discovered compound, can be cooled to a glass, as can mixtures containing more boric oxide than the diborate. The metaborate and compositions near it crystallize too readily to be quenched to a glass. In addition to the forms stable at the liquidus, sodium diborate may occur in two, and the tetraborate in one, additional form which are probably monotropic. Attempts to prepare crystalline boric oxide were not successful, and doubt is expressed as to previous claims to its crystallization. Refractive dispersions were measured for boric oxide, sodium tetraborate and sodium diborate glasses.

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, THE UNIVERSITY OF CHICAGO]

Heat Content and Heat Capacity of Aqueous Sodium Chloride Solutions

BY T. F. YOUNG AND J. S. MACHIN

Computations of activity coefficients from cryoscopic and thermal data have been greatly limited by a lack of adequate measurements.[1] This investigation was undertaken primarily to supply the heats of dilution required for a reliable determination of relative activities of sodium chloride in aqueous solutions. Because electromotive force methods[2,3] have been employed extensively in thermodynamic investigations of that electrolyte, sodium chloride is especially suitable for a critical comparison of the cryoscopic and electrical methods of evaluating activity coefficients.

The calorimetric data presented are of further interest because they furnish information concerning the variation with composition of apparent and partial molal heat capacities, and consequently have an important bearing upon the validity of the Debye–Hückel theory.[4]

The advantages of the chord-area method for the precise evaluation of partial molal properties from heats of dilution have been discussed by Young and Vogel.[5] The procedure they employed depends upon the determination of the derivative, S, of the apparent molal heat content with respect to the square root of the molality, m. Each heat of dilution experiment furnishes one average value of S which may be represented on a derivative plot by the ordinate of a horizontal line (called a "chord") extending between limits representing the initial and final values of $\sqrt{m}$, *i. e.*, $\sqrt{m_1}$ and $\sqrt{m_2}$. A special procedure was suggested by Young and Vogel[5] (p. 3037) to facilitate the drawing of a derivative curve so as to balance appropriate areas accurately. That procedure depends upon the drawing of a preliminary S curve, and the evaluation (by successive approximations, if necessary) of S', the first derivative, and S'', the second derivative of S. The final S curve is drawn in accordance with a series of points which have been plotted a distance, $P_i - \bar{P}_i$, above the center of each chord, computed from the equation

$$P_i - \bar{P}_i = - S'' (\Delta\sqrt{m})^2/24 \qquad (1)$$

where P_i represents the ordinate of a point on the derivative curve above the center of the ith chord, and $\bar{P}_i$ is the ordinate of the chord. For an application of this method it was desirable to produce chords so short that the uncertainties in values of $P - \bar{P}$ would not be large in comparison with the probable errors in the experimentally determined values of $\bar{P}$. For experiments with concentrated solutions, a dilution vessel having a volume about 0.03 that of the final diluted solution was used; for experiments with relatively dilute solutions, a larger vessel having a volume about 0.085 that of the final diluted solution was employed.

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[1] Young, *Chem. Rev.*, **13**, 103 (1933).

[2] Harned and Nims, THIS JOURNAL, **54**, 423 (1932).

[3] Brown and MacInnes, *ibid.*, **57**, 1356 (1935).

[4] Debye and Hückel, *Physik. Z.*, **24**, 185 (1923).

[5] Young and Vogel, THIS JOURNAL, **54**, 3030 (1932).

Experimental Procedure

The apparatus and procedures were similar to those described by Young and Vogel. The more important changes are described below.

Instead of the thin glass containers used in the earlier work, two silver capsules were employed. The smaller one, of about 25-cc. capacity, was used for the dilution of the more concentrated solutions. It consisted of a pure silver tube which could be closed with two spun silver caps, each provided with two small tabs for the attachment of wires. The tube was supported by a glass rod to which it was held by clamps and screws of pure silver. The larger vessel, of about 75-cc. capacity, was constructed of silver sheet and "silver solder" (largely copper and silver). Its cross section was a flattened ellipse. Rounded shoulders at the top and bottom terminated in vertical necks whose cross sections were similar in shape to, but smaller than, that of the body of the vessel. These were closed by soldered silver caps, to which wires were attached. After each experiment with this capsule the residual solution was tested with ammonium sulfide. No trace of copper was ever detected.

The covers were sealed to the body of the capsules with paraffin. For work at low temperatures the paraffin was covered with petroleum jelly to prevent leaks through small cracks produced in the paraffin. A gentle pull on a rod projecting through the calorimeter cover and attached by wires to the caps, detached first one and then the other. When blank experiments (*i. e.*, experiments with water both inside and outside the capsules) were made, no heats of opening were perceptible. To avoid errors due to lagging of the temperature of the contents of the dilution vessel, the caps were not removed for a dilution experiment until the temperature variation within the calorimeter had been reduced to less than 0.03 microvolt per minute.

The calorimeter was equipped with three tantalum propellers mounted on a single shaft. The submerged portion of the shaft was a tantalum tube on which the propellers were mounted. It was cemented to an upper portion made of glass tubing. A small synchronous motor geared directly to the stirrer rotated it at 450 revolutions per minute.

The calorimeter heater was similar to that used by Young and Vogel. Its flattened case was of platinum sealed with gold. Its leads were encased in a long thin tube of platinum–iridium, which projected through one of the openings of the calorimeter top. The tube extended to the bottom of the calorimeter where it terminated in a short U-shaped portion sealed to the bottom of the vertical case. The heater current was controlled by a semi-automatic set of switches. A manually operated switch caused the seconds pendulum of a weight driven clock, upon its next passage through a pool of mercury, to actuate an automatic switch which closed the heater circuit. Another manual switch was then closed to provide a by-pass for the current while two of the three leads to the automatic switch were interchanged. After a selected interval the pendulum, operating the automatic switch as before, opened the circuit.

Following each dilution there were usually two heating periods of three minutes each, from which the heat required for a temperature change of one microvolt was determined. The average deviation of 104 measurements from 52 respective means is 0.024%.

For work near 12.5° the thermostat was cooled by water pumped from an ice-water mixture through the copper coils immersed in the thermostat fluid (either water or an alcohol–water mixture), and returned to the source. For the measurements near 0°, brine was pumped through the coils. Temperature regulation was maintained by electrical heating and a large mercury regulator.

Materials.—The objectives of this investigation require a knowledge of the variation of the derivative, S, with temperature. It was desirable, therefore, to determine S at each of the three temperatures for solutions of as nearly the same composition as possible. Consequently, large quantities of the solutions were prepared and in general, two dilutions of each were made at each temperature. (An accident caused the omission of one duplicate at 25°.) Since the ratio of the volume of the solution in the calorimeter to the volume of the diluting water varied slightly, the centers of the chords derived from each stock solution were not quite the same. Corrections for these differences were computed and applied, as described below, but were extremely small. In some ranges of composition, analytical errors may introduce large errors into the chords[5] (p. 3036). In general, the use of the same solutions at all three temperatures reduced the effects of such errors upon the determinations of the variations of S with temperature, since partial cancellation ensued.

All solutions were prepared from distilled water and C. P. sodium chloride. All but the two most dilute were analyzed by the residue method of Richards and Hall.[6] Those two were prepared by weight dilution from more concentrated solutions. The quantities of solution (usually about 0.8 liter) and water introduced into the calorimeter were determined with weight burets.

Results

The experimental data are in Table I: $\Delta\phi H$ represents the heat absorbed in fifteen degree calories per gram formula weight of sodium chloride, t is the temperature of the solution and diluting water just before mixing; and $\sqrt{m_1}$ and $\sqrt{m_2}$ are the square roots of the initial and final molalities, respectively. The numbers of significant figures in the $\sqrt{m}$ columns were determined by the necessity for a precise computation of the difference, $\sqrt{m_2} - \sqrt{m_1}$. Because the second solution was produced by the dilution of the first, the difference, $\sqrt{m_2} - \sqrt{m_1}$, was determined to more decimal places than either $\sqrt{m}$.

Since the measurements were not performed at exactly the selected temperatures, it was necessary to apply a small correction to each determination to obtain $\overline{P}$ for one of the three temperatures, 0, 12.5 and 25°. The procedure was facilitated by the facts that solutions of the same composition were diluted in each of these temperature regions

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(6) Richards and Hall, THIS JOURNAL, **51**, 709 (1929).

and that the compositions of the respective solutions formed in each temperature range were nearly the same. For each dilution range, for example, the dilution of the 1.5742 molal solution ($\sqrt{m}$ = 1.2547) to solutions approximately 1.432 molal, the average value of the derivative $\mathrm{d}\overline{P}/\mathrm{d}t$ between 0 and 12.5 and the average value of $\mathrm{d}\overline{P}/\mathrm{d}t$ between 12.5 and 25° were computed from the data in column 4 of Table I. The two chords so obtained were plotted as ordinates with temperatures as abscissas and the $\mathrm{d}\overline{P}/\mathrm{d}t$ curve was drawn in accordance with the chord-area principle. From the straight line so obtained, a value of $\mathrm{d}\overline{P}/\mathrm{d}t$ was determined, for example, for the interval between 12.50 and 12.58°, the actual temperature of one of the observations. This value of the temperature coefficient multiplied by the difference, 12.50–12.58°, was added to the $\overline{P}$ observed at 12.58 to yield $\overline{P}$ at 12.50°. No correction at 25 or 12.5° amounted to more than two units and none at 0° to more than five units. Consequently the inaccuracy introduced by the treatment of $\mathrm{d}\overline{P}/\mathrm{d}t$ as a linear function of temperature is very small.

TABLE I

$\sqrt{m_1}$	$\sqrt{m_2}$	t	$\Delta(\phi H)$	$\overline{P}_{0.0}$
2.46569	2.42189	0.19	17.865	−410.7
	2.42229	.22	17.697	−411.0
2.35009	2.30872	.18	20.152	−490.0
	2.30840	.16	20.339	−490.4
2.12964	2.09288	.16	22.650	−618.9
	2.09281	.16	22.692	−618.9
1.89025	1.85832	.19	23.290	−733.2
	1.85801	.20	23.537	−733.9
1.57834	1.55201	.15	21.833	−832.6
	1.55243	.14	21.503	−833.1
1.25467	1.19683	.20	49.593	−862.4
	1.19682	.19	49.532	−860.9
0.90208	0.86122	.17	31.21	−768.5
	.86113	.19	31.24	−767.9
.72157	.68904	.18	20.78	−643.3
	.68891	.17	20.91	−644.3
.45192	.43164	.18	7.40	−369
	.43158	.20	7.27	−362
.31608	.30184	.20	2.28	−164
	.30187	.22	2.89	−207
	.30187	.21	1.97	−142
				$\overline{P}_{12.5}$
2.46569	2.42229	12.63	10.104	−234.5
	2.42244	12.60	10.056	−233.8
2.35009	2.30921	12.63	12.354	−304.0
	2.30920	12.64	12.376	−304.6
2.12964	2.09343	12.61	15.065	−417.7
	2.09333	12.61	15.107	−417.7
1.89025	1.85873	12.56	16.055	−510.3
	1.85883	12.58	16.014	−510.0
1.57834	1.55249	12.56	14.874	−576.4
	1.55252	12.56	14.844	−576.0
1.25467	1.19651	12.58	33.721	−581.3
	1.19667	12.57	33.519	−579.3
0.90208	0.86099	12.57	19.62	−478.8
	.86112	12.56	19.59	−459.5
.72157	.68893	12.55	12.19	−374.5
	.68879	12.55	12.37	−378.2
.45192	.43158	12.55	3.10	−153
	.43159	12.55	3.03	−150
				$\overline{P}_{25.0}$
2.46569	2.42241	25.02	3.4684	− 80.34
	2.42246	25.02	3.4699	− 80.48
2.35009	2.30936	25.03	5.861	−144.3
	2.30933	25.02	5.919	−145.4
2.12964	2.09343	25.01	9.028	−249.4
	2.09343	25.01	9.033	−249.6
1.89025	1.85891	25.01	10.439	−333.2
	1.85875	25.01	10.447	−331.8
1.57834	1.55258	25.06	9.998	−388.9
	1.55239	25.06	10.082	−389.2
1.25467	1.19674	25.03	21.983	−379.9
	1.19678	25.03	21.993	−380.2
0.90208	0.86089	25.02	11.77	−286.0
.72157	.68888	25.04	6.49	−199.1
	.68890	25.06	6.46	−198.4
.45192	.43156	25.05	0.47	− 23
	.43154	25.04	.28	− 14

The $\overline{P}$ values are given in the last column of Table I, and are plotted as chords on Fig. 1, the curves of which represent the derivative $S = \mathrm{d}(\phi H)/\mathrm{d}\sqrt{m}$ as a function of $\sqrt{m}$. The results of duplicate experiments with concentrated solutions differed so little that they are not distinguishable on the plot. Individual chords are discernible however in the dilute solution region. Measurements of the heats of dilution at 0° of the most dilute solution represented in Table I are relatively inaccurate because the temperature changes produced were very small (equivalent to galvanometer deflections of about 2 mm.). Corresponding data for 12.5 and 25° have been omitted entirely because of the availability of the equations recently derived by Young and Groenier[7] from the data obtained by Gulbransen and Robinson[8] with their calorimeter designed specially for very small thermal effects. The circles represent values calculated for 25° from Young and Groenier's equation 8 and for 12.5° from the fol-

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(7) Young and Groenier, THIS JOURNAL, **58**, 187 (1936).

(8) Gulbransen and Robinson, *ibid.*, **56**, 2637 (1934).

lowing equation which is the mean of their equations 10 and 11

$$S = 385 - 1591\sqrt{m} + 758\,m \qquad (2)$$

The accuracy of this equation is restricted, especially for relatively large molalities, by the excessive length of Gulbransen and Robinson's chords, and is further limited by the necessity for interpolation. Nevertheless, because of the superior precision of Gulbransen and Robinson's apparatus for the measurement of very small thermal effects, equation 2 was given greater weight in the drawing of the 12.5° curve near $\sqrt{m} = 0.44$ than was given to the data of Table I. If the small discrepancy apparent in this region be entirely due to errors in the observed galvanometer deflections produced by the dilution of the 0.204 molal solution ($\sqrt{m} = 0.452$), the mean error is less than 0.75 mm. In the same concentration range, the 25° data of the two investigations merge, somewhat fortuitously, with no significant discrepancy.

The final curves as shown in Fig. 1 were drawn with reference to *points* calculated, by means of equation 1, from values of S' and S'' determined from preliminary plots. The sizes of the dilution vessels had been so chosen that the average value of $P - \overline{P}$ was less than 0.04, and the largest was but 0.15, which is less than the precision of measurement. The experimental dilutions were nearly equivalent, therefore, to direct determination of the derivative, S.

For calculations involving a large scale reproduction of Fig. 1, the original data in Table I are not convenient. The dilution of the 1.5742 molal solution, for example, leads to values of S which correspond to six slightly different molalities. Each datum corresponds to a $\sqrt{m}$ which is the mean of $\sqrt{m_1}$ and $\sqrt{m_2}$ of the dilution experiment from which it was derived. Let X_j denote this mean $\sqrt{m}$ of the jth dilution. The mean of the six X_j values is 1.2257. For the small interval between each X_j and 1.2257, S' was determined from curves previously mentioned. This value of S', multiplied by $(1.2257 - X_j)$, was added to S previously computed for X_j. The sum is the derivative, S, which corresponds exactly to $\sqrt{m} = 1.2257$. All six experiments thus yielded derivatives for this same value of $\sqrt{m}$. The experiments had been so designed that all of the increments were insignificant: the largest was but 0.21.

Table II contains the resulting values of the derivative, S, corrected as described for temperature, curvature (by equation 1), and composition. These are not data read from smooth curves but

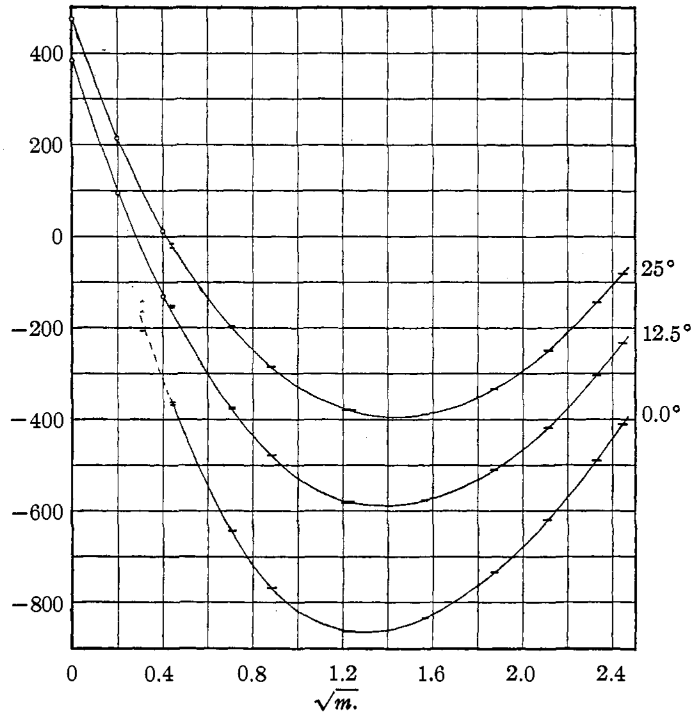

Fig. 1.

TABLE II

$\sqrt{m}$	S 0.0	12.5	25.0
2.4440	−410.5	−234.6	− 80.41
	−411.0	−233.9	− 80.57
2.3296	−489.9	−304.1	−144.4
	−490.2	−304.7	−145.5
2.1114	−618.8	−417.8	−249.5
	−618.8	−417.7	−249.7
1.8744	−733.1	−510.4	−333.3
	−733.8	−510.1	−331.8
1.5654	−832.6	−576.4	−388.9
	−833.1	−576.0	−389.3
1.2257	−862.5	−581.4	−380.0
	−861.1	−579.4	−380.3
0.8816	−768.6	−478.9	−286.1
	−767.9	−479.5	.....
.7052	−643.3	−374.5	−199.1
	−644.4	−378.3	−198.5
.4418	−369	−153	− 23
	−362	−150	− 14
.3090	−164		
	−207		
	−142		

are the original experimental quantities plus very small, usually insignificant, increments derived from smooth curves. For activity coefficient calculations a few values of S derived from the curves of Fig. 1 for round values of m are shown in Table III.

TABLE III

$\sqrt{m}$	S		
	0.0	12.5	25.0
0.3162	−196	− 39	91
.3500	−243	− 77	59
.4000	−311	−128	13
.4500	−376	−177	− 28
.5000	−435	−220	− 66
.6000	−545	−302	−136

Table II is suitable for a test of the precision of the calorimetric measurements. The average fractional discrepancy between duplicate measurements of heats of dilution of solutions more concentrated than 0.6 molal is about 0.2%, *i. e.*, the average deviation from the mean is 0.1%. The discrepancies in the data for the three most dilute solutions, *i. e.*, those producing very small temperature changes, are better expressed in terms of either equivalent temperature differences or galvanometer deflections. The average deviation from the mean of those data is equivalent to a deflection of about 0.2 mm.

Discussion

Three general methods have been used to test the validity of the Debye–Hückel theory for infinitely dilute solutions. Experimentally determined activity coefficients, heats of dilution and heat capacities have been compared with theoretical predictions. Many uni-univalent electrolytes in aqueous solution have been shown to meet the first two tests. The activity coefficients of sodium chloride have been compared by Brown and MacInnes,[3] and the heats of dilution by Young and Groenier[7] with the theoretical equations for extremely great dilutions.

From precise determinations of ϕC, the apparent molal heat capacity, Randall and Rossini[9] have calculated limiting values of the derivative, $d(\phi C)/d\sqrt{m}$, as m approaches 0. Though the dielectric constant of water has not been determined with sufficient precision to permit an accurate theoretical calculation of the limiting slope, Randall and Rossini demonstrated that their estimates were of the "proper order of magnitude" and that they showed "about the right" variations with changes of valence type. Their estimates depended upon extrapolations based upon the assumption that ϕC is *approximately* a linear function of $\sqrt{m}$. In a subsequent examination of various published data for 19 uni-univalent electrolytes, Rossini[10] concluded that ϕC "can be represented within the accuracy of the best experimental data, as a linear function of $\sqrt{m}$, from the lowest measured concentration to about 2.5 molal." Employing strictly linear extrapolations, he derived new values of the limiting slopes which are very similar to those of Randall and Rossini. Gucker and Schminke[11] also investigated several electrolytes of the 1–1 valence type, and found linear relationships between ϕC and $\sqrt{m}$ to represent their very precise measurements throughout wide ranges of concentration. For three of their solutes they found the linear relationship valid over the whole range investigated, and by extrapolation estimated the respective limiting derivatives. The largest of their values is over three times the smallest. A similar variation exists in the limiting slopes tabulated by Rossini. Randall and Rossini did not investigate the electrolytes whose limiting slopes were found in the later investigations to be the smallest. Nevertheless, the largest limiting value in their table is 65% larger than the smallest. If these differences are significant, the data are in conflict with the Debye–Hückel theory, which demands that the limiting slopes be the same for all strong electrolytes of a given valence type. It is important, therefore, to investigate the validity of the linear relationship upon which the various extrapolations were based. Gucker[12] has pointed out the difficulty of obtaining the precision necessary for this purpose from direct heat capacity measurements. The heat of dilution data, however, may be used.

If, at each temperature between 12.5 and 25°, $d(\phi C)/d\sqrt{m}$ is independent of molality, the vertical distance between the two upper curves of Fig. 1 must be constant. In Fig. 2 the solid line exhibits the difference between the two smooth S curves divided by 12.5; it therefore represents for each molality, the average value of $d(\phi C)/d\sqrt{m}$ throughout the temperature range between 12.5 and 25°. The open circles show, for comparison, data calculated directly from values of P in Table II, and the filled circles denote cor-

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(9) Randall and Rossini, THIS JOURNAL, **51**, 323 (1929).

(10) Rossini, *Bur. Standards J. Research*, **7**, 47 (1931).

(11) Gucker and Schminke, THIS JOURNAL, **54**, 1358 (1932); **55**, 1013 (1933).

(12) Gucker, *Chem. Rev.*, **13**, 111 (1933).

responding data derived from Young and Groenier's equations. The dashed line represents the constant value 14.4 which Rossini found to be valid for the various sodium chloride data at, and somewhat below, 25°. The measurements reported here and represented by the open circles, are in themselves evidence of the failure of the linear relationship,[13] but the smallness of the thermal effects observed made corroboration desirable. This has now been supplied by the measurements of Gulbransen and Robinson which reveal similar evidence of the variation of $d(\phi C)/d\sqrt{m}$ with composition. The variation observed within the concentration range of either investigation alone might not seem conclusive, because it might be ascribed to experimental error. A single horizontal line drawn through both sets of points, however, would imply the existence of very large and improbable errors, and would be untenable. Manifestly, the derivative $d(\phi C)/d\sqrt{m}$ does vary with composition.

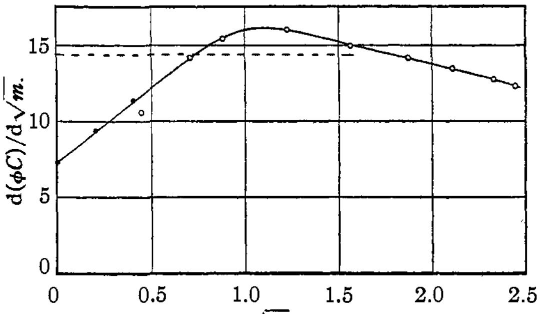

Fig. 2.

On Fig. 3 is plotted $\phi C - \phi C^\circ$ *vs.* $\sqrt{m}$. The dashed line represents Rossini's equation for temperatures between 18 and 25°; the solid line represents the integration of the solid curve of Fig. 2, *i. e.*, the average value of $\phi C - \phi C^\circ$ throughout the range between 12.5 and 25°. Because of the temperature difference the two curves should not correspond exactly. It is to be observed that their shapes are similar throughout the range between $\sqrt{m} = 0.2$ and $\sqrt{m} = 1.6$, *i. e.*, the range investigated experimentally by Randall and Rossini. Within this limited region the integrated (solid) curve is, in fact, approximately straight and its average slope does not differ greatly from that of the dashed line. Since there is some difference between the temperatures to which the two lines correspond, the agreement within the concentration range between $\sqrt{m} = 0.2$ and $\sqrt{m} = 1.6$ is quite satisfactory. There is, therefore, no conflict between Randall and Rossini's precise measurements[14] and the heats of dilution.

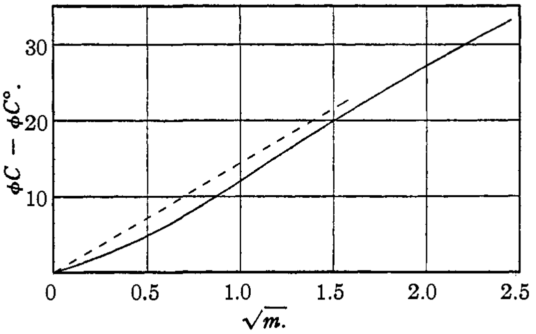

Fig. 3.

The slope of the ϕC *vs.* $\sqrt{m}$ curve for sodium chloride varies so rapidly near the origin that the limiting slope determined by linear extrapolation of apparent molal heat capacities is much larger (about twice as large) than the value derived from heats of dilution. Yet the heat capacity measurements for sodium chloride—especially those at 25°—are among the best in existence. The differences found between the limiting slopes of the various salts are, therefore, not significant and constitute no evidence of failure of the Debye–Hückel theory. That the theoretical limiting law is valid for sodium chloride at least is indicated by other data; the activity coefficients determined by Brown and MacInnes and the apparent molal heat content equations of Young and Groenier. More investigations of the latter type are desirable to supply further information concerning the variation with concentration of the heat capacities of electrolytic solutions.

These heat of dilution data have already been utilized[1] for a preliminary computation of activity coefficients from available freezing point tables. The computation revealed errors in older activity

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(13) This was pointed out at the meeting of the American Chemical Society in March, 1933; *cf.* Young, ref. 1. The purpose of Rossini's investigation of existing heat capacity data was to collect and arrange them conveniently for various thermochemical calculations. He did not discuss the relation of his equations to the Debye–Hückel theory. The influence upon his calculations of the differences between the two curves of Fig. 2 (and the corresponding curves of Fig. 3) are small and probably quite negligible.

(14) It is interesting that three of the four actual measurements (not average values) corresponding to Randall and Rossini's two smallest concentrations indicate a curvature in the expected direction. The fourth measurement yields a point which is well below even the straight line drawn by Rossini. Randall and Rossini did actually put some curvature into the line drawn to represent their measurements, but the heat capacity data were not capable of determining the change of slope quantitatively. Indeed, Rossini later represented the same data by a linear equation.

coefficient calculations introduced by the use of inaccurate and inadequate thermal data. A subsequent communication will describe the application of these dilution measurements to some freezing point determinations recently made in this Laboratory.

Summary

Differential heats of dilution to be used with cryoscopic data for the evaluation of activity coefficients of sodium chloride in aqueous solution have been obtained (by the chord-area method) from appropriate calorimetric measurements at 0, 12.5 and 25°.

These dilution data have been combined with those of Gulbransen and Robinson (extrapolated to infinite dilution by the method of Young and Groenier) to demonstrate that the apparent molal heat capacity of sodium chloride in aqueous solution is not a linear function of the square root of the molality. Many of the discrepancies between various precise measurements of the heat capacities of electrolytes, and the limiting law derived from the Debye–Hückel theory arose from linear extrapolations. Others are probably due to extrapolations which are too nearly linear. The theory is in agreement with measurements of the heats of dilution of aqueous sodium chloride solutions.

CHICAGO, ILL. RECEIVED SEPTEMBER 8, 1936

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 374]

The Normal Vapor Pressure of Crystalline Iodine[1]

BY LOUIS J. GILLESPIE AND LEWIS H. D. FRASER

The normal vapor pressure of iodine is the pressure of the pure vapor in equilibrium with pure solid or liquid iodine when this is subjected to the pressure only of the pure vapor. But few attempts have been made to measure it directly. Ramsay and Young[2] appear to have determined the pressure of air necessary to stop the sublimation of iodine at various temperatures from 58 to 113°. Haber and Kerschbaum[3] used a vibrating quartz fiber as manometer below 0 to −48°. They report some data by Naumann[4] from 19 to −40°. The precision of none of this work is within the theoretical uncertainties of the better indirect methods.

These uncertainties are due to the assumption, necessary in the indirect methods as ordinarily practiced, that iodine vapor behaves as an ideal gas—more particularly, that a mixture of iodine vapor and a permanent gas behaves as an ideal gas mixture. Gerry and Gillespie[5] showed how the uncertainties may be removed by applying thermodynamic corrections. They derived the corrections from the extensive data of Braune and Strassmann[6] and applied them to the precise indirect results of Baxter and co-workers.[7] They applied to these corrected results the rational equation of Giauque,[8] which has only one adjustable constant—the coefficient of the reciprocal temperature—and found the following equation to fit the corrected results very well

$$\log p = -3512.8/T - 2.013 \log T + 13.3740 \quad (1)$$

where p is the vapor pressure of the solid iodine in atmospheres, log is to the base 10 and $T = 273.1 + t°$.

The present paper deals with some direct measurements of the normal vapor pressure of solid iodine, of relatively high precision, made by means of a flexible metallic diaphragm to restrain the iodine vapor and devices for measuring precisely the low pressures of dry air on the opposite side of the diaphragm when the position of a pointer on the diaphragm, observed with a microscope, indicates a state of balance.

Apparatus

Corrosion experiments showed that platinum is not attacked by iodine, and gold becomes slightly tarnished, but the tarnish disappears on standing in air. These metals and glass were used to contain the iodine.

Figure 1 shows the diaphragm A, a disk of platinum-rhodium foil (4% Rh) 0.01 mm. thick with an effective diameter of 5.7 cm. It is mounted between two brass

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[1] From a thesis submitted by Mr. L. H. D. Fraser in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Ramsay and Young, *J. Chem. Soc.*, **49**, 453 (1886).

[3] Haber and Kerschbaum, *Z. Elektrochem.*, **20**, 296 (1914).

[4] Naumann, Dissertation, Berlin, 1907.

[5] Gerry and Gillespie, *Phys. Rev.*, **40**, 269 (1932).

[6] Braune and Strassmann, *Z. physik. Chem.*, **A143**, 225 (1929).

[7] Baxter, Hickey and Holmes, THIS JOURNAL, **29**, 127 (1907); Baxter and Gross, *ibid.*, **37**, 1061 (1915).

[8] Giauque, *ibid.*, **53**, 507 (1931).