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## The Heat Content of Sodium Chloride in Extremely Dilute Aqueous Solutions

BY T. F. YOUNG AND W. L. GROENIER

In their review of the heats of dilution of strong electrolytes, Lange and Robinson[1] concluded that the Debye–Hückel[2] theory was in satisfactory agreement with numerous calorimetric investigations of electrolytes in extremely dilute aqueous .solutions. They did not attempt, however, to make numerical comparisons of theoretical predictions with experiment. Agreement in order of magnitude is all that was expected.

Recently Gulbransen and Robinson[3] contributed a new and more extensive series of measurements of heats of dilution of sodium chloride solutions, from which they calculated various thermodynamic functions. These included the relative apparent molal heat content[4] (the difference between $\phi H$, the apparent molal heat content and $\phi H^0$, the limiting value of $\phi H$ at infinite dilution), which they represented as a function of the square root of $m$, the molality. Extrapolating their data to infinite dilution they estimated values of $S^0$, the limit at $\sqrt{m} = 0$ of the derivative

$$S = \mathrm{d}(\phi H)/\mathrm{d}\sqrt{m} \qquad (1)$$

When these estimates were compared with corresponding values derived from the theory of Debye and Hückel, significantly large discrepancies were observed; the theoretical values were from 14% (at 25°) to 49% (at 10°) larger than the values of the limiting slopes derived from experiment.

(1) Lange and Robinson, *Chem. Rev.*, **9**, 89 (1931).

(2) Debye and Hückel, *Physik. Z.*, **24**, 185 (1923).

(3) Gulbransen and Robinson, THIS JOURNAL, **56**, 2637 (1934); *cf.* Robinson, *ibid.*, **54**, 1311 (1932).

(4) Gulbransen and Robinson tabulated explicitly the negatives of the functions discussed here, *i. e.*, $\Delta H_\infty = -(\phi H - \phi H^0)$ and $\mathrm{d}(\Delta H_\infty)/\mathrm{d}\sqrt{m} = -S = -\mathrm{d}(\phi H)/\mathrm{d}\sqrt{m}$.

Gulbransen and Robinson's method of calculation was not designed primarily for the evaluation of the limiting derivative, $S^0$. They calculated, for each of their dilutions, the heat absorbed per mole of solute, *i. e.*, the increase in $\phi H$, the apparent molal heat content. By an ingenious addition process they then calculated the difference between $\phi H$ at a molality, $m$, selected as a temporary reference state and the $\phi H$ corresponding to the molality of each of their other solutions. For the extrapolation of their data to infinite dilution, they assumed the validity of the empirical equation

$$\phi H - \phi H^0 = S\sqrt{m} \qquad (2)$$

for the range between $\sqrt{m} = 0$ and $\sqrt{m} = 0.1$. Each value of $S$ was determined by the method of least squares and used in their evaluation of $\phi H - \phi H^0$ for various molalities. The value of $S$ thus obtained was their estimate of the limiting derivative, $S^0$. It is obvious that this procedure does not necessarily yield correct values of $S^0$ unless $S$ is actually constant between $\sqrt{m} = 0$ and 0.1. Gulbransen and Robinson observed "some evidence of continuously changing slope" and consequently recognized the uncertainties of their calculations. To make a more reliable and precise estimate of $S^0$ it is necessary to consider the variation of $S$ even for very small values of $\sqrt{m}$.

## Procedure

The chord–area method has been suggested by Young and Vogel[5] for the precise treatment of

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

TABLE I

DATA FOR APPLICATION OF CHORD–AREA METHOD

| No. | $\sqrt{m_1}$ | $\sqrt{m_2}$ | $\Delta\sqrt{m}$ | $\overline{P_i}$ | | | |
|---|---|---|---|---|---|---|---|
| | | | | 10° | 15° | 20° | 25° |
| 1 | 0.0791 | 0.0178 | −0.0612 | ... | 329.9 | 329.9 | 401.8 |
| 2 | .0791 | .0127 | − .0664 | ... | 357.1 | 381.2 | 415.9 |
| 3 | .1118 | .0252 | − .0866 | 269.0 | 334.8 | 350.9 | 355.6 |
| 4 | .1118 | .0179 | − .0939 | 263.2 | 346.3 | 343.1 | 368.6 |
| 5 | .1581 | .0358 | − .1223 | 229.7 | 270.6 | 326.1 | 336.0 |
| 6 | .1581 | .0253 | − .1328 | 230.5 | 286.2 | 345.7 | 349.5 |
| 7 | .2236 | .0503 | − .1733 | 142.0 | 200.3 | 253.4 | 294.9 |
| 8 | .2236 | .0358 | − .1878 | 153.9 | 208.2 | 262.0 | 299.3 |
| 9 | .3162 | .0712 | − .2450 | 90.2 | 133.5 | 177.5 | 228.1 |
| 10 | .3162 | .0507 | − .2655 | 99.0 | 151.8 | 189.4 | 245.2 |
| 11 | .4472 | .1005 | − .3467 | − 14.1 | 41.0 | 94.3 | 140.7 |
| 12 | .4472 | .0716 | − .3757 | 5.1 | 55.1 | 111.3 | 152.0 |
| 13 | .6356 | .1423 | − .4933 | −138.5 | − 69.7 | − 12.6 | 36.7 |
| 14 | .6356 | .1012 | − .5344 | −113.8 | − 47.7 | 12.1 | 57.3 |
| 15 | .9033 | .2062 | − .6972 | ... | ... | −124.5 | − 77.5 |
| 16 | .9033 | .1423 | − .7610 | ... | ... | − 96.8 | − 52.0 |

heat of dilution measurements. In Table I are the data necessary for the application of that method, as here employed. The first column contains numbers by which the various dilutions may be distinguished, the next three columns contain, respectively, the $\sqrt{m}$ before dilution, the $\sqrt{m}$ after dilution and $\Delta\sqrt{m}$, the difference between them. In the next four columns are values of $\overline{P}$, computed by equation 3 from the values of $-\Delta(\phi H)$ given in Gulbransen and Robinson's Table I.

$$\overline{P} = \Delta(\phi H)/\Delta\sqrt{m} \qquad (3)$$

The chord, $\overline{P}$, is the average value of $S$ throughout the composition range between $\sqrt{m_1}$ and $\sqrt{m_2}$.

When the chords had been plotted (as illustrated in Young and Vogel's second figure) it proved to be difficult to draw the derivative curves through them with the desired precision; the graphical method proved to be not well suited to these data.

Those chords which were obtained by dilution of the more concentrated solutions were very long because the experiments of Gulbransen and Robinson had been designed for another method of treatment. Because of the extremely small thermal effects involved, the chords obtained from dilution of the very dilute solutions were burdened with unavoidable experimental errors. Consequently, considerable personal judgment was required for the drawing of the derivative curve on the chord–area plot and it was desirable to introduce the method of least squares.

The plots indicated that the $S$ curves could be satisfactorily represented between $\sqrt{m} = 0$ and $\sqrt{m} = 0.64$, by the quadratic equation

$$S = S^0 + B\sqrt{m} + Cm \qquad (4)$$

The value of $S$ directly above or below the center of the $i$th chord may be represented by $P_i$. It is given by

$$P_i = S^0 + BX_i + CX_i^2 \qquad (5)$$

in which $X_i$ is the mean of $\sqrt{m_2}$ and $\sqrt{m_1}$ of the $i$th chord. The difference between $P_i$ and $\overline{P}_i$, the ordinate of the $i$th chord, is given by

$$P_i - \overline{P}_i = -S'' \delta_i^2/24 = -C\delta_i^2/12 \qquad (6)$$

in which $S''$ represents the second derivative of $S$ with respect to $\sqrt{m}$, and $\delta_i$, the change in $\sqrt{m}$ of the $i$th dilution. Equations 5 and 6 were combined to express $\overline{P}_i$ in terms of the empirical constants of equation 4, thus

$$\overline{P}_i = S^0 + BX_i + C(X_i^2 + \delta_i^2/12) \qquad (7)$$

A uniform weighting factor cannot properly be applied to the equations. If the probable errors in all values of $\Delta(\phi H)$ at any temperature were the same, the probable errors in $\overline{P}$ would be inversely proportional to $\delta$. Under those circumstances a weighting factor proportional to $\delta$ should be applied to each equation of the type of 7. This would be equivalent to the substitution of an equation involving $\Delta(\phi H)_i$ for the one involving $\overline{P}_i$. This simple weighting factor, however, would not be sufficient, for the various values of $\Delta(\phi H)$ are not equally precise. Each represents an experimental determination of the ratio of the heat absorbed, $q$, in an isothermal dilution, to $n$,

the number of moles of solute diluted. If the probable errors in all the $q$s were equal, the errors in $\Delta(\phi H)$ would be inversely proportional to $n$, and the weighting factor to apply to the $\overline{P}$ values should be proportional to $n\delta$. This factor would be correct if errors in the measurement of calorimetric thermal effects were entirely independent of the magnitude of those effects, and if errors from sources other than temperature measurements were entirely negligible. Actually, the errors in the determination of $\Delta(\phi H)$ do not fall off this rapidly with an increase of $n$. The weighting factor, $n\delta$, would, therefore, be too radical. A factor which is a compromise between $\delta$ and $n\delta$ was therefore adopted, namely, $m_2$, the molality of the residual solution of each dilution experiment. The relation of this factor to the others may be simply demonstrated. Since the calorimeter always contained approximately the same quantity of solvent, $n$ is approximately proportional to $m_2$ and therefore approximately equivalent to it as a weighting factor. The $\delta$s were obtained in two types of dilutions: (a) those in which $m_2$ was approximately $0.025\ m_1$ and (b) those, carried out in two steps, in which $m_2$ was approximately $0.05\ m_1$. For the two classes $\delta = -5.3\ \sqrt{m_2}$ and $\delta = -3.5\ \sqrt{m_2}$, respectively. Therefore, $\sqrt{m_2}$ is approximately proportional to $\delta$ and may be substituted for the latter in the weighting factor. The factor, $\delta$, is therefore approximately proportional to $m_2^{1/2}$ and the factor, $n\delta$, is approximately proportional to $m_2^{3/2}$. The factor, $m_2$, which was adopted is the geometrical mean of these.[6]

The equations obtained by the use of the method of least squares and the chord–area principle are

$$25^\circ \quad S = 476._1 - 1452._2\sqrt{m} + 730._4\ m \quad (8)$$
$$20^\circ \quad S = 451._3 - 1585._7\sqrt{m} + 894._8\ m \quad (9)$$
$$15^\circ \quad S = 413._6 - 1650._8\sqrt{m} + 924._5\ m \quad (10)$$
$$10^\circ \quad S = 355._7 - 1531._5\sqrt{m} + 591._8\ m \quad (11)$$

(6) In the formation of the *normal equations* the square of the residuals was, therefore, multiplied by $m_2^2$. The selection of the weighting factor was, necessarily, somewhat arbitrary. We also made calculations with the weaker factor $\sqrt{m_2}$, i. e., $m_2$ applied to the squares of the residuals. The agreement of the $S^0$ values with theory was not quite as good, but the mean of the four $S^0$ values so obtained, 428, was only 1% larger than the mean, 424, of the four values given in Table II. It is possible that a little better agreement with the theory would have been obtained if the factor $m_2^{3/2}$ had been used instead of $m_2$. However, in addition to the objection that this factor would be too extreme for the determination of the constants of the "most probable" quadratic equation, there is a second objection: if the $S$ curve does not quite conform to the quadratic equation within the limits of precision of the data, $m_2^{3/2}$ would seem to underweight the chords adjacent to $m = 0$, where we are particularly interested in $S$.

The corresponding curves are represented in Fig. 1, together with values of $P_i$ calculated by equation 4 from the $\overline{P}_i$ values in Table I and the empirically determined values of $C$. The agreement of the points with the curves is excellent and demonstrates the beautiful precision in the experimental determination of the minute thermal effects produced in the dilution experiments.
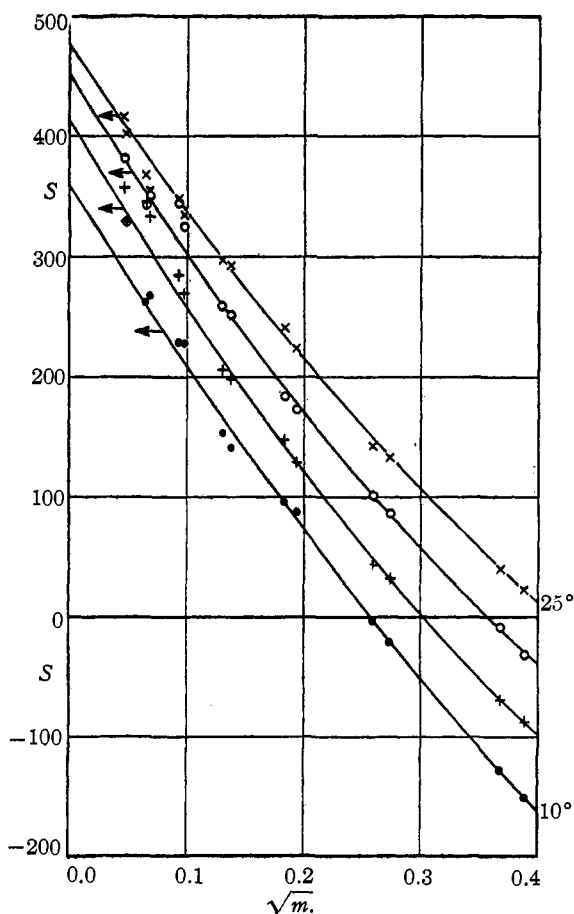


Fig. 1.—The derivative $S$; equations 8, 9, 10, and 11 are represented by the solid lines, and corresponding values of $P$ by $\times$ at 25°, $\bigcirc$ at 20°, $+$ at 15° and $\bullet$ at 10°. Arrows indicate the limits of Gulbransen and Robinson's extrapolations.

It also supports the assumption that quadratic equations are capable of representing the data for molalities between 0 and 0.4. It is possible to test further the validity of the quadratic at 20 and 25° with the aid of Gulbransen and Robinson's dilutions of their most concentrated solution (0.8 molal). By the methods described above, equations were derived from the data of all sixteen measurements at each temperature. The $S^0$ values determined for 25 and 20° are 471 and 442,

respectively. The small changes produced in the $S^0$ values by a doubling of the concentration range are a further indication of the competence of the quadratic equation to represent the data.[7] It seems unlikely that the errors in $S^0$ are much greater than 5%.[8]

## Discussion

In Fig. 1 the small arrows attached to each curve indicate the preliminary estimates of the $S^0$ values made by Gulbransen and Robinson. The reason for the divergence of the results of the two modes of calculation may now be explained. The original calculation was based on the assumption that $S$ is constant between 0 and 0.01 molal whereas the decrease of $S$ in this composition range is about 30% at 25° and 40% at 10°. The curves and arrows of Fig. 1 show that the limiting values of $S$ are from 14 to 50% larger than the original estimates.
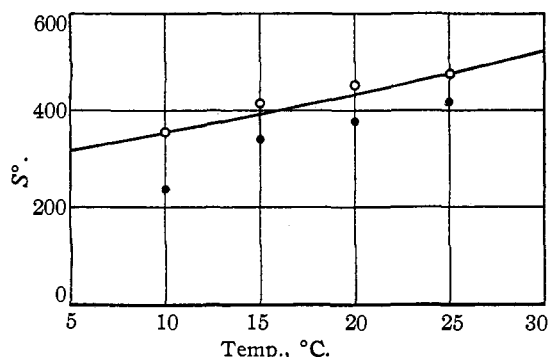


Fig. 2.—The limiting derivative $S°$; the solid line represents theoretical values, O values computed by the chord–area method, and ● the original values of $S°$.

It is now possible to compare the experimental $S^0$ values with the prediction of the Debye–Hückel theory. For this purpose values of $S^0$ were calculated from the equation derived from the theory by Scatchard[9] and by Gatty.[10] Birge's[11] esti-

mates of the fundamental constants, Wyman's[12] dielectric constant data, and specific volumes of water from "International Critical Tables"[13] were employed in the computation. As shown in Table II and Fig. 2, the agreement is excellent. The average discrepancy has been reduced from about 25% to less than 2.5% and the maximum from about 50 to 5%. The uncertainties in the theoretical values are greater than the discrepancies now existing; a 1% error in the temperature coefficient of the dielectric constant would cause an error of 4% in $S^0$ at 25° and 4.6% at 10°.[14] Values of $S^0$ calculated from the dielectric constants of Drake, Pierce and Dow[15] are larger than those calculated from Wyman's data and larger than the experimental values. The limiting values of $S$ for sodium chloride determined from the measurements of Gulbransen and Robinson are therefore in thoroughly satisfactory agreement with theory.

TABLE II
VALUES OF THE LIMITING DERIVATIVE, $S^0$

| $T$, °C. | Gulbransen and Robinson | Theory | Chord–area method |
|---|---|---|---|
| 10 | 239 | 355 | 356 |
| 15 | 340 | 393 | 414 |
| 20 | 370 | 434 | 451 |
| 25 | 418 | 477 | 476 |

The limiting derivatives of other salts studied by Lange[1] and his co-workers must be calculated by this (or an equivalent) method before further significant comparisons can be made. The empirical equations, 8, 9, 10 and 11 yield important information concerning apparent molal heat capacities. These will be discussed in a later communication from this Laboratory.

We extend our thanks to Professor Arthur C. Lunn and to Professor Walter Bartky for helpful and time-saving advice concerning the application of the method of least squares, and to Professor A. L. Robinson for his valued coöperation.

## Summary

The chord–area method of Young and Vogel has been applied to the recent heat of dilution measurements of Gulbransen and Robinson. Values of $S^0$, the limit (as $m \doteq 0$) of the derivative of the apparent molal heat content with respect to the square root of the molality, were found to be from 14 to 50% greater than indicated by the

(7) More detailed information concerning the shapes of the $S$ curves may be obtained if much shorter chords are employed. For this purpose diluting water may be put into the dilution vessel and solutions into the relatively large calorimetric space surrounding it; cf. ref. 5.

(8) The precision of the chord–area method is illustrated by the agreement of the result, 476, at 25° with the estimate, 461, made by Young and Vogel, ref. 5, from measurements of concentrated solutions and a single measurement of Lange and Messner [Naturwissenschaften, 15, 521 (1927); Z. Elektrochem., 33, 431 (1927)]. The heat absorbed during the solution of sodium chloride in an infinite amount of water was estimated from Young and Vogel's equation and the data of Lipsett, Johnson and Maass [THIS JOURNAL, 49, 925 (1927); ibid., 49, 1940 (1927)] to be 924 calorie mole⁻¹. The new equation yields 923 calorie mole⁻¹.

(9) Scatchard, THIS JOURNAL, 53, 2037 (1931).
(10) Gatty, Phil. Mag., 11, 1082 (1931).
(11) Birge, Phys. Rev. Supplement, 1, 1 (1929).

(12) Wyman, Phys. Rev., 35, 623 (1930).
(13) "International Critical Tables," McGraw-Hill Book Co., Inc., New York City, 1928, Vol. III, p. 25.
(14) Cf. Lange and Robinson, THIS JOURNAL, 52, 2811 (1930).
(15) Drake, Pierce and Dow, Phys. Rev., 35, 613 (1930).

preliminary calculations of Gulbransen and Robinson. The new $S^0$ values are in satisfactory agreement (0 to 5%) with limiting slopes calcu-

lated from the Debye–Hückel theory and Wyman's dielectric constant data.

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## On the Synthesis of Taurine

### BY FRANK CORTESE

Thus far, the most practical synthesis of taurine is that of Marvel, Bailey and Sparberg,[1] who obtained it in over-all yields of 32 to 45% from ethylene bromide, sodium sulfite and ammonia. To the other methods summarized by these authors may be added the recently described procedure of Schoeberl,[2] who obtained taurine by oxidation of cystamine in yields of 40%.

The following is an adaptation of the method of Reychler,[3] who employed, however, a somewhat inconvenient procedure.

### Experimental

β-Aminoethyl Bromide Hydrobromide.—This was prepared by Gabriel[4] by heating aminoethanol and fuming hydrobromic acid in a sealed tube at 170°. With certain precautions, the reaction may be effected at atmospheric pressure.

Ordinary 48% hydrobromic acid is distilled until 10 cc. of the distillate weighs at least 14.2 g. The relative narrowness of the boiling range is not a reliable indication of the strength of the acid. One hundred grams of colorless β-aminoethanol (b. p. 167–169° uncorr.) obtained by fractionation of commercial monoethanolamine (cork stoppers cannot be used) is slowly stirred into 700 cc. of ice cold redistilled 48% hydrobromic acid, ignoring the rise in temperature. The reaction mixture is distilled with the aid of porous plate and a Wurtz column until 185 cc. is collected. It is then gently refluxed, without reversing the condenser, for one hour, and then further distilled until another 70 cc. is collected. This procedure is repeated until further 60-, 30-, 25-, 15-, 10- and 5-cc. portions are obtained. Each fraction includes the amount of water distilled during both reflux and distillation periods. The mixture is finally refluxed for three hours. The process may be interrupted any time up to this point; 230 cc. of distillate is now collected, as crude hydrobromic acid. In all, the volume of distillate collected should not be less than 627 nor more than 633 cc. If less is distilled the yield is seriously impaired, if more, decomposition sets in, resulting in a worthless product.

Three hundred and thirty cubic centimeters of acetone is now thoroughly mixed with the residue in the flask, after it has cooled to about 70°. If necessary, crystalliza-

tion should be induced by freezing and stirring. After remaining in the refrigerator overnight, the material is filtered by suction, washed well with acetone, air-dried until the odor of acetone just vanishes and stored in a desiccator. The colorless crystals weigh 230–240 g. The filtrate concentrated to 100 cc. on the steam-bath, seeded, etc., yields another 25–40 g.; a third somewhat colored crop may be obtained from the mother liquor by concentrating to a sirup on the steam-bath, seeding, etc. The total yield varies from 290 to 303 g., or 87–90%. The first two fractions are pure β-aminoethyl bromide hydrobromide, while the last contains 5–10% unchanged aminoethanol hydrobromide, as indicated by titration with standard silver nitrate. All three crops may be used without further purification for the preparation of taurine.

β-Aminoethyl bromide hydrobromide crystallizes from a mixture of 95% alcohol and ethyl acetate either in small pointed rhombohedra or in pearly leaflets; m. p. 174–175° (corr.) with discoloration (Gabriel,[4] 172.5–173.5°).

0.6453 g. in water consumed 31.47 cc. of 0.1 N silver nitrate, equivalent to 38.98% ionizable bromine. (Calcd. 39.00%.)

Taurine.—A solution of 205 g. (1 mol.) of β-aminoethylbromide hydrobromide and 277 g. (1.1 mol.) of crystalline sodium sulfite, or an equivalent quantity of the much cheaper exsiccated variety, in 800 cc. of water is concentrated on the steam-bath to a minimum volume (fifteen to twenty-four hours; small runs take much less time). Time may be saved by refluxing for three hours and evaporating under reduced pressure. The cold moist cake is mashed well in a mortar and then thoroughly stirred with 500 cc. of concentrated hydrochloric acid. The salt residue is filtered upon a thick asbestos mat on a Büchner funnel and washed with ten 50-cc. portions of concentrated acid. (The pump should be flushed well with water afterward.) The filtrate is mixed well, decanted from any salt, concentrated with the aid of an ebullition tube in a 2-liter beaker over a free flame to 200 cc. and then mixed, while still hot, with 800 cc. of 95% alcohol. After fifteen minutes the product is filtered, washed with alcohol, air-dried and recrystallized by dissolving in four times its weight of hot water and adding five volumes of 95% alcohol. The yield of colorless practically pure taurine will be 100–102 g., or 80%. A further 6 g. may be obtained by working up the last filtrate. The use of five mols of sulfite increases the yield of taurine to 91%, but it is more inconvenient to work up the salt cake.

*Anal.* Calcd. for $C_2H_7O_3NS$: S, 25.63. Found: S, 25.64.

Taurine decomposed at 300–305° (corr.) without melt-

(1) Marvel, Bailey and Sparberg, THIS JOURNAL, **49**, 1833 (1927).
(2) Schoeberl, *Z. physiol. Chem.*, **216**, 193 (1933).
(3) Reychler, *Bull. soc. chim. Belg.*, **32**, 247 (1923).
(4) Gabriel, *Ber.*, **50**, 826 (1917).