Summary

The equivalent conductance of hydrochloric acid has been measured in 20, 45, 70 and 82% dioxane solutions at 15, 25, 35 and 45°. The experimental data closely follow the Onsager limiting slope in 20 and 45% dioxane solutions at high dilutions. Ionic association is too pronounced in 70 and 82% dioxane for convergence with the limiting slope within the accessible concentration range.

In a given solvent mixture, it was shown that the temperature dependence of the limiting conductance is linear, and the variation with viscosity can be expressed by $\Lambda_0\eta_0^s = r(s < 1)$.

The effect of the dielectric constant upon conductance and ionic association was illustrated by graphs, and by evaluation of the dissociation constant of hydrochloric acid in 70 and 82% dioxane solutions. At 25° the estimated values of the dissociation constant are 7.7×10^{-3} and $2.0 \times$ $\times 10^{-4}$ in 70 and 82% dioxane solutions, respectively. Rough values of the heat and entropy of ionization were also reported.

NEW HAVEN, CONN. RECEIVED JULY 13, 1938

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

The Heat Contents of the Salts of the Alkali Metals in Extremely Dilute Aqueous Solutions

BY T. F. YOUNG AND PAUL SELIGMANN

One of the most significant and interesting tests of the limiting law of Debye and Hückel[1] is the comparison of heats of dilution with the predictions of the theoretical equation. In their review of existing calorimetric data Lange and Robinson[2] concluded that the theory was in fairly satisfactory agreement with experiment. In various other papers, however, they and their respective co-workers have made estimates of the limit, as the concentration approaches zero, of the derivative of the apparent molal heat content with respect to the square root of the concentration ($S = \mathrm{d}\phi H/\mathrm{d}\sqrt{c}$), which differ considerably from the values computed from the modern precise dielectric constant measurements of Wyman.[3] These limiting derivatives for salts of the alkali metals vary from 36% of the theoretical value for potassium nitrate at 12.5° to 89% of the theoretical for lithium sulfate at 25°. They appear to show some significant trends: for example, the limiting derivatives of the five alkali metal sulfates decrease in the order of increasing molecular weights of the salts, whereas the theory demands that the limiting slope be the same for all salts of a given valence type.

In some recent papers of Lange and Robinson and their co-workers,[4] doubt has been expressed of the validity of extrapolations based upon the assumption that S is constant throughout a concentration range such as that between $m = 0$ and 0.01. Young and Groenier[5] have applied to the sodium chloride measurements a method of calculation which avoids the assumption of the constancy of the derivative, S. Their method possesses the further advantage that it deals directly with the measured heats of dilution; the older method[6] of Lange and Robinson was applied to a series of relative values of $-\phi H$ calculated by an addition process which obscured the actual measurements. As applied by Young and Groenier, the method also included a "chord-area" plot of the derivative, S, the property of immediate interest. This representation of the actual dilution data and the derivative on the same graph aids in the selection of a satisfactory type of equation to be used to represent the data, and in an understanding of the significance of the deviations between the derived equation and the experimental values.

In this paper are presented the results of an investigation of the limiting slopes of all salts of the alkali metals for which there are sufficient data for the determination of equations by the method of least squares.[7]

Procedure.—In each dilution experiment, q, the heat absorbed during an isothermal dilution

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

[2] Lange and Robinson, *Chem. Rev.*, **9**, 89 (1931).

[3] Wyman, *Phys. Rev.*, **35**, 623 (1930).

[4] *Cf.* Gulbransen and Robinson, THIS JOURNAL, **56**, 2637 (1934).

[5] Young and Groenier, *ibid.*, **58**, 187 (1936).

[6] For details, see Lange and Robinson, *ibid.*, **52**, 4218 (1930).

[7] We are indebted to Mr. J. C. Hesler, Mr. Fred Karush and Mr. R. P. McCormick who duplicated our calculations.

of n moles of solute is determined. The ratio q/n is the increase in the apparent molal heat content, $\Delta(\phi H)$. From a series of values of $\Delta(\phi H)$, each tabulated with the corresponding initial and final concentrations, an equation of the type

$$\phi H + C = \alpha c^{1/2} + \beta c + \gamma c^{3/2} + \ldots \qquad (1)$$

may be derived by conventional least square methods. The precision with which $\Delta(\phi H)$ is determined decreases with the amount of solute in the calorimeter, *i. e.*, with n. The probable error in $\Delta(\phi H)$ would be inversely proportional to n if all q's were determined with the same probable error, and a weighting factor proportional to n^2 would then be applicable to the squares of the residuals in the formation of the "normal equations." The probable errors do not decrease quite this rapidly with increase of n; a factor between unity and n^2 is therefore desirable. The final concentration, c_2, is approximately proportional to n and was used as the factor for the one cubic equation evaluated by this method (equation 26).

A slightly different point of view was adopted by Young and Groenier. For graphical representation of the derivative $S = \mathrm{d}(\phi H)/\mathrm{d}\sqrt{m}$ on a chord–area plot they had computed for each dilution the chord $\overline{P} = \Delta(\phi H)/\delta$, where δ is the increase in $\sqrt{c}$ accompanying the dilution. From the chords, equations of the type

$$S = S^0 + B\sqrt{m} + Cm + \ldots \qquad (2)$$

were derived. If, in the formation of the normal equations, the squares of the residuals had been multiplied by the factor $n\delta^2$, the constants obtained from the second method would be precisely equal to the equivalent ones determined by the method described in the preceding paragraph. For convenience the factor m_2^2 was used instead of $n\delta^2$, since m_2 was nearly proportional to δ^2 in the sodium chloride experiments of Gulbransen and Robinson. In this extension of the calculations to other salts, the same factor m_2^2 and its approximate equivalent c_2^2 were adopted for general use. The only data for which this factor is not appropriate are those for potassium nitrate. In the 25° experiments of Lange and Monheim[8] there were two very dissimilar series of dilutions. One series resulted in five chords which are very much shorter than the others. For any value of $X = (\sqrt{c_2} + \sqrt{c_1})/2$ (the abscissa of a chord center), c_2 of a short chord is larger than c_2 of a long chord. The simple factor c_2^2 would therefore give greater weight to the shorter chords. On the chord–area plot the short chords lie far below the curve drawn through the longer ones. Since all the short ones lie in the region of small concentrations, they affect the tilt of the least square curve and exert a disproportionately large effect upon the extrapolated slope, S^0. The ratio of c_2 of a long chord to c_2 of a short chord having the same X is about 0.62. To give equal weights to the dilutions of both series, the factors c_2^2 and $(0.62\sqrt{c_2})^4$ were applied to the squares of the residuals of the long and short chords, respectively. The same factors were also applied to Lange and Monheim's potassium nitrate measurements at 12.5°.

The largest value of X in the 10 and 15° sodium chloride data was about 0.4. For the sake of intercomparisons of the four equations, it was desirable that the concentration ranges covered by the data employed in the derivations be the same for all temperatures. Since the quadratic equations appeared to be capable of representing the derivative S throughout the whole range of the existing data, the limit adopted for X was 0.4.

In this extension of the calculations to other salts of the alkali metals, the same limit was adopted for the derivation of a set of preliminary equations. The restriction eliminated data for very few salts, since X for most of them does not exceed 0.2. Each of the preliminary equations was tested by means of a deviation plot. The deviation of the ith chord is the difference between S_i, computed by the substitution of X_i in the empirical equation, and P_i calculated from the chord, $\overline{P}_i$, by the following equation[9]

$$P_i - P_i = -C\delta_i^2/12 \qquad (3)$$

When the deviation plot showed a trend indicative of failure of the quadratic equation for the full concentration range, a new equation was derived. The new equation might be either another quadratic derived for a more limited concentration range, or it might be a cubic equation.

The deviations of only one curve, that for potassium perchlorate at 15°, seemed to show a significant trend. A new quadratic was therefore derived from all of the chords except the last pair. It was adopted as final since a new deviation plot exhibited no significant trend. When the two discarded chords were represented on the new deviation plot it became apparent that they

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[8] Lange and Monheim, *Z. physik. Chem.*, **A150**, 349 (1930).

[9] Ref. 5, equation 6.

were inconsistent with each other, and that only one of them disagreed seriously with the curve derived from the other ten. The deviation of the longer chord, which resulted from a single dilution in the calorimeter, was relatively small; the deviation for the shorter chord produced by an additional dilution was larger. When the S curve is known only approximately in the region of small concentrations, one chord may be calculated from the other. Such a calculation exposed a 4% discrepancy between the two chords. Such a large error is not to be expected in the dilution of relatively concentrated solutions, and is apparently due to an accident. If the accident had occurred in the determination of the longer chord, both would have been affected; if it occurred in the second dilution only the shorter chord would be affected. The longer chord which is in satisfactory agreement with the curve had been confirmed by duplicate measurements, the second dilution was one of the very few dilutions made by Andauer and Lange[10] which was not duplicated. It seems, therefore, that the shorter chord is the faulty one. There is, then, no evidence that the quadratic does not represent the potassium perchlorate curve satisfactorily over the whole concentration range of the data, but merely that it fails to agree satisfactorily with a chord which is almost certainly in error.

Concentration was expressed in most of the work of Lange and Robinson and their co-workers in terms of c (mole/liter). The sodium chloride data are in terms of molality (m). Though the difference is insignificant, these quantities are distinguished by their usual symbols in the equations.

The Equations.—The new equations, together with two of the sodium chloride set, are in Tables I and II. As predicted by theory, the limiting slopes of the alkali sulfates are $3^{3/2}$ times those of salts of the 1–1 valence type. The mean of five values of $S^0/3^{3/2}$ of the salts of the 1–2 type and the eleven values of S^0 for the other alkali metal salts is 47_6 at 25°. This value is about 30% larger than the mean of the limits calculated by the method of Lange, *et al.* The theoretical limit is 47_7. The complete set of curves is shown in Figs. 1 and 2 which illustrate the concordance of the empirical equations with the data and the agreement of theory with experiment. This striking agreement seems to us to be the most impressive quantitative confirmation yet received by the Debye–Hückel limiting law.

TABLE I

	25°	
$NaCl$[4,5]	$S = 476 - 1{,}452\sqrt{m} + 730m$	(4)
$NaBr$[11]	$S = 470 - 1{,}793\sqrt{c} + 1{,}498c$	(5)
$NaNO_3$[12]	$S = 454 - 2{,}645\sqrt{c} + 1{,}937c$	(6)
$NaClO_3$[12]	$S = 462 - 2{,}497\sqrt{c} + 2{,}103c$	(7)
$NaBrO_3$[12]	$S = 540 - 4{,}428\sqrt{c} + 7{,}299c$	(8)
$NaIO_3$[12]	$S = 501 - 5{,}962\sqrt{c} + 7{,}841c$	(9)
KCl[13]	$S = 444 - 1{,}447\sqrt{c} + 839c$	(10)
KBr[11]	$S = 514 - 3{,}050\sqrt{c} + 5{,}353c$	(11)
KNO_3[8]	$S = 408 - 4{,}128\sqrt{c} + 3{,}636c$	(12)
$KClO_3$[10]	$S = 568 - 5{,}797\sqrt{c} + 8{,}974c$	(13)
$KClO_4$[10]	$S = 440 - 6{,}973\sqrt{c} + 9{,}022c$	(14)
	15°	
$NaCl$[4,5]	$S = 414 - 1{,}651\sqrt{m} + 924m$	(15)
$KClO_3$[10]	$S = 409 - 4{,}903\sqrt{c} + 5{,}239c$	(16)
$KClO_4$[10]	$S = 417 - 8{,}447\sqrt{c} + 12{,}151c$	(17)
	12.5°	
KCl[13]	$S = 394 - 1{,}896\sqrt{c} + 1{,}530c$	(18)
KNO_3[8]	$S = 350 - 5{,}314\sqrt{c} + 5{,}862c$	(19)

TABLE II

	25°	
Li_2SO_4[14]	$S = 2{,}548 - 6{,}948\sqrt{c} + 4{,}958c$	(20)
Na_2SO_4[14]	$S = 2{,}432 - 14{,}896\sqrt{c} + 19{,}532c$	(21)
K_2SO_4[14]	$S = 2{,}399 - 14{,}879\sqrt{c} + 22{,}323c$	(22)
Rb_2SO_4[14]	$S = 2{,}512 - 18{,}333\sqrt{c} + 32{,}635c$	(23)
Cs_2SO_4[14]	$S = 2{,}231 - 18{,}697\sqrt{c} + 34{,}622c$	(24)

The calorimetric measurements of some of the more dilute solutions depended upon precision in temperature measurement of a few ten-millionths of a degree. Some of the curves required extrapolations over wide concentration intervals by means of an arbitrary type of equation, the quadratic power series. The remaining discrepancies between theory and the extrapolated limits, therefore, may be without significance. That they do not, in general, indicate failures of theory becomes more probable when a few of the typical cases are examined further. The two series of chords tabulated for potassium nitrate have been discussed already: one or the other must be wrong. Since the general agreement observed for all the salts suggests that the five short chords are in error, an equation was derived from the long chords only. It is in very close agreement with theory.

$$S = 449 - 4{,}578\sqrt{c} + 4{,}708c \qquad (25)$$

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[10] Andauer and Lange, *Z. physik. Chem.*, **A165**, 89 (1933).

[11] Hammerschmid and Robinson, THIS JOURNAL, **54**, 3120 (1932).

[12] Lange and Robinson, *Z. physik. Chem.*, **A148**, 97 (1930).

[13] Lange and Leighton, *Z. Elektrochem.*, **34**, 566 (1928).

[14] Lange and Streeck, *Z. physik. Chem.*, **A157**, 1 (1931).

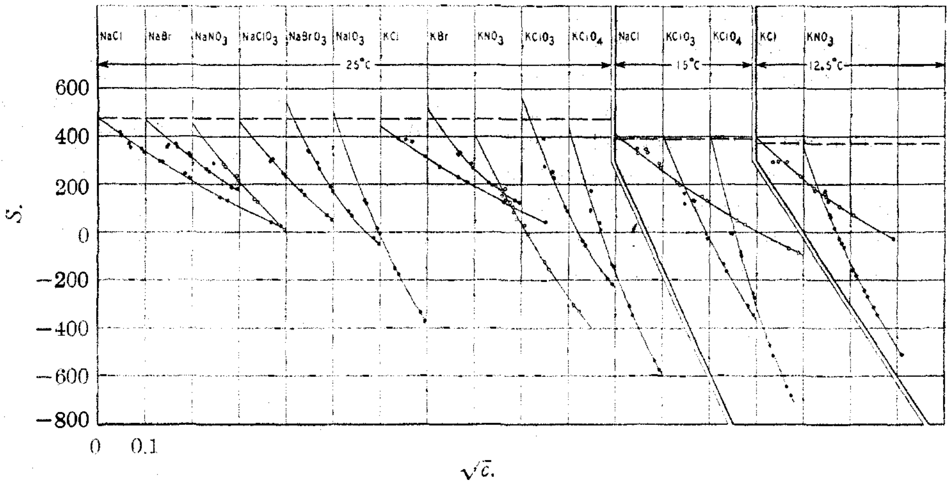

Fig. 1.—The derivative, S, *versus* $\sqrt{c}$. The curves represent the equations of Table I; the symbols ○ and ● are used to distinguish values of P associated with intersecting or adjacent curves. The origin of each successive curve lies one division to the right of the origin of its predecessor. Each horizontal interval represents an increment of 0.1 in $\sqrt{c}$. The respective theoretical limits are shown by the broken horizontal lines.

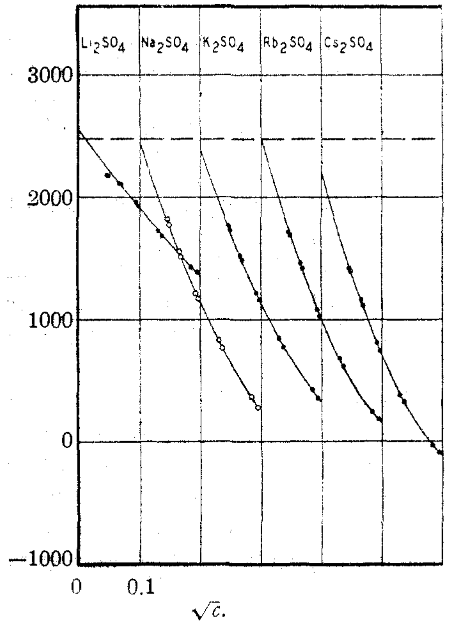

Fig. 2.—The derivative, S, versus $\sqrt{c}$. The curves represent the equations of Table II; the symbols represent values of P.

Though the potassium chloride limit is in satisfactory agreement with theory, the wide range of data available permits a further study of equation types. A cubic was determined from all ten chords

$$S = 460 - 1{,}718\sqrt{c} + 2{,}106c - 1{,}583c^{3/2} \quad (26)$$

The somewhat better agreement of the extrapolated limit with theory suggests that the quadratic may have been applied to too wide a concentration range. One developed for values of X less than 0.2 actually reverses the algebraic sign of the discrepancy.

$$S = 482 - 1{,}967\sqrt{c} + 2{,}368c \quad (27)$$

The changes in S^0 produced by these arbitrary variations of method confirm the view that differences of such magnitude are not significant. Moreover, the curves exhibiting the largest discrepancies are, in general, those which are most highly curved, and which are therefore least likely to be well fitted by an equation of arbitrarily chosen type.

The empirical equations, 4 to 24, may be used for calculations of accurate values of the partial molal and apparent molal heat contents. If, however, they are accepted (in addition to other known facts) as evidence that the theory agrees with experiment within the limits of error of the latter, a more precise set of equations may be derived with the aid of theory. Table III contains equations all having the theoretical limit, S^0. The B and C terms were computed by least square methods similar to those described above. Since fewer data are necessary for the determination of two constants the chord centers, X, were restricted to 0.2. Since the five short chords for potassium nitrate at 25° are definitely inconsistent with the theory, as well as with the other measurements, and since theory was being used as a guide for the derivation of this set of equations, the five short chords were not used. To emphasize the somewhat arbitrary character of this pro-

TABLE III

	25°	
NaCl	$S = 477 - 1{,}532\sqrt{m} + 1{,}154m$	(28)
NaBr	$S = 477 - 1{,}888\sqrt{c} + 1{,}770c$	(29)
$NaNO_3$	$S = 477 - 2{,}961\sqrt{c} + 2{,}834c$	(30)
$NaClO_3$	$S = 477 - 2{,}708\sqrt{c} + 2{,}701c$	(31)
$NaBrO_3$	$S = 477 - 3{,}562\sqrt{c} + 4{,}831c$	(32)
$NaIO_3$	$S = 477 - 5{,}635\sqrt{c} + 6{,}913c$	(33)
KCl	$S = 477 - 1{,}893\sqrt{c} + 2{,}144c$	(34)
KBr	$S = 477 - 2{,}541\sqrt{c} + 3{,}902c$	(35)
KNO_3	$(S = 477 - 5{,}006\sqrt{c} + 6{,}079c)$	(36)
$KClO_3$	$S = 477 - 4{,}527\sqrt{c} + 5{,}334c$	(37)
$KClO_4$	$S = 477 - 7{,}492\sqrt{c} + 10{,}510c$	(38)
	15°	
NaCl	$S = 393 - 1{,}411\sqrt{m} + 335m$	(39)
$KClO_3$	$S = 393 - 4{,}681\sqrt{c} + 4{,}602c$	(40)
$KClO_4$	$S = 393 - 8{,}086\sqrt{c} + 11{,}011c$	(41)
	12.5°	
KCl	$S = 374 - 1{,}569\sqrt{c} + 372c$	(42)
KNO_3	$S = 374 - 5{,}753\sqrt{c} + 7{,}522c$	(43)
	25°	
Li_2SO_4	$S = 2{,}481 - 6{,}022\sqrt{c} + 2{,}305c$	(44)
Na_2SO_4	$S = 2{,}481 - 15{,}576\sqrt{c} + 21{,}482c$	(45)
K_2SO_4	$S = 2{,}481 - 16{,}022\sqrt{c} + 25{,}599c$	(46)
Rb_2SO_4	$S = 2{,}481 - 17{,}896\sqrt{c} + 31{,}381c$	(47)
Cs_2SO_4	$S = 2{,}481 - 22{,}169\sqrt{c} + 44{,}570c$	(48)

cedure the 25° equation is enclosed in parentheses. For certain theoretical calculations based upon the assumption that the limiting law is valid, this second set of equations will be preferable to those in Tables I and II. Ion size studies, for example, are often based upon the assumption that the Debye–Hückel theory is quantitatively correct, which implies that S^0 of all salts of a given valence type must be the same.[15]

For most purposes, values of the relative partial molal and apparent molal heat contents computed from the two sets of equations do not differ appreciably, nor do they differ much from the values listed in the original tables of Lange, Robinson, *et al.* About five calories per mole is the largest difference produced by various methods of extrapolation.

A few other salts of the alkali metals have been studied, though sufficient data for them have not been published to justify the derivation of least square equations. A few dilutions of lithium chloride[16] and potassium fluoride,[17] represented on a chord-area plot indicate that these three salts obey the limiting law. Chords for rubidium fluoride[8] are erratic and badly scattered and are useless for our purpose.

For investigation of heat capacities, more dilution measurements are necessary over a temperature range and wide concentration range. Young and Machin[18] already have utilized such data for sodium chloride to demonstrate that existing specific heats do not prove the existence of a conflict between the limiting law and experiment.

At the present time no existing calorimetric data for salts of the alkali metals are in disagreement with the Debye–Hückel limiting law. Indeed, most measurements of their heats of dilution support the law with striking consistency.[19]

Summary

The method applied by Young and Groenier to the heats of dilution of aqueous sodium chloride solutions has been extended to all other salts of the alkali metals for which sufficient data are available for the application of the least square technique. The average value of the limiting derivative, S^0, for eleven salts of the 1–1 valence type at 25° and $S^0/3^{3/2}$ for five salts of the 1–2 valence type is about 30% larger than the average of the older estimates based upon an assumed linear relation between the apparent molal heat content and the square root of the concentration. The new average agrees with the theoretical value calculated from Wyman's dielectric constant measurements and the Debye–Hückel limiting law.

Since the calculated values of S^0 appear to confirm the Debye–Hückel limiting law and Wyman's measurements a second set of derivative equations have been derived in which S^0 was fixed at the theoretical value.

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[15] It already has been pointed out by Young and Vogel, THIS JOURNAL, **54**, 3030 (1932), that reasonable values of the parameter "a" may be computed from the B terms of the empirical equations. Such a calculation implies that the temperature coefficient of "a" is negligible and that certain other factors may be neglected. Lange and Robinson (Ref. 2, p. 111) have pointed out that these assumptions lead to the conclusion that the ion size of the alkali metals increases with atomic weight whereas freezing point measurements and other data indicate the reverse order.

[16] Lange and Messner, *Z. Elektrochem.*, **33**, 431 (1927).

[17] Lange and Eichler, *Z. physik. Chem.*, **129**, 285 (1927).

[18] Young and Machin, THIS JOURNAL, **58**, 2254 (1936).

[19] An incomplete investigation of salts of the alkaline earth metals of the 2–1 valence type indicates similar agreement, at least at 25°. The extrapolations seem to be of poorer precision, and afford less definite support to the Debye–Hückel theory, but no data point to failure of the theory. Existing data for salts of the 2–2 valence type *if treated by the methods described above*, certainly do not lead to limiting values in agreement with theory. *Cf.* Young, *Science*, **85**, 48 (1937).