underlying the calculated values and the analytical errors in the experimental determinations. The author is of the opinion that the cation-exchange reactions of bentonites offer an easy experimental way of determining relative activity coefficients with a fair degree of accuracy.

Summary

A method for utilizing the cation-exchange reactions of bentonites for the determination of relative activity coefficients in mixed electrolytes has been presented. The method was applied experimentally to the barium–cadmium exchange reaction; the results are in fair agreement with those calculated from published data of the activity coefficients of barium chloride and cadmium chloride solutions.

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THE INTEGRAL HEATS OF DILUTION AND THE RELATIVE PARTIAL MOLAL HEAT CONTENTS OF AQUEOUS SODIUM CHLORIDE SOLUTIONS AT 25°

BY A. L. ROBINSON

I. Introduction

The accurate measurement of heats of dilution of strong electrolytes at concentrations below 0.1 M by Lange and his co-workers[1] and the successful extrapolation of these measurements to infinite dilution permit an evaluation of the relative partial molal heat contents of the components of such solutions in cases where measurements at higher concentrations have already been made. The dilution of very dilute aqueous solutions of strong electrolytes (in general below 0.1 M) evolves heat in every case so far studied, in agreement with the interionic attraction theory,[2] so that previous extrapolations of dilution measurements to infinite dilution, even when such measurements have been extended to concentrations of a few tenths molal, are often seriously in error. For example, Lewis and Randall[3] state that the dilution of a saturated solution of sodium chloride containing one mole of the salt with a very large amount of water absorbs 606 calories at 25° and that this agrees well with the value 598 calories calculated from partial molal heat contents. The measurements on dilute sodium chloride solutions presented here combined with the results of

[1] For a review of this work see Lange and Robinson, *Chem. Rev.*, 9, 89 (1931), which contains complete references.

[2] Lange and Meixner, *Physik. Z.*, 30, 670 (1929).

[3] Lewis and Randall, "Thermodynamics," The McGraw-Hill Book Co., Inc., New York, 1923, p. 95.

other investigators on more concentrated solutions give 483 calories for this heat effect, and permit the calculation of more accurate values of integral heats of dilution and of relative partial molal heat contents from saturation to infinite dilution. These latter values are important in the calculation of activity coefficients from freezing point data.

II. Experimental

A differential adiabatic calorimeter, already described,[4,1] was employed. A thermopile with 1072 iron–constantan thermoelements was used to measure the heat effects attending the dilutions; with this thermopile and a Kipp and Zonen type Ze galvanometer the temperature changes produced by the dilutions, usually of the order of 10^{-4} degree, could be measured with an accuracy of 2×10^{-7} degree.

The sodium chloride used was Merck's best preparation. Ordinary distilled water was used in making up the solutions and for dilution, as previous investigations had shown that further purification of the water was not necessary.

The dilution pipets, one in each half of the calorimeter, contained 25 cc. of solution, and each calorimeter half held 775 cc. of water or solution, not including the pipet contents. All details of manipulation and calculation were the same as in previous investigations.

TABLE I

HEATS OF DILUTION OF SODIUM CHLORIDE SOLUTIONS AT 25°

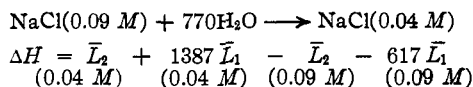| Initial concn., mole/liter	Final concn., mole/liter	Individual measurements, ΔH calories/mole NaCl				Average calories/mole NaCl
0.1	0.00308	−61.4	−61.5			−61.5 ± 0.1
.1	.00605	−53.1	−52.7			−52.9 ± .2
.05	.00154	−55.1	−53.6	−55.6	−55.4	−54.9 ± .6
.05	.00302	−49.4	−47.9	−49.1	−48.4	−48.7 ± .4
.025	.000770	−45.4	−46.2	−45.2		−45.6 ± .4
.025	.001515	−39.1	−40.7	−39.9		−39.9 ± .6
.0125	.000385	−32.8	−32.2	−34.4		−33.1 ± .9
.0125	.000754	−30.8	−29.2	−31.6		−30.5 ± .9

The first two columns of Table I give the initial and final concentrations of a dilution, respectively. The third column of the table gives the heat effects of the individual measurements (negative values of ΔH indicate heat evolved) in this concentration interval calculated per mole of sodium chloride, and the fourth column gives the average of the individual measurements and the probable error, exclusive of any systematic errors. The reproducibility of the measurements is better than 2% except at the lowest concentrations, where there is an uncertainty of 3%.
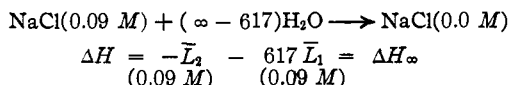
III. Discussion

The data of Table I are plotted against the square root of the molality (weight and volume concentrations differ inappreciably in this concentration range) in Fig. 1. Without the extrapolation to infinite dilution, only so-called "intermediate" heats of dilution could be read from the curve and only differences in the values of the relative partial molal heat

⁴ Lange and Monheim, Z. physik. Chem., A149, 51 (1930).

contents could be calculated. For example, ΔH here is an intermediate heat of dilution

$$NaCl(0.09\ M) + 770H_2O \longrightarrow NaCl(0.04\ M)$$

$$\Delta H = \bar{L}_2 + 1387\,\bar{L}_1 - \bar{L}_2 - 617\,\bar{L}_1$$
$$\quad\ (0.04\ M)\quad (0.04\ M)\quad (0.09\ M)\quad (0.09\ M)$$

When the final concentration of a dilution is zero, or when the measurements can be extrapolated to infinite dilution, ΔH becomes the integral heat of dilution, as

$$NaCl(0.09\ M) + (\infty - 617)H_2O \longrightarrow NaCl(0.0\ M)$$

$$\Delta H = -\bar{L}_2 - 617\,\bar{L}_1 = \Delta H_\infty$$
$$\quad\ (0.09\ M)\quad (0.09\ M)$$

The measurements were extended to $3.85 \times 10^{-4}\ M$, from which point an extrapolation to infinite dilution could be made with a probable error of less than one calorie, since below $0.12\ M$ the heats of dilution were
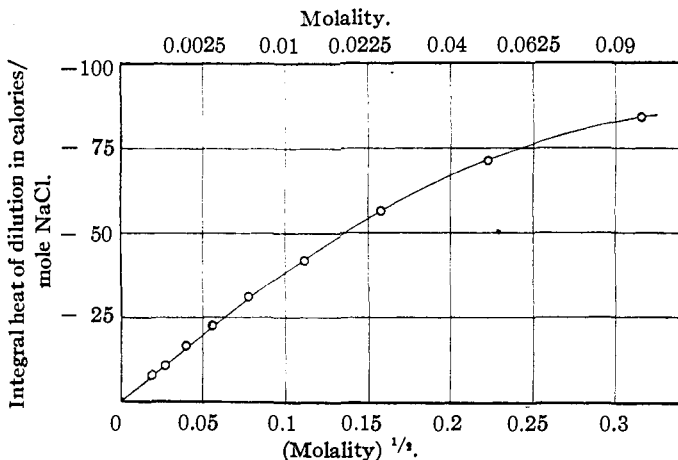

Fig. 1.—Integral heats of dilution of aqueous NaCl solutions at 25°.

found to be proportional to the square root of the molality within the experimental error of 2–3%. In this concentration region the integral heat of dilution per mole of sodium chloride is given by $\Delta H_\infty = -378\ \sqrt{m}$ calories.[5]

Lange and Messner[6] reported -23 calories as the heat of dilution, per mole of salt, of a $0.01\ M$ solution to $0.00138\ M$ at 25°. Interpolation of the results reported here gives -23.7 calories, in good agreement.

[5] The "limiting law" for the integral heat of dilution of 1–1 type salts, using Wyman's dielectric constant measurements [*Phys. Rev.*, **35**, 623 (1930)], and taking account of a correction pointed out by Scatchard [THIS JOURNAL, **53**, 2037 (1931)], is $\Delta H_\infty = -475\ \sqrt{m}$ calories per mole of salt. For a discussion of causes of deviation from the theoretical limit, see Lange and Robinson, Ref. 1.

[6] Lange and Messner, *Z. Elektrochem.*, **33**, 439 (1927).

Naudé[7] measured heats of dilution of sodium chloride in the concentration range 0.3–0.003 M at 18°. These values, when corrected to 25° using Rossini's tabulation of specific heats,[8] do not fit a smooth curve (see Fig. 2) and are evidently not of a high order of accuracy.

At higher concentrations Randall and Bisson[9] worked between 6.12 M (saturated solution) and 0.18 M, determining chiefly relative partial molal heat contents of water by direct measurement in this concentration range. Richards and Rowe[10] reported dilution measurements extending from 2.22 to 0.139 M at 20° and Pratt[11] measured intermediate heats of dilution between 2.22 and 0.25 M at 24 and 26°, as well as at other temperatures. Wüst and Lange[12] measured integral heats of solution of the salt to various concentrations down to 0.426 M at 25°, from which data intermediate heats of dilution are easily obtained.
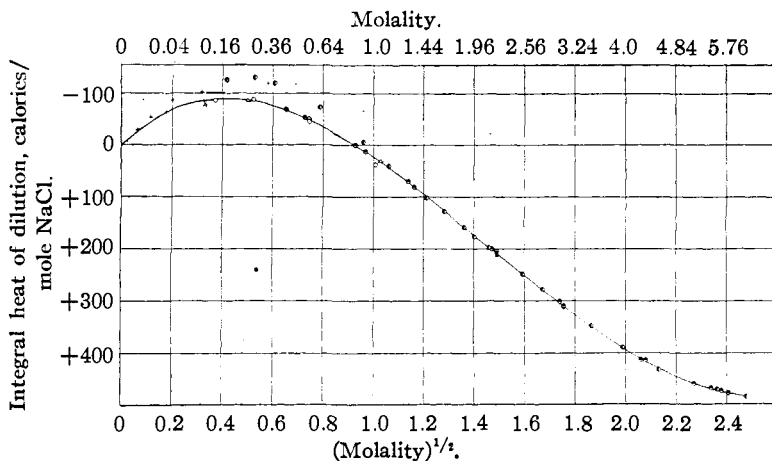

Fig. 2.—Integral heats of dilution of aqueous sodium chloride solutions at 25°: +, Naudé 18° (corrected to 25°); ○, Richards and Rowe, 20° (corrected to 25°); ◑, Randall and Bisson, 25°; △, Pratt (mean of 24° and 26°); ◓, Lange and Wüst; curve to A, these results.

To obtain integral heats of dilution for the complete concentration range up to saturation, and to calculate $\bar{L}_1$ and $\bar{L}_2$, our results (represented by the curve of Fig. 2 to A) were plotted on a large scale and fitted with the various measurements at higher concentrations. The data of Richards and Rowe were recalculated to 25°, using the temperature coefficient reported by them for possibly greater consistency, rather than the com-

[7] Naudé, Z. Elektrochem., 33, 532 (1927).

[8] Rossini, Bur. Standards J. Research, 4, 313 (1930).

[9] Randall and Bisson, THIS JOURNAL, 42, 347 (1920).

[10] Richards and Rowe, ibid., 43, 770 (1921).

[11] Pratt, J. Franklin Inst., 185, 663 (1918).

[12] Wüst and Lange, Z. physik. Chem., 116, 161 (1925).

piled specific heats of Rossini. The average of Pratt's values at 24 and 26° was used. The various measurements can be consistently combined except for the data obtained by Randall and Bisson in the more dilute region of the concentration range studied by them. The data of Lange and Wüst, Richards and Rowe and Pratt fall excellently on a smooth curve which can be joined to the measurements reported here with an uncertainty of only a few calories. Randall and Bisson added small amounts of water to definite amounts of solutions; the heat effects were very small (ranging from 0.01 to 3 calories per mole of water from 0.16 to 1.0 M according to Table III) and certainly subject to a fairly large percentage error, while the measurements of the other investigators involved much larger heat effects and are probably relatively more accurate. Moreover, they agree very well with each other, particularly so considering the different experimental techniques. The smoothed curve has therefore been drawn without considering the more dilute measurements of Randall and Bisson. From 1 M to saturation all the different sets of data agree very well. The measurements of Naudé are not of a high order of accuracy and have not been considered in drawing the portion of the curve to A.

Randall and Bisson reported that the further dilution of a 0.278 M solution produced only a small heat effect and estimated 2 calories as the amount of heat *absorbed* in the dilution from 0.278 M to infinite dilution. From the curve of Fig. 2 a value of 87 calories is read as the heat *evolved* in this process. It seems quite probable that extrapolations of heat of dilution measurements for other salts from concentrations where heat is still being absorbed by the dilution are also considerably in error.

In Table II are given the integral heats of dilution (the heat absorbed in diluting a solution containing one mole of sodium chloride at the concentration shown in the first column of the table to infinite dilution) as read from the smoothed curve of Fig. 2.

The most convenient and accurate method for obtaining values for $\bar{L}_1$ and $\bar{L}_2$ (the relative partial molal heat contents of water and sodium chloride, respectively) is that of Rossini.[13] From the definitions of $\bar{L}_1$ and $\bar{L}_2$ it can be shown that

$$\bar{L}_1 = \frac{m}{2(55.508)} \frac{d}{dm^{1/2}}(\Delta H_\infty) \text{ and } \bar{L}_2 = -\Delta H_\infty - \frac{m^{1/2}}{2} \frac{d}{dm^{1/2}}(\Delta H_\infty)$$

and from the plot of ΔH_∞ against $m^{1/2}$ in Fig. 2 values of the required slope are obtained and $\bar{L}_1$ and $\bar{L}_2$ are readily calculated. Table III gives the values of $\bar{L}_1$ and $\bar{L}_2$ so obtained and Fig. 3 shows a plot of these values against $m^{1/2}$.

The evolution of heat by the dilution of sodium chloride solutions below 0.2 M produces a minimum in the values of $\bar{L}_1$ and a maximum in the values of $\bar{L}_2$ at about 0.15 M. The values of $\bar{L}_1$ do not rise gradually

[13] Rossini, *Bur. Standards J. Research*, **6**, 799 (1931).

TABLE II		TABLE III		
INTEGRAL HEATS OF DILUTION OF AQUE-OUS SODIUM CHLORIDE SOLUTIONS AT 25°		RELATIVE PARTIAL MOLAL HEAT CONTENTS OF AQUEOUS SODIUM CHLORIDE SOLUTIONS AT 25[a]		
Concentration, moles/1000 g. H_2O	ΔH_∞ calories/mole NaCl	m, moles/1000 g. H_2O	L_1, calories/mole	L_2, calories/mole
0.0001	− 3.5	0.0001	−0.0000054	5.4
.001	−11.9	.001	− .00011	17.9
.005	−27	.005	− .0012	40.4
.01	−38	.01	− .0034	64
.05	−70	.05	− .0196	94
.1	−83	.1	− .0247	102
.2	−90	.2	− .0112	90
.4	−72	.4	.37	28
.6	−42	.6	1.05	− 48
.8	− 9	.8	1.95	−120
1.0	23	1.0	2.98	−188
1.5	105	1.5	6.39	−343
2.0	177	2.0	10.2	−466
2.5	224	2.5	13.7	−556
3.0	304	3.0	17.5	−626
3.5	355	3.5	20.3	−671
4.0	395	4.0	21.2	−688
4.5	427	4.5	20.9	−683
5.0	453	5.0	19.6	−656
5.5	470	5.5	15.8	−620
6.12	483	6.12	9.2	−570
		$L_2(s) = -930$[b]		

[a] Harned and Nims [THIS JOURNAL, **54**, 423 (1932)] report values for $\bar{L}_2$ referred to $\bar{L}_2$ (0.1 M) obtained from electromotive force measurements. In general the agreement with these results is only fair.

[b] Calculated from the data of Wüst and Lange.

from a value of zero, as previously reported,[14] but are negative up to 0.24 M, at which concentration $\bar{L}_1$ again has a zero value, and above this point increases gradually, reaching a maximum at about 4 M. $\bar{L}_2$ is also zero at infinite dilution by convention and has positive values up to about 0.45 M, at which concentration $\bar{L}_2$ again has a zero value, and above this point is negative, reaching a minimum at 4 M. This is of particular significance for the temperature coefficient of the activities of the sodium chloride and water since d ln $a_1/dT = -\bar{L}_1/RT^2$, and the temperature coefficient of the mean activity coefficient of the salt is given by d ln $f_\pm/dT = -\bar{L}_2/2RT^2$. At 25° f_{NaCl} is decreasing with rising temperature below 0.45 M and increasing above this concentration;[14a] the activity

[14] Randall and Bisson, THIS JOURNAL, **42**, 361 (1920).

[14a] The activity coefficient measurements of Harned and Nims [THIS JOURNAL, **54**, 423 (1932)], extending over the temperature range 0–40°, confirm this prediction qualitatively, although below 0.5 M the trend in the values of the activity coefficients with temperature is probably not greater than the uncertainty in these values.

of the water is increasing with rising temperature up to 0.24 M and decreasing above this concentration.   This means that a plot of the activity coefficients of sodium chloride at various temperatures against the concentration will show intersections of the curves by each other.   Since, in general, for the same concentration of salt, a more negative integral heat of dilution means a more positive value of $\overline{L}_2$ and since, in the cases
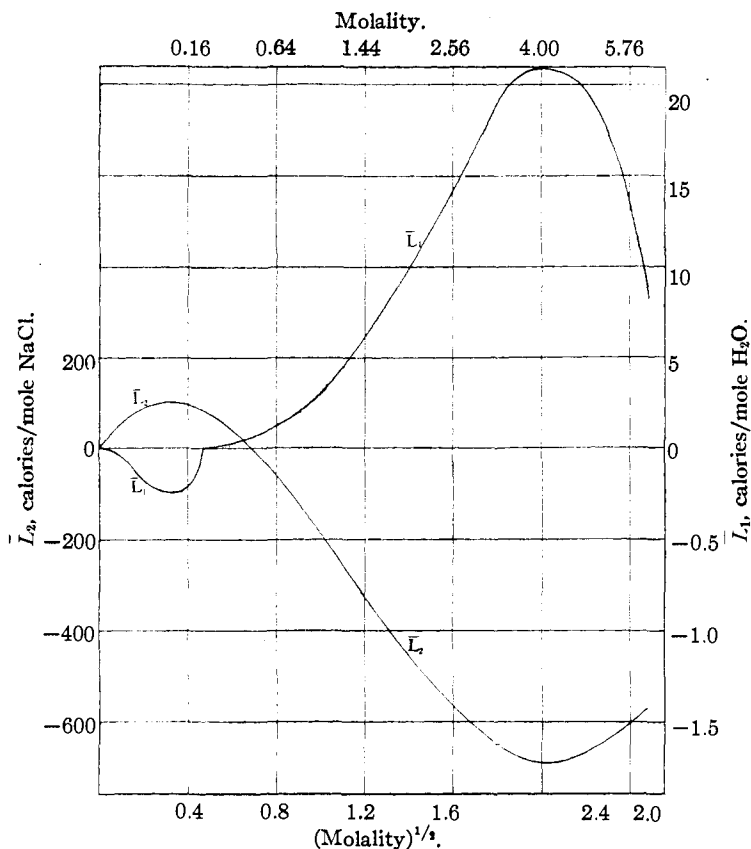

Fig. 3.—Relative partial molal heat contents in aqueous NaCl solutions at 25°

studied so far,[15] the integral heats of dilution become more negative with increasing temperature, it follows that the points of intersection of activity coefficient curves for the same salt at different temperatures will be found at higher concentrations at higher temperatures.   For example, the plot of the activity coefficients of sodium chloride at 24, 25 and 26° against the concentration should show these three curves intersecting at about 0.45 M; below 0.45 M $f_{24°}$ should have the highest value and $f_{26°}$ the smallest value, while above 0.45 M the order of the curves should be

[15] Lange and Monheim, Z. physik. Chem.. 150A, 349 (1931).

reversed. A similar plot of activity coefficients at 34, 35 and 36° should show the same reversal of order but the intersection should be at a higher concentration.

Curves representing $\bar{L}_1$ values for sodium nitrate, sodium chlorate and sodium bromate[16] plotted against $m^{1/2}$ show similar intersections below 0.1 M as do similar curves for sodium sulfate, potassium sulfate, rubidium sulfate and cesium sulfate.[17] It follows that the $\bar{L}_2$ curves for these two series of salts must also intersect and therefore the relative order of their activity coefficients may show the same reversal that has been discussed above for sodium chloride. The possibility of such a reversal would of course depend upon the actual values of the activity coefficients, as determined by freezing point measurements for instance, as well as the actual $\bar{L}_2$ values. Accurate measurements of activity coefficients have not in general been extended to the same dilution as heat of dilution measurements, so that it is not possible to discuss the question quantitatively. It seems possible, however, that anomalies observed in a comparison of the order of the integral heats of dilution of series of salts with a common ion with the order of their activity coefficients[18] may be attributable to this cause. The extension of precise activity coefficient measurements to very small concentrations would be desirable in this connection.

Summary

The intermediate heats of dilution of aqueous sodium chloride solutions have been measured in the concentration range 0.1–0.000385 M at 25° and have been combined with the results of other investigators at higher concentrations to compute the integral heats of dilution and the relative partial molal heat contents of the components from infinite dilution to saturation.

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[16] Lange and Robinson, Z. physik. Chem., **148A**, 146 (1930).

[17] Lange and Streeck, ibid., **157A**, 23 (1931).

[18] Lange and Streeck, Naturwissenschaften, **19**, 359 (1931); Lange and Robinson, Chem. Rev., **9**, 89 (1931).