As regards the mass-action law, it cannot be said that this law has been shown to be a limiting form of the conductance function in the case of aqueous solutions of strong electrolytes. It is possible that the conductance curve for potassium chloride might be fitted within the limits of error with a value $K = 0$, by slightly reducing the value of m. However, it is equally possible that values of K greater than 0.001 might be employed. In fact, they may be so employed, although they will not reproduce the experimental results quite as closely as the constants given above. Nevertheless, the curves fall within the limit of experimental error. A change of less than 0.05% in a few experimental points might admit a value of K as high as 0.01 or even 0.015. With present experimental material, however, it would be profitless to attempt a solution of this problem.

Finally, it should be borne in mind that the mass-action law is a limiting expression which is approached more or less closely, but which is never fulfilled exactly. As our experiments become more precise, the limits within which it holds constantly recede. The manner in which the limiting form is approached under given conditions depends upon the nature of the solvent and that of the electrolyte while, for a given combination of solvent and electrolyte, it depends upon the temperature. In the case of solutions which exhibit a K', C-curve concave toward the C-axis, the limiting value is approached asymptotic to the K'-axis.

WORCESTER, MASS.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF ILLINOIS.]

A STUDY OF THE HEATS OF DILUTION OF CERTAIN AQUEOUS SALT SOLUTIONS.[1]

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A. Introduction.

1. Purpose of the Investigation.—A series of investigations[2] undertaken in this laboratory with the object of studying ionic relationships in aqueous solutions of mixed strong electrolytes has indicated the formation of higher order compounds in the ionization process, in harmony with Werner's ideas in regard to its mechanism.

The method of investigation in the papers referred to has been to study the equilibria between aqueous and metallic solutions, using mixed salt

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[1] From a thesis submitted to the Graduate School of the University of Illinois by Allen Edwin Stearn in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] G. McP. Smith, *Am. Chem. J.*, **37**, 506 (1907); THIS JOURNAL, **32**, 502 (1910); **35**, 39 (1913); Smith and Ball, *Ibid.*, **39**, 179 (1917); Smith and Braley, *Ibid.*, **39**, 1545 (1917); **40**, 197 (1918); Smith and Rees, *Ibid.*, **40**, 1802 (1918).

solutions and liquid amalgams. The measurement of some colligative property of aqueous solutions seemed to offer a means of testing these ideas from another point of attack, and consequently it was planned in this investigation to measure the reversible molal heats of dilution of certain mixed salt solutions and to compare these with the heats of dilution of solutions of the single salts.

2. **Heats of Dilution.**—The reversible molal heat of dilution, L_D, of an aqueous solution at any concentration is represented by the difference in the heats of vaporization of one mol of water from a solution of that concentration and from pure water.

Thus: $L_D = \bar{L}_v - L_v$.

Here L_D is the reversible molal heat of dilution, $\bar{L}_v$ is the heat of vaporization of one mol of water from the solution in question, and L_v is the heat of vaporization of one mol of water from pure water.

But $$L = RT^2 \frac{d(ln\ p)}{dT}.$$

Or $$L_D = RT^2 \frac{d\ ln\ p/p_0}{dT}.^{1}$$

Without a large mass of experimental data on the partial vapor pressure of water in solutions of various concentrations and at various temperatures, there is no method of calculating the value of L_D without assuming Raoult's law for cases for which we know it does not hold. For dilute solutions where Raoult's law does hold the ratio p/p_0 approaches unity so that L_D is zero. In concentrated solutions, however, "or in dilute solutions where the process of dilution is associated with the formation of new molecular complexes, or with the decomposition of those already occurring, the heat of dilution may have a positive or negative value."[2]

If, now, one should measure the reversible molal heat of dilution for a given concentration of solutions of single salts, and then for an equivalent concentration of a solution of the mixed salts, one might expect to find the value in the latter case to be somewhere near the sum of the other values unless affected by the formation of new molecular complexes.

B. Materials.

The strontium chloride was in the form of "pure crystals." Most of the material was recrystallized once from water. This procedure in the light of our results seems unnecessary when it is considered that the heat effects in solutions as concentrated as 0.2 N are so small as to be hardly measureable. The sodium and potassium chlorides were of various brands, all labeled C. P. These materials are easy to obtain in a state of high purity, and inasmuch as small amounts of impurities have no effect

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[1] Kirchhoff, *Pogg. Ann.*, **104**, (1856); *Ges. Abh.*, p. 492.

[2] Nernst, "Theoretical Chemistry," Trans. 6th Ger. Ed., p. 143.

on the results in this work, it was considered unnecessary to purify them further.

C. Apparatus.

The apparatus was a very slight modification of the adiabatic calorimeter of MacInnes and Braham.[1] The instrument itself was that actually employed by Braham, as were the thermometers, Wheatstone bridge, standard cells, etc.

A calorimetric determination of a positive heat effect consisted of measuring the change in resistance of a coil of platinum wire due to the direct dilution of a certain quantity of solution of a certain concentration with a certain quantity of water. Next, a carefully measured quantity of electrical energy was introduced into the solution and the corresponding change in resistance of the same coil measured. For negative heats a slightly different procedure was followed where these heats were comparatively large. In such cases the procedure was to introduce electrical energy into the solution at a carefully measured rate slightly more rapidly than it was taken up in dilution, so that the solution did not cool down below the temperature of the surroundings. The reason for this is that it is much easier to adjust the surroundings to a rising temperature in the calorimeter by means of heating coils, than to a decreasing temperature in the calorimeter where the cooling of the surroundings could not be closely regulated with any degree of satisfaction. After finishing the run as described above, one can calculate the number of calories corresponding to the electrical energy introduced, and the actual number of calories corresponding to the increase in temperature as measured by the change in resistance of the thermometer. The difference is the number of calories due to the heat of dilution. By this procedure the heat capacity of the calorimeter is measured as a part of every determination, and thus inaccuracies due to calculations from questionable data on specific heats of solutions, water equivalent of the calorimeter, slightly varying conditions of the experiments, uncertainties arising from the calibration of the thermometer, etc., are eliminated. Thus by a simple proportion the heat of dilution can be obtained at once. For if H_D is the heat due to dilution, expressed in joules, then

$$H_D : EIT = R_D : R_E,$$

where E is electromotive force, I the current, and T the time in seconds during which the current is passed through the calorimeter heater. R_D and R_E are the changes in temperature, in resistance units, due respectively to the dilution and to the electrical heating.

Or $$-H_D \text{ (in calories)} : \frac{EIT}{J} = R_D : R_E$$

where J represents Joule's equivalent, 4.184 joules per calorie.

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[1] MacInnes and Braham, This Journal, 39, 2110 (1917).

Since the relation between the change in resistance and the temperature change is not linear, any large values of R_D or R_E would have to be corrected by means of the relation

$$\Delta t = \frac{100}{(R_{100} - R_0)\left(1 + \frac{d'}{100} - \frac{2d'T}{100^2}\right)} \Delta R$$

in which R_{100} is the resistance of the thermometer in steam at 760 mm. pressure, R_0 is its resistance in melting ice, and d' is an empirical constant. MacInnes and Braham determined R_{100} and R_0 for the thermometers employed, and used for d' the value 1.47, recommended by the Bureau of Standards. They found, however, that with the values of R_D and R_E of the magnitude met with in their work, which were even greater than those met with in this investigation, the correction was too small to affect their numerical results in any way; so that if $\Delta R = 0.02395$, then $\Delta t = 0.2395$, just 10 times the numerical value of ΔR.

D. Method.

The salt solutions were made on the basis of gram equivalents of anhydrous salt per 1000 g. of water. Their concentration was ascertained by a Volhard determination of the chlorine. The salts used were sodium chloride, potassium chloride and strontium chloride; and the concentrations at which the heats of dilution were determined were 0.2, 0.4, 0.8, 1.6 and 3.2 weight normal.[1] Points on the strontium chloride curve were also obtained for concentrations of 1.2, 2.0, 2.4 and 2.8 wt. N. Mixed salt solutions of NaCl : $^1/_2$ $SrCl_2$,NaCl : KCl, KCl : $^1/_2$ $SrCl_2$,and KCl : $SrCl_2$ were also run at the above mentioned concentrations. These solutions were prepared by diluting a volume of the solution of one of the salts with an equal volume of the solution of the same concentration of the other salt. Thus one volume of 0.8 wt. N potassium chloride and one volume of 0.8 wt. N sodium chloride were mixed and called 0.8 wt. N of the mixed salt.

The value of the reversible molal heat of dilution was obtained by diluting the solution of a definite concentration with decreasing amounts of water, and plotting the heat effects obtained against the number of mols of water added. The curve was found to be a straight line (within this region) so that, by extrapolation to zero mols of water added, the value of the reversible molal heat of dilution at the particular concentration could be obtained.

Accuracy.—The very small values of the heat effects in the case of the more dilute solutions necessitated only approximate results here. MacInnes and Braham state that heat effects of from 50 to 60 calories

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[1] Weight normal or wt. N is the number of gram equivalents of anhydrous salt per 1000 g. of water.

can be measured with an accuracy of from 4 to 5%.[1] With a total heat effect of from 5 to 20 calories one should not expect much more than 30 to 50% accuracy. In these cases, however, an error of even 100% would change the point on the curve of the concentration plotted against the molal heat effect to such a slight extent that the curve itself would be unaffected. In the case of the larger heat effects, running as high as 600 to 700 calories, the heat change can be measured to within 0.25 to 0.5%, so that the error of the reversible heat value should not be greater than 1 to 2%.

Some justification for the assumption that the molal heat values obtained by diluting a certain quantity of solution with varying amounts of water give a straight line when plotted against the number of mols of water of dilution is given in Fig. 1. The data for these curves are taken from Tables IV and VII. According to Thomsen[2] "the value of the thermal change on dilution always varies with variations in the quantity of water of dilution, and this variation, whether positive or negative, seems to have the character of a hyperbolic function of the quantity of water added." As will be seen, the region of the curve on which the experimental data represented in all the subsequent curves fall is so far from the vertex that the change of slope of the curve has become vanishingly small, and it is practically a straight line. (In Fig. 1, mols of water of dilution per 10,000 g. of solution are plotted as abscissas, and the molal heat effects as ordinates.)

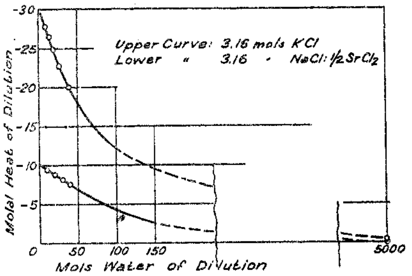

Fig. 1.—Change of molal heat effect with the number of mols of water of dilution over a wide range.

E. Experimental Results.

Tables I to VIII give the data for the heats of dilution of various salt solutions and mixtures. Table I gives in considerable detail the results of a run including resistance readings, results of potentiometer readings, etc. Table I is for the case of a negative heat effect, and a sample calculation from the data included in the table is appended.

In this table, "Time" is the time in seconds during which heat is passed through the calorimeter heater; "Res." is the resistance of the thermometer in ohms; "R" is the change of resistance of the thermometer in ohms multiplied by 10^5; "Sol. G." represents the number of grams of solution to be diluted; "Mols H_2O" represents the number of mols of water (assuming 18 g. to the mol) with which the solution was diluted;

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[1] It may be stated that to measure the change of resistance due to dilution or to the electrical energy passed into the calorimeter it was *not* necessary to shift a plug in the resistance box.

[2] Pattison Muir, "**Elements of Thermal** Chemistry," p. 167.

"Amp." is the current in amperes through the heating coil of the calorimeter; "E. M. F." is the voltage drop across the terminals of this same coil; "Cal." is the number of calories of electrical energy introduced.

The total heat effect of the dilution is given in calories as well as the molal heat effect. The latter value is obtained from the former by dividing it by the number of mols of water of dilution.

A few curves representative of the method of extrapolation are given. Mols of water of dilution are plotted as abscissas and molal heat effects as ordinates. Fig. 2 gives the curve for 2.9 wt. *N* $SrCl_2$ and that for 0.8 wt. *N* KCl. The size of the plotted point gives an estimate of the probable accuracy of each point. The radius of the circle represents the variation in the molal heat of dilution due to a variation of 0.00001 ohm in the resistance measurement. In the remainder of the data, the values obtained by drawing similar curves are given but the curves themselves are not included.

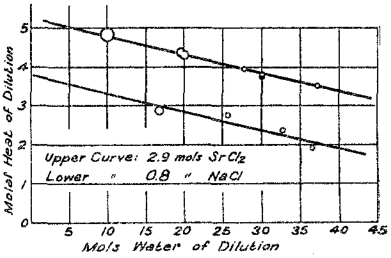

Fig. 2.—Molal heat effect as a function of the amount of water of dilution. (NOTE: Read the ordinates as negative for the NaCl curve.)

Tables III to IX give a condensed summary of some 50 tables of the type of Table I.

TABLE I.—HEAT OF DILUTION OF 3.2 WT. *N* NaCl.

Time. Sec.	Res. Ohms.	$\Delta R \times 10^5$. Ohms.	Sol. G.	H_2O. Mols.	Current. Amp.	E. M. F. Volts.	Free energy. cal.	Total ht. effect. cal.	Heat effect per mol. cal.
	27.41500								
	3205		10,586	27.4					
300		670			2.322	6.635	1105		
	3875								
300		1315			2.305	6.58	1099		
	5190							—546	—19.9
	27.43500								
	2795		10,586	18.45					
300		810			2.335	6.66	1115		
	3605								
300		1260			2.334	6.66	1115		
	4865							—398	—21.6
	27.44500								
	2862		10,586	11.22					
300		946			2.33	6.65	1111		
	3808								
300		1235			2.335	6.66	1115		
	5043							—258	—22.95[a]

Reversible Molal Heat of Dilution, L_D —25.0 cal.

Sample Calculation. If 1115 cals. produce a change in resistance of 1235 units, then 1111 cals. would produce in the same amount of the same solution a change of resistance of 1231 units. The change measured, however, was only 946 units. A quantity of heat, therefore, equivalent to that represented by a change of resistance of 1231 minus 946 or 285 units was used up by dilution. Therefore if 1235 units are equivalent to 1115 cals., 285 units would be equivalent to 258 cals. This value, then would represent the heat effect due to dilution with 11.22 mols of water. The molal heat effect would then be 258 divided by 11.22, or 22.95 cals. The sign would, of course, be negative.

TABLE II.—HEAT OF DILUTION OF NaCl SOLUTIONS.

Concentration. Wt. *N*.	Solution. G.	Water of dilution. Mols.	Total heat of dilution. cal.	Molal heat of dilution. cal.	Reversible molal heat of dilution. L_D cal.
3.2	10,586	27.4	—546	—19.9	
		18.45	—398	—21.6	
		11.22	—258	—22.95	—25.0
1.6	8,280	34.83	—245	—7.04	
		22.06	—179	—8.06	
		11.75	—102	—8.67	
		7.83	—71.1	—9.08	—9.80
0.8	7,986	36.45	—70.0	—1.92	
		32.86	—77.8	—2.37	
		25.65	—70.9	—2.76	
		16.75	—48.44	—2.89	—3.93
0.4	7,900	37.72	—29.62	—0.79	
		25.58	—24.09	—0.94	
		21.5	—25.38	—1.18	
		16.5	—21.15	—1.28	
		12.47	—17.16	—1.38	
		8.86	—12.48	—1.41	—1.60
0.2	9,300	28.8	—17.64	—0.61	
		23.4	—17.9	—0.765	
		18.11	—13.4	—0.74	
		14.6	—10.0	—0.69	—0.85

TABLE III.—HEAT OF DILUTION OF KCl SOLUTIONS.

Concentration. Wt. *N*.	Solution. G.	Water of dilution. Mols.	Total heat of dilution. cal.	Molal heat of dilution. cal.	Reversible molal heat of dilution. L_D cal.
3.16	8,410	39.0	—781.0	—20.03	
		26.55	—604.3	—22.76	
		19.4	—484.0	—24.94	
		14.4	—382.2	—26.48	
		9.4	—261.2	—27.79	—30.0
1.6	8,000	40.0	—289.5	—7.24	
		30.0	—246.7	—8.22	
		20.0	—177.2	—8.87	
		10.0	—103.3	—10.33	—10.80
0.8	8,000	40.0	—70.68	—1.77	
		30.0	—64.9	—2.16	
		20.0	—48.8	—2.44	
		10.0	—27.8	—2.78	—3.20

TABLE III (*continued*).

Concentration. Wt. *N*.	Solution. G.	Water of dilution. Mols.	Total heat of dilution. cal.	Molal heat of dilution. cal.	Reversible molal heat of dilution. L_D cal.
0.4	8,000	34.95	−15.0	−0.43	
		30.0	−13.42	−0.45	
		25.0	−14.1	−0.564	
		20.0	−12.44	−0.622	
		15.0	−10.0	−0.67	−0.95
0.2	7,850	40.0	−2.74	−0.069	
		38.2	−2.92	−0.076	
		34.0	−3.2	−0.094	
		30.0	−3.1	−0.103	
		30.0	−3.25	−0.108	−0.24

TABLE IV.—HEAT OF DILUTION OF $SrCl_2$ SOLUTIONS.

Concentration. Wt. *N*.	Solution. G.	Water of dilution. Mols.	Total heat of dilution. cal.	Molal heat of dilution. cal.	Reversible molal heat of dilution. L_D cal.
3.2	10,000	35.0	189.0	5.4	
		15.0	95.7	6.4	7.2
2.9	9,500	37.2	129.8	3.49	
		30.0	112.4	3.75	
		30.0	114.1	3.80	
		27.7	109.2	3.95	
		20.0	86.33	4.31	
		19.5	85.44	4.38	
		10.0	48.5	4.85	5.40
2.4	10,000	35.0	33.7	0.96	
		25.0	32.5	1.29	2.10
2.0	10,000	35.0	35.5	1.01	
		25.0	31.0	1.23	1.75
1.55	10,000	40.0	23.64	0.59	
		30.0	21.4	0.71	
		30.0	20.92	0.70	
		20.0	17.3	0.86	1.11
1.2	10,000	35.0	18.9	0.54	
		25.0	16.3	0.65	0.90
0.8	10,000	40.0	15.4	0.38	
		30.0	13.0	0.44	
		20.0	10.0	0.50	0.62
0.425	10,000	40.0	11.16	0.28	
		30.0	10.07	0.34	
		20.0	7.4	0.37	0.50
0.2	10,000	40.0	7.88	0.20	
		30.0	6.81	0.23	
		20.0	4.0^{+}	0.2^{+}	0.25 ±

TABLE V.—HEAT OF DILUTION OF NaCl : KCl SOLUTIONS.

Concentration. Wt. *N*.	Solution. G.	Water of dilution. Mols.	Total heat of dilution. cal.	Molal heat of dilution. cal.	Reversible molal heat of dil. L_D. Obs.	Reversible molal heat of dil. L_D. Calc.
3.2	10,000	40.0	—780.0	—19.5		
		30.0	—658.0	—21.9		
		20.0	—468.0	—23.4		
		10.0	—256.0	—25.6	—27.8	—20.6
1.6	10,000	40.0	—286.6	—7.16		
		30.0	—230.7	—7.70		
		20.0	—165.1	—8.30		
		10.0	—88.6	—8.86	—9.40	—7.13
0.8	10,000	40.0	—58.54	—1.46		
		30.0	—52.6	—1.75		
		20.0	—39.25	—1.96		
		10.0	—23.8	—2.38	—2.60	—2.55
0.4	10,000	35.0	—21.0	—0.60		
		25.0	—16.0	—0.65		
		15.0	—10.4	—0.70	—0.77	—1.01
0.2[a]	10,000	40.0	—7.2	—0.18		
		30.0	—5.8	—0.19	—0.2	—0.55

[a] Another run gave a non-measureable result probably due to the fact that equilibrium between the solution and the dilution water had not been reache.d

TABLE VI.—HEAT OF DILUTION OF NaCl : 1/2 SrCl$_2$ SOLUTIONS.

Concentration. Wt. *N*.	Solution. G.	Water of dilution. Mols.	Total heat of dilution. cal.	Molal heat of dilution. cal.	Reversible molal heat of dil. L_D. Obs.	Reversible molal heat of dil. L_D. Calc.
3.2	10,000	40.0	—303.0	—7.58		
		30.0	—246.6	—8.22		
		20.0	—177.0	—8.85		
		10.0	—95.0	—9.50	—10.20	—8.70
1.6	10,000	40.0	—108.8	—2.72		
		30.0	—93.8	—3.13		
		20.0	—70.2	—3.51		
		10.0	—36.6	—3.65	—4.20	—3.30
0.8	10,000	40.0	—28.2	—0.70		
		30.0	—25.7	—0.86		
		15.0	—16.1	—1.07	—1.30	—1.18
0.4	10,000	40.0	—8.65	—0.22		
		20.0	—6.0	—0.30	—0.40	—0.60
0.2	10,000	40.0	—5.0	—0.12		
		25.0	—3.0	—0.12	—0.1	—0.2

TABLE VII.—HEAT OF DILUTION OF KCl : 1/2 $SrCl_2$ SOLUTIONS.

Concentration. Wt. N.	Solution. G.	Water of dilution. Mols.	Total heat of dilution. cal.	Molal heat of dilution. cal.	Reversible molal heat of dil. L_D.	
					Obs.	Calc.
3.2	10,000	40.0	—575.0	—14.37		
		30.0	—472.0	—15.70		
		20.0	—343.5	—17.2		
		10.0	—189.0	—18.9	—20.5	—9.7
(Duplicate Run)						
3.2	10,000	35.0	—514.8	—14.72		
		25.0	—412.0	—16.48		
		15.0	—269.3	—17.95	—20.7	
1.6	10,000	40.0	—168.5	—4.21		
		30.0	—142.0	—4.75		
		20.0	—102.0	—5.10		
		10.0	—54.3	—5.43	—6.0	—2.6
(Duplicate Run)						
1.6	10,000	35.0	—150.5	—4.30		
		25.0	—121.3	—4.86		
		15.0	—77.0	—5.15	—6.0	
0.8	10,000	40.0	—32.4	—0.81		
		30.0	—27.9	—0.93		
		20.0	—20.2	—1.01	—1.22	—0.53
0.4	On four dilutions there was no certain effect measured.					
					—0.00	—0.00
0.2	Since the 0.4 wt. N solution gave a value which was too small to be measured, no dilutions were made on this solution. The observed value may be safely assumed to be zero. The calculated value is zero.					

TABLE VIII.—HEAT OF DILUTION OF KCl : $SrCl_2$ SOLUTIONS.

Concentration. Wt. N.	Solution. G.	Water of dilution. Mols.	Total heat of dilution. cal.	Molal heat of dilution. cal.	Reversible molal heat of dil. L_D.	
					Obs.	Calc.
3.2	10,000	35.0	—375.0	—10.66		
		25.0	—297.1	—11.88		
		15.0	—184.6	—12.30	—14.0	—3.9
1.6	10,000	35.0	—96.06	—2.75		
		25.0	—86.47	—3.46		
		15.0	—60.80	—4.06	—5.2	—0.6
0.8	10,000	35.0	—18.6	—0.53		
		25.0	—16.5	—0.66		
		15.0	—15.6	—1.04	—1.3	—0.0

F. Discussion.

Figs. 3 to 7 show graphically the change of the reversible molal heat of dilution with the concentration for the various solutions studied. The concentrations expressed in terms of weight normality, are plotted as abscissas; while the heats of dilution in calories per mol of water of dilution, are plotted as ordinates. Fig. 3 shows this for the 3 single salts, by means of curves, plotted to the same scale. Figs. 4 to 7 show the change of the heat of dilution of the various salt mixtures with their concentrations. There are 2 curves in each of these 4 figures. The one labeled "Obs." gives the curve as it was observed experimentally, while the one marked "Calc." is plotted from data calculated on the assumption that the heat of dilution of a mixed salt solution is equal to the sum of the heats of dilution of solutions of the various constituents at concentrations equivalent to their concentrations in the mixed solution.

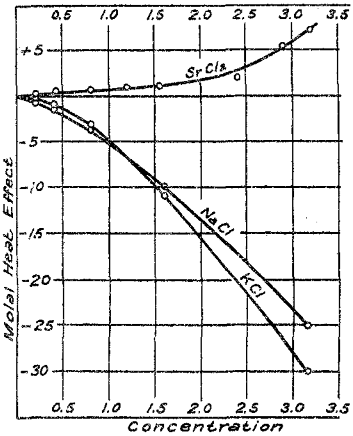

Fig. 3.—Reversible molal heat of dilution as a function of the concentration for solutions of the salts $SrCl_2$, NaCl and KCl.

It will be noted at once that, without exception, the observed values lie on a curve which, except at low concentrations, is significantly lower than the curve for the calculated values. This holds even in the case of the mixed sodium and potassium salts where one might expect the least deviation from the calculated values; and is in harmony with the conclusion[1] that the ion-fraction of one of the metallic constituents increases with increasing total salt concentration, since the two curves, which practically coincide at low concentrations, diverge more and more as the total salt concentration increases. The curve, to be sure, does not indicate which of the ion-fractions increases.

There seems to be no simple relation between the two curves. In the case of the mixture NaCl : 1/2 $SrCl_2$ the divergence is even less than in the case of NaCl : KCl where the least divergence might be expected. These experimental curves, then, seem to be influenced by 3 factors. There are the specific effects of the two salt components, and there is also the very apparent effect of a third species of molecular aggregate, in all probability a molecular complex of the two salts with varying amounts of water. The concentration of these complexes, in equilibrium with their simple components, will be low at low total salt concentrations, and the specific effect on the curve will be slight in that region so that the two curves should tend to come together at low concentrations. This is, as is observed, the case. As the total salt concentration increases, the concentration of these complexes correspondingly increases and the curve is given a component of slope characteristic of them and depending on two things; namely, their individual "heats of dilution" at the concentration at which they occur, which will depend primarily perhaps on their heats of formation; and the rate of change of their concentration with

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[1] Smith and Ball, This Journal, 39, 179 (1917).

the total salt concentration, or in other words, the value of their equilibrium constant.

Thus, if the value of k in the expression

$$\frac{[(\mathrm{KCl})_x \,.\, (\mathrm{NaCl})_y]}{(\mathrm{KCl})^x\,(\mathrm{NaCl})^y} = k$$

is large, and if the complex $[(\mathrm{KCl})_x \,.\, (\mathrm{NaCl})_y]$ has a high heat of dilution we would expect the slope of the experimental curve to be widely divergent from that of the calculated curve, since a substance of high heat of dilution is being rapidly produced with increasing total salt concentration. If the value of k is small the curves will diverge less rapidly.

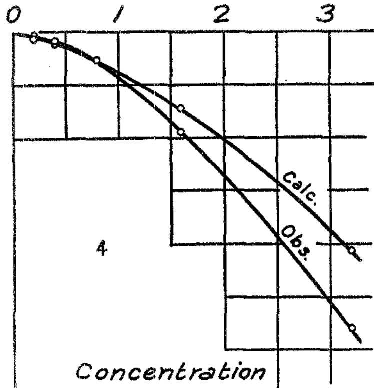

Fig. 4.—Reversible molal heat of dilution as a function of the concentration for the mixed salt solution NaCl:KCl.

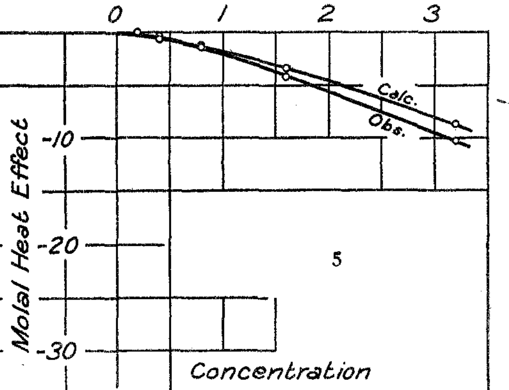

Fig. 5.—Reversible molal heat of dilution as a function of the concentration for the mixed salt solution NaCl·1/2 SrCl₂.

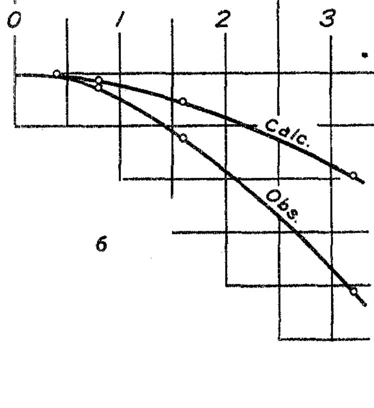

Fig. 6.—Reversible molal heat of dilution as a function of the concentration for the mixed salt solution KCl:1/2 SrCl₂.

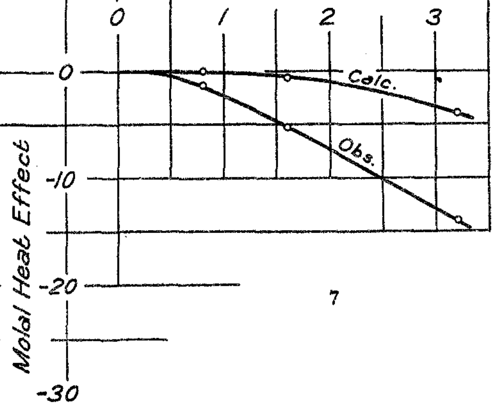

Fig. 7.—Reversible molal heat of dilution as a function of the concentration for the mixed salt solution KCl: SrCl₂.

Table IX gives the results of a short series of experiments in which very large quantities of water of dilution, 5.555 mols H_2O and 10,000 g. of solution, were used. The same tendencies will be noticed as before. In each of the 3 cases of mixed salt solutions the observed value of the molal heat effect is greater (negatively) than the calculated value, a relationship which agrees with those brought out in the curves.

TABLE IX.

Salt.	Conc.	Heat effect. Obs.	Heat effect. Calc.
$SrCl_2$	3.2 wt. *N*	+161	.....
KCl	3.2 wt. *N*	—948	.....
NaCl	3.2 wt. *N*	—1116	.....
NaCl : KCl	3.2 wt. *N*	—1010	—825
NaCl : 1/2 $SrCl_2$	3.2 wt. *N*	—406	—390
KCl : 1/2 $SrCl_2$	3.2 wt. *N*	—542	—350

The assumption of these complexes is not out of harmony with experimental data. The substances $2KCl.SrCl_2$ and $2NaCl.SrCl_2$ have both been prepared and isolated[1] and ions of the type $(SrCl_4)^{--}$ and $(BaCl_4)^{--}$ have been referred to as probably existing in solution.[2] Indeed it seems probable that there are very few types of compounds which do not tend to form "higher order compounds."[3]

As was stated in the introduction, according to Nernst the existence of a measurable heat of dilution seems due to the existence of complexes which are formed or decomposed with dilution.[4]

The thermodynamic expression for the reversible molal heat of dilution, L_D, is

$$L_D = RT^2 \frac{d \ln p/p_0}{dT},$$

where p is the vapor pressure of the solution, and p_0 is the vapor pressure of the pure solvent at the same temperature. For a negative value of L_D, as in the case of potassium and sodium chlorides, the equation tells us that the ratio p/p_0 decreases with the temperature. Thus, if p/p_0 decreases with increasing temperature, it means that p increases more slowly than p_0 with the temperature, and from Raoult's law this would indicate that at higher temperatures there is an increase in the degree of ionization of the salt. A. A. Noyes[5] found experimentally, however, that for salts of this type the opposite was true, namely that the degree of ionization actually decreased with the temperature. There must, therefore, be some factor which aids in determining what this value shall be, other than simple ionization. The heats of ionization can be obtained from a knowledge of the rate of change of the degree of ionization with the temperature, from the relation

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[1] Berthelot and Ilosvay, *Ann. chim.*, [5] **29**, 318 (1885).

[2] Noyes and Falk, THIS JOURNAL, **33**, 1455 (1911).

[3] A. Werner, *Neuere Anschauungen a. d. Gebiete d. Anorg. Chemie*, (1913).

[4] *Loc. cit.*

[5] A. A. Noyes, *Carnegie Inst. Pub.*, **63**, 339 (1907).

$$\frac{d\,ln\,K}{dT} = \frac{Q}{RT^2}.$$

The values calculated from this relationship, however, do not seem to agree with those observed. For instance, Arrhenius gives the energy equation for the ionization of dissolved potassium chloride[1] as

$$KCl = K^+ + Cl^- + 362 \text{ cal.},$$

whereas, when calculated, the value of the heat of ionzation is found to be —2,000 calories. According to Senter, "it seems that the process of ionization must be attended by some exothermic reaction which more than compensates for the heat presumably absorbed in splitting up the molecules." Van der Waals,[2] as well as Werner, has suggested that ionization in aqueous solution is essentially a hydration process and thus the energy necessary for its completion may come from the combination between the ions and water. The heats of ionization are small in comparison with the heats of hydration. Thomsen[3] has found values as high as 8,000 calories per mol. of water combining to form a hydrate. Of the two effects, therefore, this one would predominate. The order of magnitude of the heats of formation of higher order complexes of mixed salts is also great enough to overshadow any ionization effect. A few examples are taken from Pattison Muir's, "Elements of Thermal Chemistry," Appendix I:

$$SiF_4(aq) + 2KF(aq) = K_2SiF_6(aq) + 23{,}000 \text{ cal.}$$
$$NaF + HF = NaHF_2 + 17{,}000 \text{ cal.}$$
$$NH_3 + HCl = NH_4Cl + 42{,}000 \text{ cal.}$$
$$AuBr_3(aq) + HBr(aq) = HAuBr_4(aq) + 7{,}700 \text{ cal.}$$

These heats are all positive. Now it will be noted in the curves in Figs. 4 to 7 that the deviations of the observed values from those calculated are always toward a larger negative heat. That is, with dilution, the complexes existing in the solution are broken up with the absorption of heat.

G. Summary.

1. The reversible molal heat of dilution has been determined for solutions of the single salts, sodium, potassium and strontium chlorides at various concentrations ranging from 3.2 wt. N to 0.2 wt. N, and also for solutions of the mixed salts NaCl : KCl, NaCl : $^1/_2$ $SrCl_2$, KCl : $^1/_2$ $SrCl_2$, and KCl : $SrCl_2$ for the above mentioned range of concentration.

2. The heats of dilution of sodium and potassium chlorides are negative. This fact in the light of the equation

$$L_D = RT^2\,\frac{d\,ln\,p/p_0}{dT},$$

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[1] Senter, *Outlines of Physical Chemistry,* p. 344.

[2] Van der Waals, *Z. physik. Chem.,* **8,** 215 (1891).

[3] Pattison Muir, "Elements of Thermal Chemistry," p. 167.

in which L_D is the molal heat of dilution, indicates an increase in the degree of ionization with the temperature, contrary to the experimental results of A. A. Noyes, unless explained on the basis of the decomposition with dilution, of complexes existing in the solution.

3. The heats of dilution for the solutions of the mixed salts bear no simple additive relation to the heat effects of the single components at equivalent concentrations.

4. The results have been explained on the basis of the conception of higher order compounds as put forth by A. Werner.

URBANA, ILL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

A STUDY OF THE HEATS OF DILUTION OF SOLUTIONS OF BARIUM CHLORIDE AND BARIUM-SODIUM CHLORIDE MIXTURE.[1]

BY G. McP. SMITH, ALLEN E. STEARN AND R. F. SCHNEIDER.

Received August 5, 1919.

In connection with some work done in this laboratory on the heats of dilution of mixed salt solutions of strontium chloride with certain of the alkali chlorides,[1] it was thought to be of interest to measure the reversible molal heats of dilution of solutions of barium chloride and of equivalent mixtures of barium and sodium chlorides, and thus to ascertain whether the results obtained in the case of strontium were unique. The behavior of the barium chloride solution itself would be of interest, inasmuch as the strontium chloride in solution behaves differently from the two uni-univalent salts, sodium chloride and potassium chloride. This is due, perhaps to the bivalent strontium and to its ionization in partial stages to intermediate ions such as the $SrCl^+$ ion. In concentrated solutions this intermediate ion is perhaps almost the only simple ionic form of the strontium.

The sodium and barium chlorides were of various brands, all labeled C. P. Previous work[2] along this same line as well as this work has shown that the heat effects in solutions as concentrated as 0.2 weight normal are so small as to be hardly measurable. Thus, inasmuch as small amounts of impurities have no effect on the results in this work, it was considered unnecessary to purify the salts further.

The apparatus used and the method of measurement were the same as in the work to be described in the next paper.[3]

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[1] From a thesis submitted to the College of Liberal Arts and Sciences of the University of Illinois by R. F. Schneider in partial fulfilment of the requirements for the degree of Bachelor of Science, 1919.

[2] See Wells and Smith, in the February issue.

[3] *Ibid.*