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]

---

[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.*

Experimental Data.

Tables I and II give the heats of dilution of the various solutions studied. For more complete detail regarding the data taken and the methods of calculation of the molal heat effects, see the previous paper.

TABLE I.—HEAT OF DILUTION OF $BaCl_2$ 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. cal.
3.2	10,000	35	—102.0	—2.9[a]	
		35	—95.0	—2.7[a]	
		25	—43.7	—1.8[a]	—2.9[a]
2.8	10,000	35	—26.75	—0.77	
		25	—22.0	—0.88	
		15	—15.3	—1.02	—1.20
1.6	10,000	35	—13.75	—0.394	
		20	— 7.15	—0.41	—0.435

[a] These results are not to be relied on to any great extent, owing to the fact that at this concentration the solution is almost at its saturation point. The most probable indication of the value of the reversible molal heat of dilution is the first or second dilution giving a value of between —2.9 and —3.0 cal./mol.

TABLE II.—HEAT OF DILUTION OF $NaCl:{}^1/_2BaCl_2$ SOLUTIONS.

Concentration. Wt. *N*.	Solutions. G.	Water of dilution. Mols.	Total heat of dilution. cal.	Molal heat of dilution. cal.	Reversible molal heat of dilution. cal.	
					Obs.	Calc.
3.2	10,000	35	—276.5	— 7.89		
		25	—232.0	— 9.3		
		15	—172.2	—11.48	—14.1	—10.25
1.6	10,000	35	—138.0	— 3.94		
		25	—106.2	— 4.25		
		15	— 66.4	— 4.50	—4.93	—3.98
0.8	10,000	35	— 55.2	— 1.57		
		25	— 40.7	— 1.63		
		15	— 25.42	— 1.69	—1.78	—1.50
0.4	10,000	40	— 12.05	— 0.30		
		25	— 13.35	— 0.38		
		15	— 12.6	— 0.50	—0.75	—0.78

Discussion.

Fig. 1 gives the graphical representation of the results of the heats of dilution as taken from the tables. Reversible molal heat effects are plotted as ordinates against concentration, expressed in weight normality, as abscissas.

The barium chloride curve seems to be divisible into two distinct regions; the one up to a concentration of about 1.5 *N* and the other up through the higher concentrations. Comparison with the curve for strontium chloride (see previous paper), which was much more thoroughly worked out experimentally, shows two regions perfectly analogous

---

[1] *Loc. cit.*

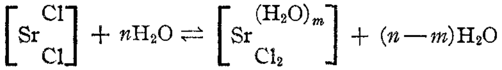
to these.[1] This type of curve is distinct from the type found for the uni-univalent alkali chlorides, the slope of which changes gradually and evenly over the entire length.

The abrupt change of slope in the case of the two bi-univalent salts comes at about the concentration where conductivity data indicate 50% ionization.

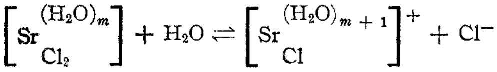
According to Harkins[2] the only type of ionization in solutions of this concentration would be $BaCl_2 \rightleftharpoons BaCl^+ + Cl^-$ and $SrCl_2 \rightleftharpoons SrCl^+ + Cl^-$. The break in the curve, then, seems to come at the point where the above reactions have nearly completed themselves, going from left to right, and the reaction $BaCl^+ \rightleftharpoons Ba^{++} + Cl^-$, or $SrCl^+ \rightleftharpoons Sr^{++} + Cl^-$ is beginning. The equilibrium constant for the second set of reactions is so much smaller than that for the first set that the former would in all probability be completed before the latter would have proceeded to any appreciable extent. Obviously such a condition would correspond to a measured degree of ionization of about 50%.

As will be suggested in the later paper, the heat effects measured seem too large to be accounted for by heats of ionization. If we consider the effects as due to hydration some idea as to the mechanism is suggested in the following, which will help explain the experimental curve.

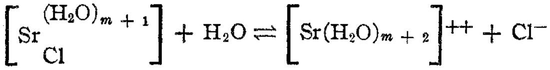
The ionization of strontium chloride has been considered to be due to reactions between water and the salt as follows:[3]



$$\left[\mathrm{Sr}^{\mathrm{Cl}}_{\mathrm{Cl}}\right] + n\mathrm{H_2O} \rightleftharpoons \left[\mathrm{Sr}^{(\mathrm{H_2O})_m}_{\mathrm{Cl_2}}\right] + (n-m)\mathrm{H_2O} \qquad (1)$$



$$\left[\mathrm{Sr}^{(\mathrm{H_2O})_m}_{\mathrm{Cl_2}}\right] + \mathrm{H_2O} \rightleftharpoons \left[\mathrm{Sr}^{(\mathrm{H_2O})_{m+1}}_{\mathrm{Cl}}\right]^+ + \mathrm{Cl}^- \qquad (2)$$



$$\left[\mathrm{Sr}^{(\mathrm{H_2O})_{m+1}}_{\mathrm{Cl}}\right] + \mathrm{H_2O} \rightleftharpoons \left[\mathrm{Sr(H_2O)}_{m+2}\right]^{++} + \mathrm{Cl}^- \qquad (3)$$

Equation 2 represents the effect of diluting a concentrated solution. The ease with which the first chloride ion is formed is great compared to that with which the second one leaves the strontium. In other words, the equilibrium constant of the reaction represented by Equation 2 is much larger than that represented by Equation 3. The mass action of one mol of water will therefore be comparatively large, and the equilibrium will be significantly disturbed to the right resulting in a hydration effect which will furnish a comparatively large amount of heat. The

---

[1] The signs of the heat effects in the two curves are opposite, that of $SrCl_2$ being positive and that of $BaCl_2$ being negative. That fact does not change any of the considerations, however. It merely means that hydration is in one case exothermic and in the other case endothermic.

[2] W. D. Harkins, This Journal, 33, 1807 (1911); Harkins and Paine, *Ibid.*, 38, 2709 (1916).

[3] G. McP. Smith and E. A. Rees, This Journal, 40, 1844 (1918).

change of mass action per mol of water added with the concentration will also be great since, with a large equilibrium constant, a given decrease in concentration will throw Reaction 2 much nearer to completion than Reaction 3. It should also be borne in mind that in going from 3.2 *N* to 1.6 *N* the number of mols of water available for mass action effect per mol of salt increases 135%, while in going from 0.4 *N* to 0.2 *N* the number of available mols of water per mol of salt increases only 103%.[1] If Reactions 2 and 3 proceeded with equal ease this effect would tend to make the curve change slope gradually with the concentration. In the case of the uni-univalent salts the curves, as was pointed out, actually do become steeper with a gradual change of slope over their entire length.

When Reaction 2 has reached completion and Reaction 3 comes into prominence as the only one whose influence is felt, the mass action of one mol of water is small and the molal heat effect is consequently small. Moreover, a comparatively large change in concentration will not shift the equilibrium nearly so much as in the case of Reaction 2 so that one would not expect much change of molal heat effect with the concentration. The curves for both strontium and barium chlorides show very small molal heat effects at low concentrations, and these increase only slowly with the concentration; while at a point corresponding to about 50% ionization, or a point at which practically all the strontium or barium is in the form of intermediate ions, the curves suddenly become steeper, the heat effects begin to be larger, and increase rapidly with the concentration.

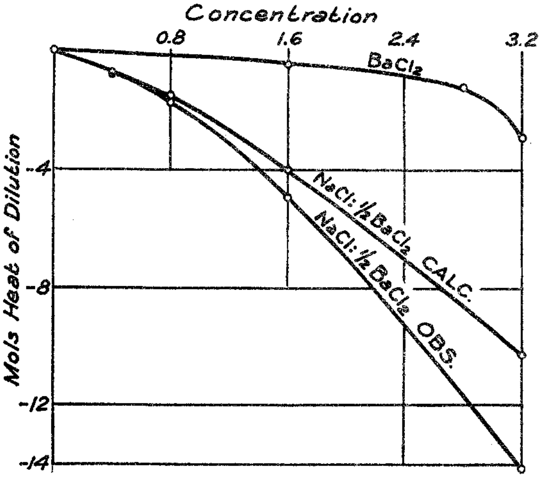


Fig. 1.

The two lower curves in Fig. 1 are for solutions of the mixed salt NaCl: 1/2 $BaCl_2$. The curve marked "Obs." is the one plotted from experimental data. The other one marked "Calc." is plotted from data calculated from the sum of the heats of dilution of the separate constitu-

---

[1] In 3.2 *N* solution there are 55.5/3.2 or 17.3 mols of water per mol of salt. The strontium is hydrated on the average with 4.5 mols of water leaving 12.8 mols of free solvent per mol of salt. In the same way in 1.6 *N* solution there are about 30 mols of free solvent per mol of salt. The increase is some 135%. From 0.4 *N* to 0.2 *N*, however, the increase will be found to be only about 103%.

ents at their respective concentrations in the mixture. It is seen that with increasing concentration these two curves diverge more and more. For a more detailed discussion of this type of curve see the next paper. Briefly, this divergence seems explicable only on the assumption that with increasing concentration there is an increasing tendency to form higher order complexes between the various salt constituents due to their mass action. Thus, at low concentrations, where these complexes would be present only in small amounts, their specific effect should be negligible, and the two curves should tend to coincide. This is actually the case.

Summary.

1. The reversible molal heat of dilution has been determined for solutions of barium chloride of 3.2, 2.8, and 1.6 weight normal, and for solutions of the mixed salt NaCl: 1/2 $BaCl_2$ at 3.2, 1.6, 0.8, and 0.4 weight normal.
2. The heats of dilution of the mixed salt bear no simple additive relation to the heat effects of the simple components at equivalent concentrations.
3. The behavior of barium chloride in this respect is found to be analogous to that of strontium chloride.
4. These results can be explained on the basis as the results obtained with the mixed strontium salts, namely on the basis of the formation of higher order compounds.

URBANA, ILL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE BROOKLYN POLYTECHNIC INSTITUTE.]

THE SEPARATION OF ZIRCONIUM AND TITANIUM AS THE PHOSPHATES.

BY JAMES BROWN AND H. T. MADDEN.

Received September 2, 1919.

In a previous paper,[1] one of us made use of the Hillebrand method[2] of separating zirconium from titanium by precipitation of the former by use of hydrogen peroxide and alkaline phosphate in a faintly acid solution. The titanium, when large in amount, was determined as a difference or by the permanganate method, and by the colorimetric method when small amounts were present. The work recorded in the present paper was undertaken with the object of making a direct gravimetric determination of the titanium in the filtrate from the zirconium phosphate precipitation.

The standard solutions employed were prepared from pure potassium zirconium fluoride (K_2ZrF_6), and from pure potassium titanium fluoride

---

[1] THIS JOURNAL, **39**, 2358 (1917).

[2] "Analysis of Silicate and Carbonate Rocks," U. S. Geol. Surv., *Bull.*, **422**, 141 (1910).