silicate, sodium phosphate (tribasic), disodium phosphate, sodium tungstate, and sodium arsenate.

Conclusions.

It has been shown that when cerium is titrated by means of potassium permanganate, zinc oxide or magnesium oxide are the best neutralizing agents. Fairly good results may also be obtained by using borax or sodium bicarbonate, while sodium carbonate, though yielding fair results, is still less satisfactory. The other reagents worked with are unsatisfactory so far as accurate results are concerned.

It has been shown that under proper conditions, the method is capable of giving very accurate results.

The method is also suitable for the determination of trivalent cerium in the presence of tetravalent cerium.

MADISON, WISCONSIN.

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., CHEMICAL LABORATORY OF HARVARD COLLEGE.]

CHANGES IN VOLUME UPON SOLUTION IN WATER OF THE HALOGEN SALTS OF THE ALKALI METALS. II.

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Received November 15, 1915.

In earlier papers[1] data were given for the changes in volume upon solution in water of the chlorides, bromides and iodides of lithium, sodium and potassium at various concentrations, and by the use of these data, together with a few observations upon rubidium and caesium halides by Buchanan, a tentative hypothesis was proposed as to the reasons for the direction and magnitude of the observed effects. At the time when the earlier paper was published the desirability was evident of additional data covering wider ranges of concentration and different temperatures, as well as the examination of other salts and other solvents. In the present paper are presented new data for the halogen salts of all five alkali metals, covering nearly all concentrations from saturation down, for temperatures between 0° and either 50°, 70° or 100°.

The experimental method was in outline as follows: A weighed amount of salt was dissolved in nearly a minimum quantity of water and the volume of the solution was adjusted to a mark in a 50 cc. flask at the highest temperature employed. The flask was then cooled to room temperature and weighed. The adjusting of the volume and weighing were then carried out at several lower temperatures. Next the solution was transferred quantitatively to a 100 cc. flask and the operations were repeated at the same temperatures, beginning with the highest. Then 250 cc., 500 cc.

[1] Baxter, Boylston, Mueller, Black and Goode, THIS JOURNAL, 23, 901 (1911); Baxter, *Ibid.*, 23, 922 (1911).

and 1000 cc. flasks were used. From the volumes of the flasks, and the volumes of the water and salt employed, the change in volume may be calculated for each solution at each temperature. These new data duplicate the earlier results only at 25°, and at this temperature they cover wider ranges of concentration and include six new salts, the halides of rubidium and caesium.

Apparatus.

The Flasks.—These were ordinary graduated flasks, the necks of which had been constricted at the point of graduation to secure greater accuracy in setting. The minimum interior diameter of the constriction varied from about 3 mm. with the 50 cc. flask to 6 mm. with the 1000 cc. flask. The volumes of these flasks at the different temperatures were determined by finding the water content. In order to do this, after the flask had been weighed dry and empty, it was filled with water and immersed in a water thermostat long enough to ensure constant temperature. This period was in practise usually as long as two or three hours, although with the smaller flasks so long a period was really unnecessary. Constancy in the position of the meniscus was considered to indicate that the flask and contents had reached the temperature of the bath. Before the volume of the water was finally adjusted,[1] the neck of the flask was dried by aspirating air through the upper portion. The flask was then stoppered, cooled or warmed to room temperature, usually rapidly by immersion in water, cleansed and dried on the outside, and finally weighed. From the apparent weights of water the volumes were calculated by multiplying by the following factors:

0°	25°	50.04°	70.19°	100°
1.001191	1.004001	1.01316	1.02389	1.04454

the densities of water[2] being assumed to be at

0°	25°	50.04°	70.19°	100°
0.999868	0.997071	0.98805	0.97771	0.95838

As is to be expected, owing to the prolonged contact with water or aqueous solutions, the weights of the empty flasks slowly decreased with time. In one year the 50 cc. flask lost in weight 6 mg., the 1000 cc. flask 37 mg., and the others in proportion. Since a considerable percentage of these losses must have occurred on the outside of the flask, the change in the cubical content, owing to solution of the glass, could hardly have exceeded 0.01 cc. even with the largest flask. On the other hand, the volumes of the flasks, which were subjected to three careful standardizations at intervals of several months, seemed to show at first a perceptible

[1] The final reading was always made with the stopper of the flask removed, for the insertion of the stopper frequently produces enough pressure to alter the position of the meniscus.

[2] Landolt-Börnstein-Roth, "Tabellen," 1912.

increase owing, apparently, to readjustment of the glass itself at the higher temperatures. This change amounted to about 0.005 cc. in the 50 cc. flask and to about 0.05 cc. in the liter flask. In using the flasks the value obtained in the standardization nearest in point of time to the experiment was used.

The cubical coefficients of expansion of the different flasks were found to be essentially the same, and to increase slightly with rising temperature. The following table gives these values:

	25 cc.[1]	50 cc.	100 cc.	250 cc.	500 cc.	1000 cc.	Average.
70.19–50.04°	0.04311	0.0435	0.04310	0.04300	0.04321	0.0315	0.04318
50.04–25.00°	283	29	278	282	280	289	284
25.00– 0.00°	290	28	294	291	273	288	286

The flasks were always weighed by substitution, the 25 cc. and 50 cc. flasks upon an ordinary analytical balance sensitive to 0.1 mg., the larger flasks on a balance sensitive to 1 mg. with a load of 1 kg. All the weights were standardized by the substitution method described by Richards.[2]

The Thermostats.—The thermostats were controlled by large mercury-toluene regulators which had two fingers well separated. Heat was supplied only by incandescent electric light bulbs in the 25° bath. In the 50°, 70° and 100° baths small gas flames below the baths furnished the greater part of the necessary heat, while the finer adjustment of temperature was effected by incandescent electric light bulbs controlled by the regulator. The baths were thoroughly stirred by four-inch fan propellers and were insulated by several thicknesses of asbestos paper. The baths contained distilled water except in the case of the 100° bath which was filled with concentrated calcium nitrate solution. The 0° bath was obtained by using distilled water with a large amount of washed cracked ice.

No appreciable differences in temperature could be detected in different parts of the various baths. The 0° and 25° baths remained constant within 0.01° at all times. The 50° and 70° baths were somewhat less so, but the fluctuations were never more than a few hundredths of a degree. These fluctuations could have had a perceptible effect only in the case of the larger flasks. But there the large quantity of material would respond so slowly to fluctuations that these must have been largely compensated. The 100° bath was much less satisfactory, and could not be depended upon to remain constant within less than 0.1°.

The thermometers were calibrated to hundredths of a degree by comparison with one standardized by the Physikalish-Technische Reichsanstalt, correction being made in the usual way for exposed thread.

[1] This flask was used in work described in a subsequent paper to appear in the February number of THIS JOURNAL.

[2] THIS JOURNAL, 22, 144 (1900).

Purification of Materials.

The usual processes of distillation and crystallization were employed in the preparation of the pure salts and the reagents used in their preparation. *Water* was doubly distilled, once from alkaline permanganate, once from very dilute sulfuric acid with the use of tin condensers. *Nitric acid* was distilled through a platinum condenser with rejection of the first third of the distillate. Constant boiling *hydrochloric acid* was distilled through a quartz condenser. In order to eliminate chlorine, *bromine* was distilled from solution in concentrated aqueous potassium bromide. A portion of the product was converted into potassium bromide by addition to a solution of recrystallized potassium oxalate, and the remainder was distilled a second time from solution in this purer potassium bromide. Iodine was expelled from bromides made from this bromine by boiling the aqueous solutions with an excess of bromine. *Hydrobromic acid* was prepared by passing thoroughly washed hydrogen sulfide gas into the purified bromine covered with water. The solution was mechanically separated from the bromide of sulfur, and the sulfuric acid formed in the reaction was precipitated by barium hydroxide. After filtration the acid was doubly distilled with rejection of extreme fractions. *Iodine* was freed from chlorine and bromine by one distillation from concentrated aqueous potassium iodide. The product was washed with water and once distilled with steam. From this iodine *hydriodic acid* was prepared by reduction with thoroughly scrubbed hydrogen sulfide in the presence of much water. After the precipitated sulfur had been coagulated by heating, it was removed by filtration and the solution was freed from sulfur compounds and hydrocyanic acid by long continued boiling.

To prepare *lithium chloride*, the commercial carbonate was thoroughly washed with water and then dissolved in hydrochloric acid, a slight excess of carbonate being used to precipitate basic impurities. After the solution had been boiled and filtered, a slight excess of acid was added and the chloride was three times crystallized, twice in a quartz dish, once in platinum. In these crystallizations, and in all others, very efficient centrifugal drainage in platinum Gooch crucibles was employed.

The lithium carbonate used in making *lithium bromide* was more carefully freed from alkali metals at the start. It was first dissolved in nitric acid. The solution was boiled with an excess of carbonate and filtered, acidified with nitric acid and the salt was twice crystallized. The nitrate was now converted to carbonate by fusion in a platinum dish with four equivalents of twice crystallized oxalic acid.[1] Since the product was found to be free from both nitrate and oxalate, the carbonate was then dissolved in an excess of hydrobromic acid in a quartz dish. After the solution had been boiled and filtered, the salt was twice crystallized.

[1] Wells, *Am. Chem. J.*, **26**, 265 (1891).

Lithium iodide was prepared by dissolving washed lithium carbonate in the pure hydriodic acid solution, boiling the solution with an excess of carbonate, filtering, acidifying with hydriodic acid and crystallizing. Owing to slight decomposition of lithium iodide in concentrated aqueous solution, the salt and its solutions were colored faintly yellow with a very small amount of free iodine.

C. P. *sodium chloride* was twice precipitated from aqueous solution in a quartz dish by conducting hydrochloric acid gas to the surface of the solution through a quartz tube. The gas was generated by boiling C. P. fuming acid.

To prepare sodium bromide, *sodium carbonate* was freed from impurities by three crystallizations in platinum. The carbonate was converted to oxalate by means of a slight excess of twice crystallized oxalic acid, and the oxalate to bromide by an excess of bromine which had been freed from chlorine as already described. The latter reaction was brought to completion by protracted boiling in a quartz flask. During this boiling any iodine contained originally by the bromine must have been expelled. No test for oxalate could be obtained in the solution by the addition of calcium chloride. The solution was next evaporated to dryness and fused in a platinum dish. The residue was dissolved in water, the solution was filtered and the salt was twice crystallized in platinum.

Sodium iodide was prepared from the pure sodic carbonate exactly as with the bromide. The reaction of the oxalate with iodine runs much more slowly than that with bromine, so that prolonged boiling with an excess of iodine in the quartz flask was necessary.

Potassium chloride, *bromide* and *iodide* were prepared exactly as the sodium salts, except that the starting point for the bromide and iodide was recrystallized potassium oxalate.

Merck's *rubidium chloride* was three times recrystallized from aqueous solution, the solubility of the salt being much diminished by saturating the solution with hydrochloric acid gas. The final mother liquor, when tested spectroscopically, was found to contain only very small amounts of all the other alkali metals.

The *bromide* and *iodide* of rubidium were prepared from the purified chloride as follows: The chloride was converted to nitrate by protracted boiling with a large excess of nitric acid in a quartz flask. Then the nitrate was mixed with four equivalents of oxalic acid and the mixture was fused in a platinum dish. The resulting carbonate was neutralized with oxalic acid and the oxalate was converted into bromide and iodide as in the cases of the corresponding salts of sodium and potassium.

We are very greatly indebted to Professor H. L. Wells, of Yale University, who kindly loaned us 200 g. of very pure caesium nitrate for preparing the *caesium halides*. The caesium nitrate was converted to chloride by prolonged boiling in a quartz flask with continual addition of redistilled hydrochloric acid. The solution was next evaporated to dryness in a platinum dish and the caesium chloride was fused. Then the residue was dissolved, the solution was filtered and the salt twice crystallized.

To obtain the *bromide* and *iodide* of caesium the nitrate was ground with four equivalents of pure oxalic acid and the mixture was fused in a platinum dish.[1] The resulting carbonate was dissolved in a slight excess of pure hydrobromic or hydriodic acid, the solutions were evaporated to dryness and the residues were fused in a platinum dish. After solution of the residues in water and filtration, the salts were twice crystallized from aqueous solution in platinum vessels.

Preparation of the Salts for Weighing.

Especial pains were taken in drying the salts before weighing them in preparation for making up the solutions. The chlorides, with the exception of lithium chloride, were fused in a weighed platinum crucible, and the crucible and contents were weighed. Treated in this way the salts do not become appreciably basic. Since the bromides and iodides of the alkalies become somewhat basic when fused in air, these salts instead were dried without fusion. The salts were first heated for two hours in an electric air bath at 250°. Next they were powdered by gentle grinding in an agate mortar, and again were heated to 250° for two hours. After a second grinding, a suitable amount of salt was placed in a weighed platinum crucible and heated for a third period of two hours at 250°. Then the crucible with its contents was cooled and weighed. Salts when treated in this way gave essentially neutral solutions.

Since neither of the foregoing methods is applicable to the halides of lithium, both because they become decidedly basic when fused in the air and because of the hygroscopic nature of the dry salts, instead of weighing the salts, the halogen content of the most dilute solution was found by precipitation with silver nitrate and weighing the silver halide. This was done by weighing out in small flasks portions of the solution, diluting to one liter in large glass-stoppered Erlenmeyer flasks, and adding a dilute solution of a slight excess of silver nitrate containing much free acid. After coagulation by occasional shaking, the silver halide was washed by decantation and collected on a weighed platinum sponge crucible. Dilute silver nitrate solution was used in washing the silver chloride, very dilute nitric acid for the silver bromide and iodide. Finally, however, all three salts were rinsed in the crucibles with ice-cold distilled water. The crucibles and contents were dried for at least four hours at 250° before being weighed.

[1] Wells. *Loc. cit.*

Method of Procedure.

The method of conducting a series of experiments to find the change in volume during solution was as follows: A sufficient quantity of salt to prepare a very nearly saturated solution at 25° was dried as previously described Then it was dissolved in a minimum amount of hot water and transferred to the 50 cc. flask through a funnel with a capillary stem long enough to extend through the constricted portion of the neck of the flask. In order to prevent the salt from crystallizing and clogging the capillary, the bulb of the flask and greater portion of its neck were immersed in a bath of hot water. The crucible was rinsed many times with small portions of hot water and the rinsings were transferred to the flask. If the flask was not already nearly full, it was filled to the neck (but not to the graduation) and gently agitated until the solution was homogeneous. Then it was immersed very nearly to the graduation in the thermostat at the highest temperature to be employed. When the solution had very nearly reached the temperature of the thermostat, water was added nearly to the graduation and the solution was again well agitated without wetting the neck of the flask above the graduation. Finally, the volume of the solution was adjusted exactly to the graduation by adding water slightly above the graduation and evaporating the excess of water in a current of air. If the flask was not already at 25° it was stoppered and transferred to the bath at that temperature in preparation for weighing. The outside of the flask was cleansed, usually with the use of very dilute ammonia, and after being wiped with a damp cloth, to avoid creating electrical charges, the flask was left in the balance case for one-half hour before being weighed by substitution. The empty dry flasks were always treated and weighed in a similar fashion before each series of experiments. Some difficulty was experienced from the appearance of minute bubbles on the inside of the flask when filled with solutions. These bubbles were so small and adhered so tenaciously that tapping the flask sharply was never sufficient entirely to remove them. By the use of water which had been freshly boiled in a Jena glass flask, together with sharp tapping with a glass rod it was possible to prevent the difficulty.

As soon as the flask had been filled and weighed at the highest temperature employed, the operations were repeated at the lower temperatures in succession. After the experiment at 0° had been completed the contents of the flask were quantitatively transferred to the flask next larger in size. The volume was adjusted and the solution was weighed at the same temperatures, beginning with the highest one. If, as sometimes happened, the salt began to crystallize before the lowest temperature was reached with the most concentrated solution, the whole was immediately transferred to the flask next larger in size.

In the first series of determinations with rubidium chloride at 25°, and with potassium chloride and lithium iodide at various temperatures, duplicate determinations were made, but since the results obtained in these experiments always lay along a smooth curve, with the other salts only one series of experiments was considered necessary.

The computation of the change in volume during solution was carried out as follows: First, the weight of salt was corrected to vacuum by adding the following vacuum corrections[1] per gram of substance:

	Cl. g.	Br. g.	I. g.
Ag	0.00007	0.00004	0.00007
Na	0.00042	0.00025	0.00019
K	0.00046	0.00030	0.00024
Rb	0.00029	0.00023	0.00021
Cs	0.00018	0.00013	0.00013

To correct the weight of the solution to vacuum was not always easy, for only when the volume of the solution was adjusted at 25° was the volume at the time of weighing, and hence the density, accurately known. When the volume was adjusted at a higher or at a lower temperature the method finally adopted for finding the density at room temperature was to divide the weight of the solution by the volume occupied at 25° by the water content of the flask at the temperature in question. This method assumes the same rate of expansion and contraction with the temperature for the solutions and for water. But in the more concentrated solutions, where this assumption is less nearly true, the vacuum correction is a much smaller percentage of the whole than in the less concentrated solutions which resemble water more nearly.

To find the weight of water in the solution the weight of salt corrected to vacuum is subtracted from the weight of solution corrected to vacuum.

The volume of the salt was found from the densities determined directly as described in a subsequent paper to appear in the February issue of THIS JOURNAL or calculated from the cubical coefficient of expansion. Since the cubical coefficient of expansion of lithium halides has not been determined, the assumption was made that these salts are not far different in this respect from the corresponding sodium salts. This assumption seems warranted since the coefficients of expansion of all the chlorides examined are nearly the same, and this is also the case for bromides and iodides. The volume of the water was computed from the weight by means of the densities given on page 78. The difference between the sum of the volumes of the salt and the water and the volume of the flask is the change in volume.

In Table III are given the data for each experiment as well as the computed change in volume per gram of salt and per gram molecule of salt. The absolute densities of the solutions also are included, although they play no part in the necessary computations. No experiments are omitted

[1] Found, except in the case of the silver salts, from the densities given on page 78.

from this table except three series known to have been made with impure water. Following the tables are curves showing change in volume during solution per gram of salt at different gram molecular concentrations. In these curves the change in volume in cubic centimeters per *gram* of salt is plotted vertically against the concentration in *mols* per liter horizontally.

It must be obvious that these curves furnish a very accurate means of computing the density of any solution of any of the salts at any temperature between the extremes. The density of the solution is equal to

$$\frac{\text{weight of solution}}{\text{volume of solution}} = \frac{\text{weight of water} + \text{weight of salt}}{\text{volume of water} + \text{volume of salt} \pm \text{change in volume during solution}}$$

If the percentage composition is known (*i. e.*, the weights of water and salt) the volume of water, volume of salt and approximate change in volume during solution can be calculated, and thus the approximate volume of the solution. From the weight of salt and approximate volume of the solution the concentration is given nearly enough so that the exact change in volume may be found from the curves. In case the temperature in question does not correspond to any one of the curves, by plotting change in volume for the given concentration at the different temperatures, against temperature, the value for the desired temperature may be obtained. In case concentration is known at the outset (*i. e.*, weight of salt and volume of solution) there can be calculated in order: change in volume during solution, volume of salt, volume of water, weight of water and density of solution.

TABLE I.

	Sp. gr. 70.19°/4°.	Sp. gr. 50.04°/4°.	Sp. gr. 25.00°/4°.	Sp. gr. 0.00°/4°.	Cubical coeff. of expansion, 25°–50°.
NaCl	...	2.156	2.161	2.168	0.000106
NaBr	3.186[1]	3.194	3.203	3.213	0.000119
NaI	...	3.653[1]	3.665	3.677[1]	0.000136
KCl	1.978	1.981	1.987	1.992	0.000117
KBr	...	2.740	2.749	2.756	0.000125
KI	...	3.114	3.123	3.133	0.000114
RbCl	...	2.792	2.798	2.806	0.000082
RbBr	...	3.340	3.349	3.358	0.000101
RbI	...	3.542	3.550	3.560	0.000092
CsCl	3.952	3.961	3.974	3.988	0.000136
CsBr	4.406[1]	4.418	4.433	4.449	0.000137
CsI	4.480[1]	4.493	4.509	4.525	0.000146
LiCl	2.059[1]	2.063[1]	2.068	2.073[1]	0.00010[2]
LiBr	3.446[1]	3.454[1]	3.464	3.474[1]	0.00012[2]
LiI	4.038[1]	4.048[1]	4.061	4.074[1]	0.00013[2]

[1] Calculated from coefficient of expansion. See a subsequent paper to appear in the February issue of THIS JOURNAL.

[2] Assumed.

The weight of salt could be determined within a milligram without the least difficulty, but the accuracy in weighing the solutions diminished with increasing dilution. The weight of the 50 cc. flask and contents is probably accurate to one milligram in every case, but the weight of the 1000 cc. flask and contents is certainly not fixed more accurately than within 0.01 g., although even this represents only 0.001% in the weight of the solution. The accuracy with which the solutions were weighed obviously corresponds to an accuracy in measuring the change in volume during solution of about 0.001 cc. with the smallest, and of about 0.01 cc. with the largest flasks. That is, the change in volume was found about ten times more accurately with the smallest than with the largest flask.

TABLE II.—ANALYSES OF LITHIUM HALIDE SOLUTIONS.

All weights reduced to vacuum standard.

Salt.	Total wt. of soln. Grams.	Wt. of sample. Grams.	Wt. of silver halide. Grams.	Wt. of lithium halide in orig. soln. Grams.
LiCl	1017.65	50.833	4.8923	28.973
		50.930	4.9026	28.971
		50.941	4.9028	28.972
			Average,	28.972
	969.74	50.412	2.0710	11.785
		50.390	2.0705	11.787
			Average,	11.786
LiBr	1041.74	52.087	6.1275	56.680
		52.165	6.1363	56.676
		52.141	6.1338	56.679
			Average,	56.678
LiI	1041.89	26.043	2.4358	55.555
		26.046	2.4360	55.556
			Average,	55.556
	1038.36	25.941	2.2237	50.744
		25.911	2.2222	50.768
		25.928	2.2215	50.720
			Average,	50.744

To prepare the most dilute LiCl solution, 490.45 g. were diluted to the volume of the liter flask, which therefore contained 13.963 g. of salt.

To prepare the most dilute LiBr solution, 536.50 g. were diluted to the volume of the liter flask, which therefore contained 29.190 g. of salt.

The following results are in good agreement with those previously obtained, the only differences of importance occurring where new values for the specific gravities of the solid salts are employed, as in the case of sodium bromide.

The noticeable features of the tables and curves seem to be as follows:

Lithium and cesium halides in general produce expansion during solution. Lithium chloride is the exception, but at high concentrations and temperatures between 25° and 50° even this salt produces expansion.

TABLE III.

Salt.	Temp.	Molal conc.	Wt. of salt.	Wt. of soln.	Wt. of water.	Volume of salt.	Volume of water.	Volume of soln.	Density of soln.	Change in volume.	Change per gram of salt.	Change per mol of salt.
LiCl.....	100.0°	11.1537	11.786	30.280	18.494	5.743	19.292	24.922	1.21495	—0.113	—0.0096	— 0.27
		5.6023	..	54.328	42.542	..	44.378	49.617	1.09495	—0.504	—0.0428	— 1.40
		2.7934	..	102.520	90.734	..	94.650	99.509	1.03026	—0.884	—0.0750	— 2.08
		1.1219	..	245.525	233.739	..	243.826	248.332	0.99098	—1.237	—0.1050	— 2.92
		0.2770	..	969.739	957.953	..	999.294	1003.377	0.96648	—1.660	—0.1410	— 3.92
	70.19°	6.8731	28.972	112.680	83.708	14.071	85.617	99.417	1.13341	—0.271	—0.0094	— 0.40
		2.7541	..	258.936	229.964	..	235.209	248.104	1.04366	—1.176	—0.0406	— 1.72
		1.3698	..	504.576	475.604	..	486.452	498.834	1.01151	—1.689	—0.0583	— 2.47
		0.6816	..	997.354	968.382	...	990.471	1002.453	0.99491	—2.089	—0.0721	— 3.06
		0.3285	13.963	988.590	974.627	6.782	996.858	1002.453	0.98617	—1.187	—0.0850	— 3.61
	50.04°	13.7929	28.972	63.625	34.653	14.044	35.072	49.540	1.28433	+0.424	+0.0146	+ 0.62
		6.8774	..	113.279	84.307	..	85.327	99.355	1.14014	—0.016	—0.0006	— 0.03
		2.7558	..	260.875	231.903	..	234.706	247.954	1.05211	—0.796	—0.0275	— 1.17
		1.3707	..	508.956	479.984	..	485.787	498.512	1.02095	—1.319	—0.0456	— 1.93
		0.6821	..	1006.570	977.598	..	989.418	1001.817	1.00474	—1.645	—0.0568	— 2.41
		0.3287	13.963	998.025	984.062	6.769	995.959	1001.817	0.99622	—0.911	—0.0652	— 2.76
	25.00°	13.8030	28.972	63.968	34.996	14.010	35.099	49.504	1.29218	+0.395	+0.0137	+ 0.58
		6.8822	..	113.925	84.953	..	85.203	99.286	1.14744	+0.073	+0.0025	+ 0.11
		2.7577	..	262.750	233.778	..	234.465	247.779	1.06042	—0.696	—0.0240	— 1.02
		1.3716	..	512.915	483.943	..	485.365	498.163	1.02961	—1.212	—0.0419	— 1.78
		0.6826	..	1014.716	985.744	..	988.640	1001.094	1.01361	—1.556	—0.0537	— 2.28
		0.3290	13.963	1006.263	992.300	6.752	995.215	1001.094	1.00516	—0.873	—0.0625	— 2.65
	0.00°	6.8872	28.972	114.437	85.465	13.975	85.476	99.213	1.15345	—0.238	—0.0082	— 0.35
		2.7597	..	263.813	234.841	..	234.872	247.599	1.06549	—1.248	—0.0431	— 1.83
		1.3726	..	514.681	485.709	..	485.773	497.823	1.03386	—1.925	—0.0665	— 2.82
		0.6831	..	1017.644	988.672	..	988.803	1000.375	1.01726	—2.403	—0.0830	— 3.52
		0.3292	13.963	1008.780	994.817	6.736	994.948	1000.375	1.00840	—1.309	—0.0938	— 3.98
LiBr.....	70.19°	13.162	56.678	88.194	31.516	16.442	32.234	49.575	1.77900	+0.899	+0.0159	+ 1.38
		6.5635	..	136.855	80.177	..	82.006	99.417	1.37658	+0.969	+0.0171	+ 1.49

LiBr.....	70.19°	2.6300	..	282.703	226.025	..	231.181	248.104	1.13945	+0.481	+0.0085	+ 0.74
		1.3081	..	528.175	471.497	..	482.253	498.834	1.05882	+0.139	+0.0025	+ 0.22
		0.6509	..	1020.890	964.212	..	986.208	1002.453	1.01839	—0.197	—0.0035	— 0.30
		0.3352	29.190	1001.187	971.997	8.468	994.168	1002.453	0.99874	—0.183	—0.0063	— 0.55
	50.04°	13.172	56.678	88.536	31.858	16.409	32.244	49.540	1.78716	+0.887	+0.0156	+ 1.36
		6.5676	..	137.570	80.892	..	81.870	99.355	1.38463	+1.076	+0.0190	+ 1.65
		2.6316	..	284.767	228.089	..	230.847	247.954	1.14847	+0.698	+0.0123	+ 1.07
		1.3089	..	532.664	475.986	..	481.741	498.512	1.06851	+0.362	+0.0064	+ 0.55
		0.6513	..	1030.232	973.554	..	985.325	1001.817	1.02836	+0.083	+0.0015	+ 0.13
		0.3355	29.190	1010.717	981.527	8.451	993.394	1001.817	1.00888	—0.028	—0.0010	— 0.09
	25.00°	13.181	56.678	89.014	32.336	16.362	32.431	49.504	1.79812	+0.711	+0.0125	+ 1.09
		6.5721	..	138.397	81.719	..	81.959	99.286	1.39392	+0.965	+0.0170	+ 1.48
		2.6335	..	286.836	230.158	..	230.834	247.779	1.15763	+0.583	+0.0103	+ 0.89
		1.3099	..	536.850	480.172	..	481.583	498.163	1.07766	+0.218	+0.0038	+ 0.33
		0.6518	..	1038.558	981.880	..	984.765	1001.094	1.03742	—0.033	—0.0006	— 0.05
		0.3357	29.190	1019.059	989.869	8.427	992.777	1001.094	1.01795	—0.110	—0.0038	— 0.33
	0.00°	6.5770	56.678	139.133	82.455	16.314	82.466	99.213	1.40237	+0.433	+0.0076	+ 0.66
		2.6354	..	288.158	231.480	..	231.511	247.599	1.16381	—0.246	—0.0043	— 0.38
		1.3108	..	538.870	482.192	..	482.256	497.823	1.08245	—0.747	—0.0132	— 1.14
		0.6523	..	1041.735	985.057	..	985.187	1000.375	1.04134	—1.126	—0.0199	— 1.73
		0.3359	29.190	1021.738	992.548	8.402	992.679	1000.375	1.02135	—0.706	—0.0242	— 2.10
LiI......	70.19°	8.3718	55.556	88.894	33.337	13.764	34.097	49.575	1.79312	+1.714	+0.0309	+ 4.14
		4.1747	..	137.368	81.811	..	83.677	99.415	1.38176	+1.974	+0.0355	+ 4.75
		1.6728	..	282.800	227.243	..	232.427	248.106	1.13984	+1.915	+0.0345	+ 4.61
		0.8320	..	528.014	472.457	..	483.235	498.816	1.05853	+1.817	+0.0327	+ 4.38
		0.4140	..	1020.514	964.957	..	986.969	1002.453	1.01802	+1.720	+0.0310	+ 4.15
	50.04°	8.3777	..	89.309	33.752	13.728	34.160	49.540	1.80277	+1.652	+0.0297	+ 3.98
		4.1773	..	138.263	82.706	..	83.706	99.355	1.39161	+1.921	+0.0346	+ 4.63
		1.6738	..	285.140	229.583	..	232.359	247.950	1.14999	+1.863	+0.0335	+ 4.48
		0.8326	..	532.791	477.234	..	483.004	498.504	1.06878	+1.772	+0.0319	+ 4.27
		0.4143	..	1030.159	974.602	..	986.385	1001.820	1.02829	+1.707	+0.0307	+ 4.11

TABLE III (*continued*).

Salt.	Temp.	Molal conc.	Wt. of salt.	Wt. of soln.	Wt. of water.	Volume of salt.	Volume of water.	Volume of soln.	Density of soln.	Change in volume.	Change per gram of salt.	Change per mol of salt.
LiI......	25.00°	8.3838	..	89.823	34.266	13.681	34.366	49.504	1.81446	1.457	0.0262	3.50
		4.1802	..	139.284	83.727	..	83.973	99.286	1.40286	1.632	0.0294	3.93
		1.6750	..	287.447	231.890	..	232.571	247.779	1.16009	1.527	0.0275	3.68
		0.8331	..	537.201	481.644	..	483.059	498.156	1.07838	1.416	0.0255	3.41
		0.4146	..	1038.759	983.202	..	986.090	1001.094	1.03762	1.323	0.0238	3.18
	0.00°	4.1833	..	140.161	84.604	13.633	84.615	99.212	1.41274	0.964	0.0173	2.32
		1.6762	..	288.866	233.309	..	233.340	247.597	1.16668	0.624	0.0112	1.50
		0.8337	..	539.244	483.687	..	483.751	497.806	1.08324	0.422	0.0076	1.02
		0.4149	..	1041.893	986.336	..	986.466	1000.374	1.04150	0.275	0.0050	0.66
	70.19°	7.6466	50.744	85.361	34.615	12.572	35.405	49.575	1.72186	1.598	0.0315	4.21
		3.8131	..	133.939	83.193	..	85.090	99.415	1.34727	1.753	0.0345	4.62
		1.5279	..	279.389	228.643	..	233.858	248.106	1.12609	1.676	0.0330	4.42
		0.7600	..	524.599	473.853	..	484.662	498.816	1.05169	1.582	0.0312	4.17
		0.3782	..	1017.115	966.369	..	988.412	1002.453	1.01463	1.469	0.0289	3.87
	50.04°	7.6521	..	85.781	35.035	12.539	35.459	49.540	1.73155	1.542	0.0308	4.07
		3.8154	..	134.842	84.096	..	85.113	99.355	1.35717	1.703	0.0336	4.49
		1.5289	..	281.725	230.979	..	233.772	247.950	1.13622	1.639	0.0323	4.32
		0.7604	..	529.362	478.616	..	484.403	498.504	1.06190	1.562	0.0308	4.12
		0.3784	..	1026.750	976.004	..	987.804	1001.817	1.02489	1.474	0.0290	3.89
	25.00°	7.6576	..	86.300	35.554	12.496	35.659	49.504	1.74329	1.349	0.0266	3.56
		3.8181	..	135.852	85.106	..	85.356	99.286	1.36829	1.434	0.0283	3.79
		1.5299	..	284.013	233.267	..	233.952	247.779	1.14624	1.331	0.0262	3.51
		0.7610	..	533.752	483.006	..	484.425	498.156	1.07146	1.235	0.0243	3.25
		0.3787	..	1035.300	984.554	..	987.447	1001.094	1.03417	1.151	0.0227	3.04
	0.00°	7.6630	..	86.813	36.067	12.452	36.072	49.469	1.75490	0.945	0.0185	2.49
		3.8209	..	136.692	85.946	..	85.957	99.212	1.37778	0.803	0.0158	2.12
		1.5310	..	285.368	234.622	..	234.653	247.597	1.15255	0.492	0.0097	1.30
		0.7615	..	535.727	484.981	..	485.045	497.806	1.07618	0.309	0.0061	0.82
		0.3789	..	1038.358	987.612	..	987.742	1000.374	1.03797	0.180	0.0035	0.47

NaCl....	50.04°	5.1383	14.881	58.287	43.406	6.902	43.932	49.540	1.17656	—1.294	—0.0870	— 5.08
		2.5620	..	107.827	92.946	..	94.070	99.355	1.08527	—1.617	—0.1087	— 6.36
		1.0266	..	254.912	240.031	..	242.934	247.954	1.02804	—1.882	—0.1265	— 7.40
		0.5106	..	502.562	487.681	..	493.578	498.512	1.00812	—1.968	—0.1323	— 7.73
		0.2541	..	999.994	985.113	..	997.023	1001.817	0.99818	—2.108	—0.1416	— 8.28
	25.00°	5.1420	..	58.836	43.955	6.886	44.084	49.504	1.18851	—1.466	—0.0985	— 5.76
		2.5638	..	108.842	93.961	..	94.237	99.286	1.09625	—1.837	—0.1235	— 7.22
		1.0273	..	257.213	242.332	..	243.045	247.779	1.03807	—2.152	—0.1446	— 8.46
		0.5110	..	506.986	492.105	..	493.551	498.163	1.01771	—2.274	—0.1528	— 8.94
		0.2543	..	1008.572	993.691	..	996.610	1001.094	1.00747	—2.402	—0.1615	— 9.44
	0.00°	5.1456	..	59.328	44.447	6.864	44.453	49.469	1.19930	—1.848	—0.1242	— 7.26
		2.5657	..	109.613	94.733	..	94.745	99.213	1.10483	—2.396	—0.1610	— 9.42
		1.0281	..	258.487	243.606	..	243.638	247.599	1.04397	—2.903	—0.1951	—11.42
		0.5113	..	508.923	494.042	..	494.107	497.823	1.02230	—3.148	—0.2115	—12.36
		0.2545	..	1011.547	996.666	..	996.798	1000.375	1.01117	—3.287	—0.2209	—12.91
NaBr....	70.19°	5.4672	27.895	68.684	40.789	8.755	41.719	49.575	1.38546	—0.899	—0.0322	— 3.31
		2.7263	..	117.648	89.753	..	91.800	99.417	1.18338	—1.138	—0.0408	— 4.20
		1.0924	..	263.250	235.355	..	240.723	248.104	1.06105	—1.374	—0.0493	— 5.07
		0.5433	..	508.498	480.603	..	491.566	498.834	1.01937	—1.487	—0.0533	— 5.48
		0.2704	..	1001.013	973.118	..	995.315	1002.453	0.99856	—1.617	—0.0580	— 5.97
	50.04°	5.4711	..	69.189	41.294	8.734	41.793	49.540	1.39663	—0.987	—0.0354	— 3.64
		2.7280	..	118.648	90.753	..	91.850	99.355	1.19418	—1.229	—0.0441	— 4.54
		1.0931	..	265.701	237.806	..	240.681	247.954	1.07157	—1.461	—0.0524	— 5.39
		0.5437	..	513.379	485.484	..	491.353	498.512	1.02982	—1.575	—0.0565	— 5.82
		0.2705	..	1010.769	982.874	..	994.757	1001.817	1.00894	—1.674	—0.0600	— 6.18
	25.00°	5.4750	..	69.787	41.892	8.709	42.015	49.504	1.40972	—1.220	—0.0438	— 4.51
		2.7298	..	119.747	91.852	..	92.122	99.286	1.20608	—1.545	—0.0554	— 5.70
		1.0939	..	268.098	240.203	..	240.909	247.779	1.08200	—1.839	—0.0660	— 6.79
		0.5441	..	517.899	490.004	..	491.444	498.163	1.03962	—1.990	—0.0714	— 7.35
		0.2707	..	1019.448	991.553	..	994.466	1001.094	1.01833	—2.081	—0.0746	— 7.68
	0.00°	5.4789	..	70.359	42.464	8.682	42.470	49.469	1.42228	—1.683	—0.0603	— 6.21

TABLE III (*continued*).

Salt.	Temp.	Molal conc.	Wt. of salt.	Wt. of soln.	Wt. of water.	Volume of salt.	Volume of water.	Volume of soln.	Density of soln.	Change in volume.	Change per gram of salt.	Change per mol of salt.
NaBr....	0.00°	2.7319	..	120.644	92.749	..	92.761	99.213	1.21601	—2.230	—0.0800	— 8.23
		1.0947	..	269.521	241.626	..	241.658	247.599	1.08854	—2.741	—0.0983	—10.11
		0.5444	..	519.945	492.050	..	492.115	497.823	1.04444	—2.974	—0.1066	—10.97
		0.2709	..	1022.601	994.706	..	994.837	1000.374	1.02222	—3.145	—0.1128	—11.61
NaI......	70.19°	0.3425	51.467	1018.482	967.016	14.128	989.074	1002.453	1.01599	—0.749	—0.0146	— 2.18
	50.04°	6.9297	..	86.923	35.456	14.089	35.885	49.540	1.75460	—0.434	—0.0084	— 1.26
		3.4553	..	136.307	84.840	..	85.866	99.355	1.37192	—0.600	—0.0117	— 1.75
		1.3845	..	283.314	231.847	..	234.650	247.954	1.14261	—0.785	—0.0153	— 2.29
		0.6886	..	531.008	479.541	..	485.339	498.512	1.06519	—0.916	—0.0178	— 2.67
		0.3427	..	1028.366	976.899	..	988.710	1001.817	1.02650	—0.982	—0.0191	— 2.86
	25.00°	6.9347	..	87.607	36.140	14.043	36.246	49.504	1.76970	—0.785	—0.0152	— 2.28
		3.4577	..	137.580	86.113	..	86.366	99.286	1.38569	—1.123	—0.0218	— 3.27
		1.3855	..	285.969	234.502	..	235.191	247.779	1.15413	—1.455	—0.0283	— 4.24
		0.6891	..	535.776	484.309	..	485.732	498.163	1.07550	—1.612	—0.0313	— 4.69
		0.3429	..	1037.370	985.903	..	988.800	1001.094	1.03624	—1.749	—0.0340	— 5.10
	0.00°	6.9396	..	88.265	36.798	13.997	36.803	49.469	1.78425	—1.331	—0.0258	— 3.87
		3.4602	..	138.736	87.269	..	87.281	99.213	1.39837	—2.065	—0.0401	— 6.01
		1.3865	..	287.801	236.334	..	236.365	247.599	1.16237	—2.763	—0.0537	— 8.05
		0.6896	..	538.328	486.861	..	486.925	497.823	1.08136	—3.099	—0.0602	— 9.02
		0.3432	..	1041.056	989.589	..	989.720	1000.375	1.04067	—3.342	—0.0650	— 9.74
KCl.....	100.0°	4.101	15.171	56.552	41.381	7.693	43.167	49.617	1.13977	—1.243	—0.0820	— 6.11
		2.0448	..	104.678	89.507	..	93.370	99.509	1.05194	—1.554	—0.1024	— 7.63
		0.8213	..	247.608	232.437	..	242.468	248.332	0.99938	—1.829	—0.1205	— 8.99
		0.2028	..	971.866	956.695	..	997.982	1003.377	0.96860	—2.298	—0.1514	—11.30
	70.19°	4.5922	16.970	58.256	41.286	8.580	42.228	49.563	1.17539	—1.245	—0.0734	— 5.47
		2.2896	..	107.198	90.228	..	92.286	99.406	1.07839	—1.460	—0.0860	— 6.41
		0.9174	..	252.891	235.921	..	241.301	248.083	1.01938	—1.799	—0.1060	— 7.90
		0.2710	20.250	992.582	972.332	10.239	994.511	1002.348	0.99026	—2.402	—0.1187	— 8.84
	50.04°	2.2910	16.970	108.202	91.232	8.566	92.335	99.348	1.08912	—1.553	—0.0915	— 6.82

KCl.....	50.04°	0.9180	..	255.286	238.316	..	241.197	247.943	1.02962	—1.820	—0.1072	— 8.06
		0.2711	20.250	1002.343	982.093	10.222	993.957	1001.773	1.00057	—2.406	—0.1188	— 8.86
	25.00°	2.2926	16.970	109.138	92.168	8.540	92.439	99.275	1.09935	—1.704	—0.1004	— 7.48
		0.9187	..	257.474	240.504	..	241.211	247.745	1.03927	—2.006	—0.1182	— 8.81
		0.2713	20.250	1010.864	990.614	10.191	993.526	1001.053	1.00980	—2.664	—0.1316	— 9.82
	0.00°	2.2942	16.970	109.789	92.819	8.519	92.831	99.208	1.10664	—2.142	—0.1262	— 9.43
		0.9192	..	258.578	241.608	..	241.640	247.602	1.04433	—2.557	—0.1507	—11.22
		0.2715	20.250	1013.792	993.542	10.166	993.671	1000.385	1.01340	—3.452	—0.1705	—12.70
	70.19°	3.3433	12.358	55.702	43.344	6.248	44.333	49.575	1.12359	—1.006	—0.0814	— 6.06
		1.6672	..	104.626	92.268	..	94.372	99.415	1.05242	—1.205	—0.0975	— 7.26
		0.6680	..	250.155	237.797	..	243.221	248.106	1.00826	—1.363	—0.1103	— 8.22
		0.3337	..	493.254	480.896	..	491.865	496.679	0.99310	—1.434	—0.1160	— 8.64
		0.1653	..	987.845	975.487	..	997.737	1002.452	0.98543	—1.533	—0.1240	— 9.24
	50.04°	3.3457	..	56.151	43.793	6.238	44.323	49.540	1.13345	—1.021	—0.0826	— 6.16
		1.6682	..	105.559	93.201	..	94.328	99.355	1.06244	—1.211	—0.0980	— 7.30
		0.6685	..	252.538	240.180	..	243.084	247.950	1.01850	—1.372	—0.1110	— 8.28
		0.3339	..	498.060	485.702	..	491.574	496.360	1.00343	—1.446	—0.1170	— 8.72
		0.1654	..	997.561	985.203	..	997.114	1001.820	0.99575	—1.532	—0.1240	— 9.24
	25.00°	3.3481	..	56.628	44.270	6.219	44.400	49.504	1.14391	—1.115	—0.0902	— 6.72
		1.6694	..	106.477	94.119	..	94.396	99.286	1.07243	—1.329	—0.1075	— 8.02
		0.6689	..	254.710	242.352	..	243.064	247.779	1.02797	—1.504	—0.1216	— 9.07
		0.3342	..	502.321	489.963	..	491.402	496.019	1.01271	—1.602	—0.1296	— 9.68
		0.1656	..	1006.001	993.643	..	996.562	1001.094	1.00490	—1.687	—0.1365	—10.17
	0.00°	3.3505	..	56.995	44.637	6.204	44.643	49.469	1.15214	—1.378	—0.1123	— 8.37
		1.6706	..	107.052	94.694	..	94.706	99.212	1.07902	—1.698	—0.1374	—10.24
		0.6694	..	255.679	243.321	..	243.353	247.597	1.03264	—1.960	—0.1586	—11.82
		0.1657	..	1008.702	996.344	..	996.475	1000.374	1.00832	—2.305	—0.1865	—13.90
	70.19°	4.1696	15.412	57.402	41.990	7.792	42.948	49.575	1.15788	—1.165	—0.0756	— 5.64
		2.0792	..	106.397	90.985	..	93.060	99.417	1.07021	—1.435	—0.0932	— 6.94
		0.8331	..	251.972	236.560	..	241.954	248.104	1.01559	—1.642	—0.1066	— 7.94
		0.4144	..	497.203	481.791	..	492.781	498.834	0.99673	—1.739	—0.1128	— 8.41

TABLE III (*continued*).

Salt.	Temp.	Molal conc.	Wt. of salt.	Wt. of soln.	Wt. of water.	Volume of salt.	Volume of water.	Volume of soln.	Density of soln.	Change in volume.	Change per gram of salt.	Change per mol of salt.
KCl.....	70.19°	0.2062	..	989.660	974.248	..	996.470	1002.453	0.98724	—1.809	—0.1174	— 8.75
KBr.....	50.04°	4.5983	27.113	67.335	40.222	9.895	40.708	49.540	1.35920	—1.063	—0.0392	— 4.66
		2.2928	..	116.753	89.640	..	90.724	99.355	1.17511	—1.264	—0.0466	— 5.55
		0.9187	..	263.811	236.698	..	239.560	247.954	1.06395	—1.501	—0.0554	— 6.60
		0.4570	..	511.474	484.361	..	490.217	498.512	1.02600	—1.600	—0.0590	— 7.02
		0.2274	..	1008.829	981.716	..	993.585	1001.817	1.00700	—1.663	—0.0613	— 7.30
	25.00°	4.6017	..	67.865	40.752	9.863	40.872	49.504	1.37090	—1.231	—0.0454	— 5.40
		2.2944	..	117.778	90.665	..	90.931	99.286	1.18625	—1.508	—0.0556	— 6.62
		0.9194	..	266.080	238.967	..	239.670	247.779	1.07386	—1.754	—0.0647	— 7.70
		0.4573	..	515.866	488.753	..	490.189	498.163	1.03554	—1.889	—0.0696	— 8.29
		0.2276	..	1017.381	990.268	..	993.178	1001.094	1.01627	—1.947	—0.0718	— 8.55
	0.00°	2.2961	..	118.510	91.397	9.838	91.409	99.213	1.19450	—2.034	—0.0750	— 8.93
		0.9200	..	267.289	240.176	..	240.208	247.599	1.07952	—2.447	—0.0902	—10.74
		0.4576	..	517.642	490.529	..	490.594	497.823	1.03981	—2.609	—0.0962	—11.45
		0.2277	..	1020.219	993.106	..	993.237	1000.375	1.01984	—2.700	—0.0996	—11.85
KI......	50.04°	5.5632	45.755	80.991	35.236	14.693	35.662	49.540	1.63486	—0.815	—0.0178	— 2.96
		2.7739	..	130.441	84.686	..	85.710	99.355	1.31288	—1.048	—0.0229	— 3.80
		1.1115	..	277.443	231.688	..	234.489	247.954	1.11893	—1.228	—0.0268	— 4.46
		0.5529	..	525.125	479.370	..	485.166	498.512	1.05339	—1.347	—0.0294	— 4.89
		0.2751	..	1022.473	976.718	..	988.527	1001.817	1.02062	—1.403	—0.0307	— 5.09
	25.00°	5.5672	..	81.599	35.844	14.651	35.949	49.504	1.64833	—1.096	—0.0239	— 3.98
		2.7758	..	131.570	85.815	..	86.067	99.286	1.32516	—1.432	—0.0313	— 5.20
		1.1123	..	279.895	234.140	..	234.828	247.779	1.12962	—1.700	—0.0371	— 6.16
		0.5532	..	529.688	483.933	..	485.355	498.163	1.06328	—1.843	—0.0403	— 6.65
		0.2753	..	1031.233	985.478	..	988.373	1001.094	1.03011	—1.930	—0.0422	— 6.97
	0.00°	5.5712	..	82.143	36.388	14.604	36.393	49.469	1.66049	—1.528	—0.0334	— 5.55
		2.7779	..	132.481	86.726	..	86.737	99.213	1.33532	—2.128	—0.0465	— 7.72
		1.1131	..	281.389	235.634	..	235.665	247.599	1.13647	—2.670	—0.0584	— 9.70
		0.5536	..	531.818	486.063	..	486.127	497.823	1.06829	—2.908	—0.0635	—10.55

KI.....	0.00°	0.2755	..	1034.453	988.698	..	988.829	1000.375	1.03406	−3.058	−0.0668	−11.08
RbCl....	50.04°	6.5223	39.068	75.822	36.754	13.992	37.199	49.540	1.53052	−1.651	−0.0423	− 5.12
		3.2521	..	125.542	86.474	..	87.520	99.355	1.26357	−2.157	−0.0552	− 6.68
		1.3031	..	272.785	233.717	..	236.543	247.954	1.10014	−2.581	−0.0661	− 8.00
		0.6482	..	520.571	481.503	..	487.325	498.512	1.04425	−2.805	−0.0718	− 8.68
		0.3225	..	1018.037	978.969	..	990.805	1001.817	1.01619	−2.980	−0.0763	− 9.23
	25.00°	6.0890	36.439	74.552	38.113	13.023	38.225	49.495	1.50625	−1.753	−0.0481	− 5.82
		3.0357	..	124.675	88.236	..	88.496	99.275	1.25585	−2.244	−0.0616	− 7.44
		1.2165	..	273.163	236.724	..	237.420	247.745	1.10260	−2.698	−0.0740	− 8.95
		0.6054	..	522.663	486.224	..	487.653	497.774	1.05000	−2.902	−0.0796	− 9.63
		0.3011	..	1024.613	988.174	..	991.077	1001.053	1.02354	−3.047	−0.0836	−10.10
		4.0487	24.229	66.318	42.089	8.659	42.213	49.495	1.33989	−1.377	−0.0568	− 6.87
		2.0185	..	116.227	91.998	..	92.268	99.275	1.17076	−1.652	−0.0682	− 8.24
		0.8089	..	264.491	240.262	..	240.968	247.745	1.06759	−1.882	−0.0776	− 9.39
		0.4026	..	513.860	489.631	..	491.070	497.774	1.03232	−1.955	−0.0806	− 9.75
		0.2002	..	1015.780	991.551	..	994.464	1001.053	1.01471	−2.070	−0.0854	−10.32
		4.9833	29.822	70.108	40.286	10.658	40.404	49.495	1.41647	−1.567	−0.0526	− 6.36
		2.4845	..	120.113	90.291	..	90.556	99.275	1.20990	−1.939	−0.0650	− 7.86
		0.9956	..	268.470	238.648	..	239.349	247.745	1.08365	−2.262	−0.0759	− 9.18
		0.4955	..	517.918	488.096	..	489.530	497.774	1.04047	−2.414	−0.0810	− 9.80
		0.2464	..	1019.819	989.997	..	992.906	1001.053	1.01875	−2.511	−0.0842	−10.18
	0.00°	3.2568	39.068	127.256	88.188	13.922	88.200	99.213	1.28265	−2.909	−0.0744	− 9.01
		1.3050	..	276.347	237.279	..	237.310	247.599	1.11611	−3.633	−0.0930	−11.25
		0.6491	..	526.894	487.826	..	487.890	497.823	1.05840	−3.989	−0.1021	−12.35
		0.3230	..	1029.616	990.548	..	990.679	1000.375	1.02923	−4.226	−0.1082	−13.08
RbBr....	50.04°	5.1739	42.387	80.118	37.731	12.691	38.187	49.540	1.61724	−1.338	−0.0316	− 5.22
		2.5798	..	129.645	87.258	..	88.313	99.355	1.30487	−1.649	−0.0389	− 6.43
		1.0337	..	276.713	234.326	..	237.159	247.954	1.11598	−1.896	−0.0448	− 7.41
		0.5142	..	524.413	482.026	..	487.854	498.512	1.05196	−2.033	−0.0480	− 7.94
		0.2559	..	1021.814	979.427	..	991.268	1001.817	1.01996	−2.142	−0.0506	− 8.37
	25.00°	5.1777	..	80.658	38.271	12.657	38.383	49.504	1.62932	−1.536	−0.0363	− 6.00

TABLE III (*continued*).

Salt.	Temp.	Molal conc.	Wt. of salt.	Wt. of soln.	Wt. of water.	Volume of salt.	Volume of water.	Volume of soln.	Density of soln.	Change in volume.	Change per gram of salt.	Change per mol of salt.
RbBr....	25.00°	2.5816	..	130.653	88.266	..	88.525	99.286	1.31593	—1.896	—0.0448	— 7.41
		1.0345	..	279.020	236.633	..	237.328	247.779	1.12608	—2.206	—0.0521	— 8.62
		0.5145	..	528.829	486.442	..	487.871	498.163	1.06156	—2.365	—0.0558	— 9.23
		0.2560	..	1030.376	987.989	..	990.893	1001.094	1.02925	—2.456	—0.0580	— 9.60
	0.00°	2.5835	..	131.424	89.037	12.623	89.049	99.213	1.32467	—2.459	—0.0580	— 9.59
		1.0352	..	280.287	237.900	..	237.931	247.599	1.13202	—2.955	—0.0698	—11.54
		0.5149	..	530.704	488.317	..	488.382	497.823	1.06605	—3.182	—0.0751	—12.41
		0.2562	..	1033.359	990.972	..	991.103	1000.375	1.03297	—3.351	—0.0791	—13.08
RbI.....	50.04°	5.5699	58.600	92.362	33.762	16.540	34.170	49.540	1.86439	—1.170	—0.0200	— 4.24
		2.7772	..	141.839	83.239	..	84.245	99.355	1.42760	—1.430	—0.0244	— 5.18
		1.1129	..	288.857	230.257	..	233.041	247.954	1.16496	—1.627	—0.0278	— 5.90
		0.5535	..	536.534	477.934	..	483.712	498.512	1.07627	—1.740	—0.0297	— 6.31
		0.2754	..	1033.889	975.289	..	987.080	1001.817	1.03201	—1.803	—0.0308	— 6.54
	25.00°	2.7792	..	142.964	84.364	16.502	84.612	99.286	1.43992	—1.828	—0.0312	— 6.63
		1.1136	..	291.323	232.723	..	233.407	247.779	1.17574	—2.130	—0.0364	— 7.72
		0.5539	..	541.107	482.507	..	483.924	498.163	1.08620	—2.265	—0.0387	— 8.22
		0.2756	..	1042.641	984.041	..	986.932	1001.094	1.04150	—2.340	—0.0399	— 8.49
	0.00°	2.7813	..	143.868	85.268	16.461	85.279	99.213	1.45009	—2.527	—0.0431	— 9.16
		1.1144	..	292.804	234.204	..	234.236	247.599	1.18257	—3.098	—0.0529	—11.24
		0.5543	..	543.245	484.645	..	484.709	497.823	1.09124	—3.347	—0.0571	—12.12
		0.2758	..	1045.934	987.334	..	987.464	1000.375	1.04554	—3.550	—0.0606	—12.87
CsCl.....	70.19°	7.5180	62.715	94.409	31.694	15.869	32.416	49.575	1.90437	+1.290	+0.0206	+ 3.46
		4.2990	35.862	75.010	39.148	9.074	40.041	49.575	1.51306	+0.460	+0.0128	+ 2.16
		2.1437	..	124.010	88.148	..	90.158	99.417	1.24737	+0.185	+0.0052	+ 0.87
		0.8590	..	269.603	233.741	..	239.071	248.104	1.08665	—0.041	—0.0011	— 0.19
		0.4272	..	514.879	479.017	..	489.942	498.834	1.03214	—0.182	—0.0051	— 0.85
		0.2126	..	1007.337	971.475	..	993.628	1002.453	1.00487	—0.249	—0.0069	— 1.17
	50.04°	7.5233	62.715	94.820	32.105	15.833	32.494	49.540	1.91401	+1.213	+0.0193	+ 3.26
		4.3020	35.862	75.447	39.585	9.054	40.065	49.540	1.52295	+0.421	+0.0117	+ 1.98

CsCl.....	50.04°	2.1451	..	124.921	89.059	..	90.136	99.355	1.25732	+0.165	+0.0046	+ 0.78
		0.8596	..	271.969	236.107	..	238.961	247.954	1.09685	−0.061	−0.0017	− 0.29
		0.4275	..	519.648	483.786	..	489.637	498.512	1.04240	−0.179	−0.0050	− 0.84
		0.2127	..	1017.005	981.143	..	993.009	1001.817	1.01516	−0.246	−0.0069	− 1.15
	25.00°	7.5288	62.715	95.322	32.607	15.782	32.703	49.504	1.92554	+1.019	+0.0162	+ 2.75
		4.3051	35.862	75.939	40.077	9.024	40.195	49.504	1.53400	+0.285	+0.0079	+ 1.34
		2.1465	..	125.864	90.002	..	90.266	99.286	1.26769	−0.004	−0.0001	− 0.02
		0.8601	..	274.178	238.316	..	239.017	247.779	1.10654	−0.262	−0.0073	− 1.23
		0.4278	..	523.938	488.076	..	489.510	498.163	1.05174	−0.371	−0.0103	− 1.74
		0.2129	..	1025.487	989.625	..	992.532	1001.094	1.02437	−0.462	−0.0129	− 2.17
	0.00°	4.3082	..	76.364	40.502	8.992	40.507	49.469	1.54367	−0.030	−0.0008	− 0.14
		2.1481	..	126.519	90.657	..	90.669	99.213	1.27523	−0.448	−0.0125	− 2.10
		0.8608	..	275.272	239.410	..	239.442	247.599	1.11177	−0.835	−0.0233	− 3.92
		0.4281	..	525.604	489.742	..	489.807	497.823	1.05581	−0.976	−0.0272	− 4.58
		0.2130	..	1028.223	992.361	..	992.492	1000.375	1.02784	−1.109	−0.0310	− 5.21
CsBr.....	70.19°	4.1801	44.084	82.094	38.010	10.006	38.877	49.575	1.65596	+0.692	+0.0157	+ 3.34
		3.0665	32.340	73.206	40.866	7.340	41.798	49.575	1.47667	+0.437	+0.0135	+ 2.85
		1.5292	..	122.071	89.731	..	91.780	99.417	1.22787	+0.297	+0.0092	+ 1.95
		0.6127	..	267.552	235.212	..	240.576	248.104	1.07839	+0.188	+0.0058	+ 1.24
		0.3048	..	512.742	480.402	..	491.357	498.834	1.02788	+0.137	+0.0042	+ 0.90
		0.1517	..	1005.211	972.871	..	995.056	1002.453	1.00275	+0.057	+0.0018	+ 0.36
	50.04°	4.1831	44.084	82.559	38.474	9.978	38.940	49.540	1.66651	+0.622	+0.0141	+ 3.00
		3.0687	32.340	73.676	41.336	7.320	41.837	49.540	1.48720	+0.383	+0.0118	+ 2.52
		1.5301	..	123.024	90.684	..	91.782	99.355	1.23823	+0.253	+0.0078	+ 1.66
		0.6131	..	269.953	237.613	..	240.487	247.954	1.08872	+0.147	+0.0045	+ 0.96
		0.3050	..	517.592	485.252	..	491.121	498.512	1.03827	+0.071	+0.0022	+ 0.47
		0.1518	..	1014.970	982.630	..	994.514	1001.897	1.01313	−0.017	−0.0005	− 0.01
	25.00°	4.1861	44.084	83.094	39.010	9.945	39.125	49.504	1.67853	+0.434	+0.0099	+ 2.09
		3.0709	32.340	74.192	41.852	7.295	41.975	49.504	1.49871	+0.234	+0.0072	+ 1.54
		1.5312	..	123.981	91.641	..	91.910	99.286	1.24873	+0.081	+0.0025	+ 0.53
		0.6136	..	272.163	239.823	..	240.528	247.779	1.09841	−0.044	−0.0014	− 0.29

TABLE III (*continued*).

Salt.	Temp.	Molal conc.	Wt. of salt.	Wt. of soln.	Wt. of water.	Volume of salt.	Volume of water.	Volume of soln.	Density of soln.	Change in volume.	Change per gram of salt.	Change per mol of salt.
CsBr.....	25.00°	0.3052	..	521.898	489.558	..	490.996	498.163	1.04765	−0.128	−0.0040	− 0.84
		0.1519	..	1023.423	991.083	..	993.995	1001.094	1.02230	−0.196	−0.0061	− 1.29
	0.00°	3.0731	..	74.608	42.268	7.269	42.274	49.469	1.50818	−0.074	−0.0023	− 0.49
		1.5323	..	124.596	92.256	..	92.268	99.213	1.25584	−0.324	−0.0100	− 2.13
		0.6140	..	273.169	240.829	..	240.861	247.599	1.10327	−0.531	−0.0164	− 3.49
		0.3054	..	523.466	491.126	..	491.191	497.823	1.05151	−0.637	−0.0197	− 4.19
		0.1520	..	1026.026	993.686	..	993.817	1000.375	1.02564	−0.711	−0.0220	− 4.67
CsI......	70.19°	2.8931	37.252	76.883	39.631	8.315	40.534	49.575	1.55084	+0.726	+0.0195	+ 5.06
		1.4427	..	125.694	88.442	..	90.459	99.417	1.26431	+0.643	+0.0173	+ 4.48
		0.5781	..	271.120	233.868	..	239.201	248.104	1.09277	+0.588	+0.0158	+ 4.10
		0.2875	..	516.330	479.078	..	490.003	498.834	1.03507	+0.516	+0.0138	+ 3.60
		0.1431	..	1008.692	971.440	..	993.593	1002.453	1.00622	+0.545	+0.0146	+ 3.80
	50.04°	2.8952	..	77.386	40.134	8.291	40.620	49.540	1.56209	+0.629	+0.0169	+ 4.39
		1.4436	..	126.695	89.443	..	90.525	99.355	1.27517	+0.539	+0.0145	+ 3.76
		0.5784	..	273.574	236.322	..	239.180	247.954	1.10333	+0.483	+0.0130	+ 3.37
		0.2877	..	521.209	483.957	..	489.810	498.512	1.04553	+0.411	+0.0110	+ 2.86
		0.1432	..	1018.539	981.287	..	993.155	1001.817	1.01669	+0.371	+0.0100	+ 2.59
	25.00°	2.8973	..	77.989	40.737	8.262	40.857	49.504	1.57541	+0.385	+0.0103	+ 2.68
		1.4446	..	127.712	90.460	..	90.726	99.286	1.28630	+0.298	+0.0080	+ 2.08
		0.5789	..	275.858	238.606	..	239.307	247.779	1.11332	+0.210	+0.0056	+ 1.46
		0.2879	..	525.588	488.336	..	489.771	498.163	1.05505	+0.130	+0.0035	+ 0.91
		0.1433	..	1027.064	989.812	..	992.720	1001.094	1.02594	+0.112	+0.0030	+ 0.78
	0.00°	1.4456	..	128.392	91.140	8.232	91.152	99.213	1.29411	−0.171	−0.0046	− 1.19
		0.5793	..	276.940	239.688	..	239.720	247.599	1.11850	−0.353	−0.0095	− 2.46
		0.2881	..	527.224	489.972	..	490.037	497.823	1.05906	−0.446	−0.0120	− 3.11
		0.1434	..	1029.748	992.496	..	992.627	1000.375	1.02936	−0.484	−0.0130	− 3.37

Sodium and potassium chlorides produce the greatest contraction during solution, between 0.1 and 0.2 cc. per gram of salt except at the highest temperatures and concentrations.

With the other salts the contractions both per gram and per gram molecule vary irregularly between fairly narrow limits, at 25° between 0.02 and 0.09 cc. per gram of salt.

In the case of salts of the same metal with different halogens, the contraction is always greatest with chlorides and least with iodides. The only exception to this rule noted in the earlier paper, sodium bromide, has disappeared owing to the use of the new value of the density of the solid salt.

In general, contraction increases and expansion diminishes with increasing dilution. This increase in contraction with increasing dilution is greatest with chlorides and least with iodides. It is also noticeable that the rate of increase is greatest with lithium chloride, and much less for rubidium and caesium chlorides than for the corresponding salts of sodium and potassium. Bromides of the different metals show no marked differences in the rate of increase, and the same is true of the iodides.

Lithium iodide and lithium bromide in very concentrated solutions at 25° and above, show *increasing expansion with increasing dilution.*

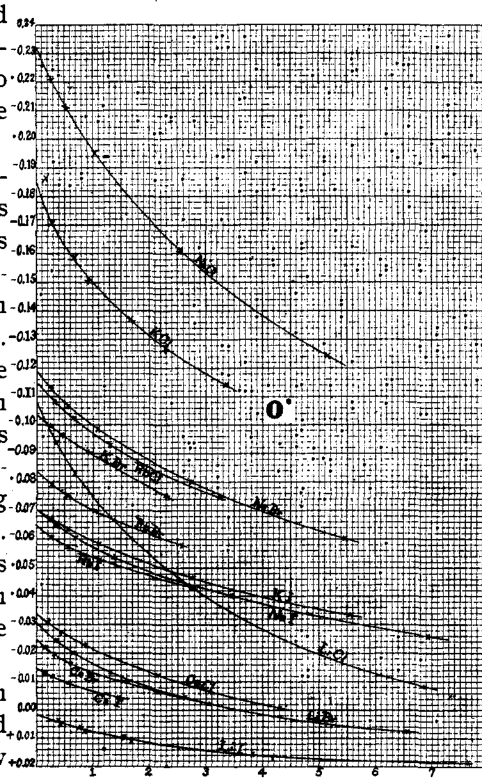

Fig. 1.

All the curves seem to approach the horizontal axis with increasing concentration, *i. e.*, in most cases the greater the change in volume, the steeper the curve. With unlimited solubility necessarily a zero value for change in volume would eventually be reached, when the water disappeared from the solution. But this point is far beyond the practical limits of solubility even with the most soluble salts.

From 0° to 50° all the salts examined except lithium chloride and up to 70° most of the salts at a given concentration show diminishing contraction or increasing expansion with rising temperature. In the case of both lithium chloride and bromide, however, the contraction is greater at 70°

than at 50° and with lithium chloride it is least at 25° and even greater at 100° than at 0°. Potassium chloride also shows greater contraction at 100° than at 25°.

In the earlier paper a suggestion was advanced as to the causes of these varied changes in volume during solution, based upon the hypothesis of compressible atoms previously proposed by T. W. Richards. While the earlier paper should be consulted for details, the main features of the explanation are summed up below.

It was pointed out that, since the solution of salts in water is accompanied sometimes by an increase, sometimes by a decrease in volume, *at least two* important influences must be at work, one producing expansion, the other contraction. Experimentally the resultant of the combined effects is observed. As the chief cause of expansion, it was suggested that, since

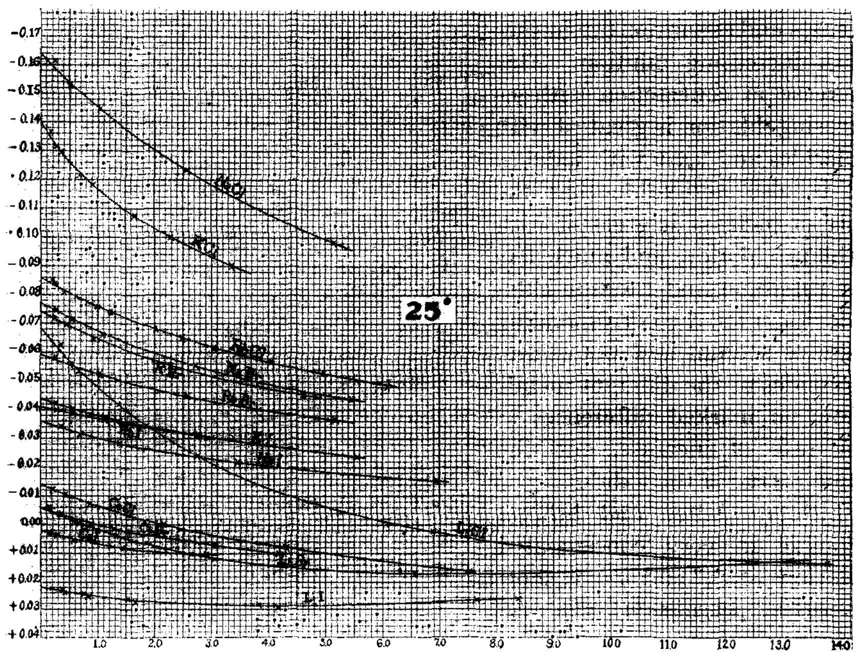

Fig. 2.

the *formation* of the solid salts in question from the solid or liquid elements is accompanied by a very marked contraction, from 15% with lithium iodide to 56% with caesium chloride,[1] the *dissociation* of the salts during solution should tend to produce a corresponding expansion.[2]

[1] See Table V on page 96.

[2] In a paper published nearly a year later than the first one of this series, Heydweiller suggests dissociation as a cause for expansion during solution but without giving any idea of the magnitude of the effect to be expected. *Ann. Physik*, **37**, 762 (1912).

As the chief cause of contraction was proposed the combination of the ions and the molecules with water, *i. e.*, ionic or molecular hydration.[1]

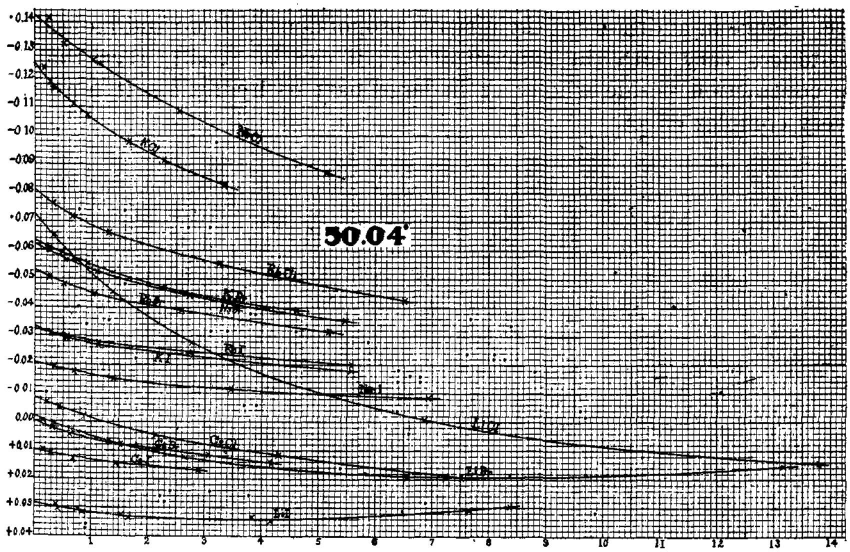

Fig. 3.

The magnitude of this effect may be expected to vary with (1) the extent of the hydration, *i. e.*, the quantities of material concerned, (2) the magnitude of the affinities involved, (3) the compressibilities of the metals and

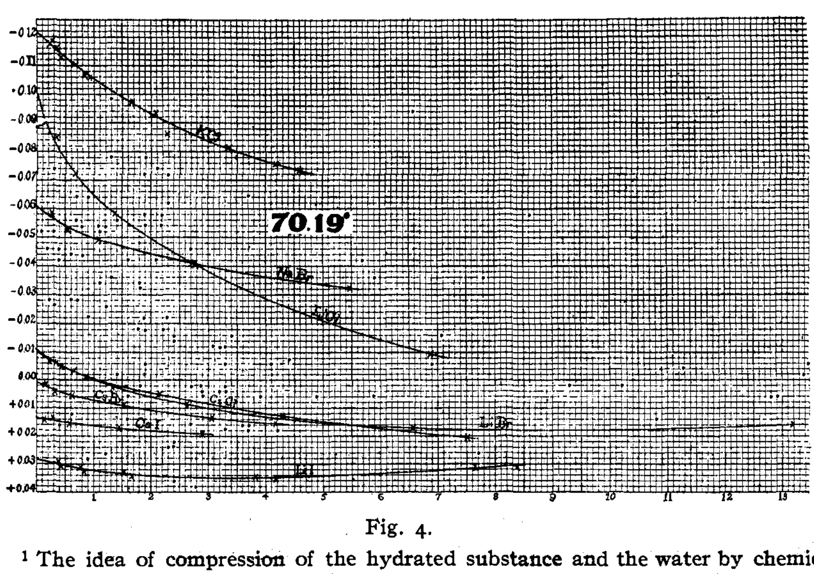

Fig. 4.

[1] The idea of compression of the hydrated substance and the water by chemical combination was first proposed by Richards (*Proc. Amer. Acad.*, 37, 13 (1901)).

halogens, and of the water. Furthermore the extent of the hydration is undoubtedly not constant for any one ionic or molecular species, but (4) increases with increasing dilution and (5) decreases with rising temperature. Since in addition (6) the relative proportions of ionic and molecular substances vary with the concentrations, it can be readily seen that if the contraction is due wholly or in large part to hydration, it must be a very complex effect.

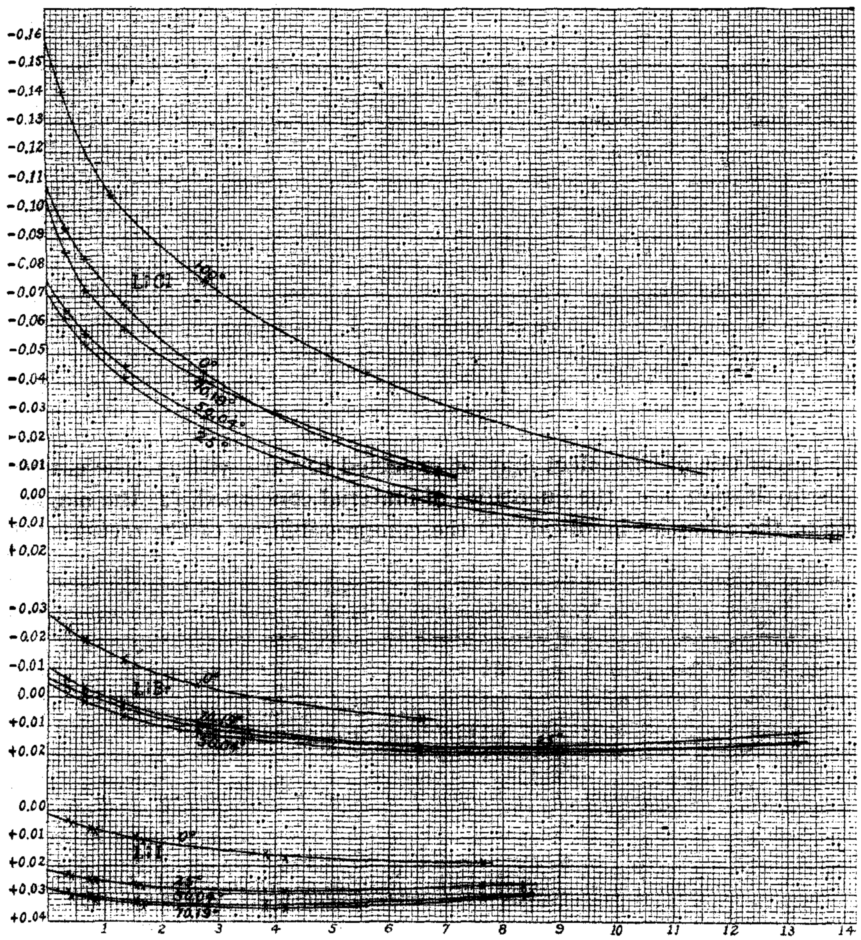

Fig. 5.

It was further pointed out that, since the molecules are already in a state of great compression, the effect of hydration in further compressing them must be small. For this reason, if for no other, the resultant change in volume during solution produced by the molecules should at any rate be less than that produced by the ions. Furthermore, judging from the fact that few of the salts in question form solid hydrates at ordinary temperatures and that even these hydrates are not particularly stable, the molecular hydration cannot be very extensive in most cases. This is in accord with the general trend of all the curves toward low values for change in volume as the concentration increases, *i. e.*, as the proportion of salt in the molecular condition increases.

It was also shown that the effects observed in fairly dilute solution are in accord with the compressibilities of the elements involved and the water, the relative hydration of the ions,[1] the affinities of the elements for each other and for water, and the change in volume during the formation of the solid salt from the elements.

It was emphasized that although the varying polymerization of water undoubtedly plays some part in the change, it certainly is not the determining factor, since the observed effects are not in accord with those to be expected if the change in volume is due wholly to changing polymerization of the water.

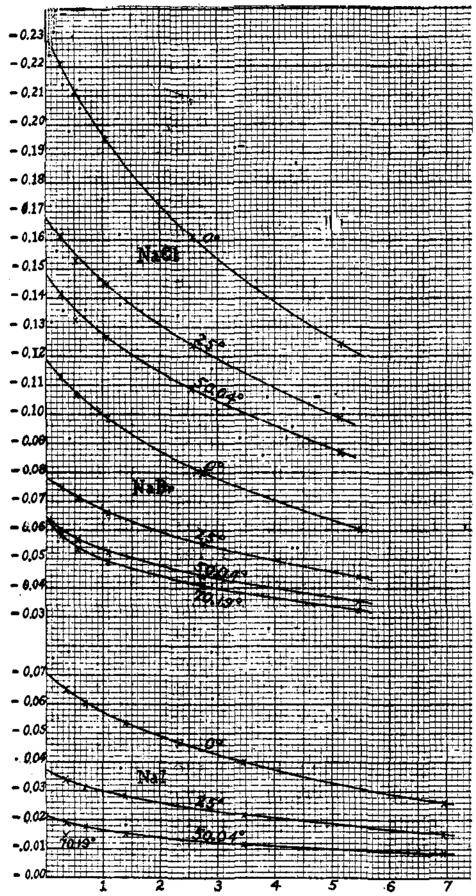

Fig. 6.

An interesting comparison of the different salts was obtained by finding the algebraic sum of (*a*) the change in volume in the formation of the solid salt from the solid or liquid elements, and (*b*) the change in volume during solution. This sum, which is negative for all fifteen salts, represents the contraction in the formation of the solution from water and the free elements. Obviously, in very dilute solution the sum represents the change in volume in the formation of ions from the free elements and water, while in more concentrated solutions it refers to both ionized and un-ionized substances in varying proportions.

[1] Washburn and Millard have recently found the caesium ion to be more highly hydrated than the chloride ion, although less hydrated than the potassium ion. THIS JOURNAL, 37, 694 (1915).

Owing to the availability of new data, the following tables, which give the values of the sum $a + b$, together with the data from which the computations are made, are reprinted from the earlier paper with the necessary corrections.

TABLE IV.

Element.	At. wt. Ag=107.88.	Sp. gr.[1]	At. vol. cc.	Compressibility[2] megabars $\times 10^6$.	Heat of oxidation. Kilogram calories.	Heat of combination with hydrogen.[4] Kilogram calories.
Li......	6.94	0.534	13.1	9.0	143(2M + O)[3]	..
Na.....	23.00	0.971	23.7	15.6	101(2M + O)[3]	..
K......	39.10	0.862	45.4	31.7	87(2M + O)[3]	..
Rb.....	85.45	1.532	55.8	40.0	84(2M + O)[3]	..
Cs.....	132.81	1.87	71.0	61.0	83(2M + O)[3]	..
Cl......	35.46	1.412	25.0	95.0	—18(Cl_2O)	22.0
Br.....	79.92	3.121	25.6	52.0	...	8.4
I.......	126.92	4.94	25.7	13.0	45(I_2O_5)	—6.0

TABLE V.

Salt.	Mol. wt.	Sp. gr.[5] fused salt at 25°.	Sum of at. vols. cc.	Mol. vol. cc.	Contraction in formation of solid = a. cc.	Change in vol.[6] during soln. at 25° = b. cc.	$a + b$. cc.	Compressibility[7] megabars $\times 10^6$.
LiCl....	42.40	2.068	38.1	20.5	—17.6	—2.03	—19.6	...
LiBr....	86.86	4.364	38.7	25.1	—13.6	+0.16	—13.4	...
LiI.....	133.86	4.061	38.8	33.0	— 5.8	+3.40	— 2.4	...
NaCl....	58.46	2.162	48.7	27.0	—21.7	—8.48	—30.2	4.1
NaBr....	102.92	3.203	49.3	33.1	—17.2	—6.94	—24.1	5.1
NaI.....	149.92	3.665	49.4	40.9	— 8.5	—4.50	—13.0	6.9
KCl.....	74.56	1.988	70.4	37.5	—32.9	—8.71	—41.6	5.0
KBr.....	119.02	2.749	71.0	43.3	—27.7	—7.72	—35.4	6.2
KI......	166.02	3.123	71.1	53.2	—17.9	—6.31	—24.2	8.6
RbCl....	120.91	2.798	80.8	43.2	—37.6	—9.19	—46.8	...
RbBr....	165.37	3.349	81.4	49.4	—32.0	—8.70	—40.7	...
RbI.....	212.37	3.550	81.5	59.8	—21.7	—7.86	—29.6	...
CsCl....	168.27	3.974	96.0	42.4	—53.6	—1.09	—54.7	...
CsBr....	212.73	4.433	96.6	47.9	—48.7	0.00	—48.7	...
CsI.....	259.73	4.509	96.7	57.6	—39.1	+1.77	—37.3	...

[1] For the specific gravities of the alkali metals see Richards and Brink, THIS JOURNAL, **29**, 117 (1907).

[2] Richards, Stull and Bonnet, *Pub. Carnegie Inst.*, **76**, 15 (1907); Richards and Stull, *Ibid.*, **7** (1903); Richards, THIS JOURNAL, **37**, 1643 (1915).

[3] Abegg, "Handb. d. anorg. Chem.," Vol. II, Part I.

[4] Landolt-Börnstein-Roth, "Tabellen," 1912.

[5] For the specific gravities of the salts of sodium, potassium rubidium, and caesium, see a subsequent paper to appear in the February number of THIS JOURNAL; for those of the lithium salts, see Baxter, *Am. Chem. J.*, **31**, 559 (1904).

[6] The values refer to molal solutions and are obtained by multiplying values taken from the curves on page 92 by the molecular weights.

[7] Richards and Jones, THIS JOURNAL, **31**, 158 (1909). If the most recent value of the compressibility of mercury is used these values become slightly larger.

The sum $a + b$, which represents, in cubic centimeters, the contraction produced in the formation of the solution from one gram atom each of the free metal and halogen and the water, was previously found to be additive for lithium, sodium, and potassium salts at 1 molal concentration and below. Values are given in Table VI for all fifteen salts at various concentrations up to five molal, at 25°, which show not only that the property is additive for the rubidium and cesium salts as well, but also that the additive relationship holds for all fifteen salts at high concentrations.

In connection with these tables it is interesting to note that since the values are obtained from the expression (Atomic Volume of Metal + Atomic Volume of Halogen — Molecular Volume of Salt) + (Molecular Volume of Salt + Volume of Water — Volume of Solution), they are independent of the molecular volumes (and hence the specific gravities) of the solid salts, and that while the absolute values are dependent on both the atomic volumes of the free elements and the observed change in volume during solution, the additive relationships depend upon the latter alone.

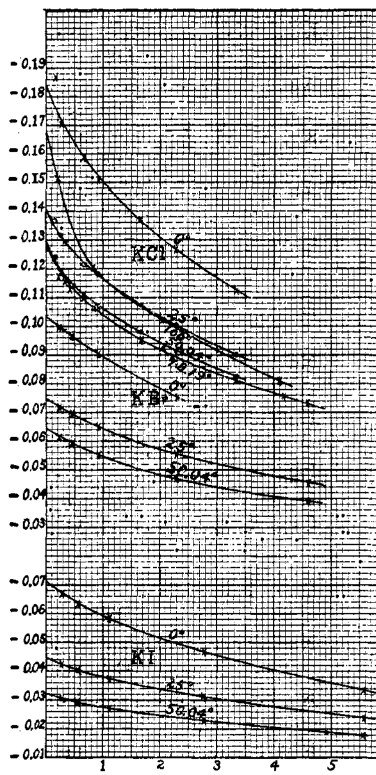

Fig. 7.

It is not surprising to find the additive relationships holding closely at the lower concentrations, where the greater portion of the salt is in the ionic state, but that these relationships should hold so closely at concentrations as high as 5 molal is curious, to say the least. The fact that the curves representing change in volume at different concentrations are far from parallel makes the relationship all the more striking. The obvious significance of this feature is that the change in volume which takes place when the free elements become dissolved *molecules* of salt also is an additive property.

It is difficult to believe that this coincidence is a chance one. The cause may be sought first in the probability, previously emphasized, that the change in volume produced by the undissociated molecules at high concentrations at any rate is small, and second in the fact that the molecular volumes of the solid salts themselves are not far from additive, as Table VII shows.

Table VI.

	Cl.	Dif.	Br.	Dif.	I.
		Infinite Dilution.			
Li	20.5	6.4	14.1	11.3	2.8
Dif.	10.8		11.0		11.1
Na	31.3	6.2	25.1	11.2	13.9
Dif.	12.0		11.4		11.3
K	43.3	6.8	36.5	11.3	25.2
Dif.	4.7		5.3		5.2
Rb	48.0	6.2	41.8	11.4	30.4
Dif.	8.0		8.2		8.2
Cs	56.0	6.0	50.0	11.4	38.6
		1 Molal.[1]			
Li	19.6	6.2	13.4	11.0	2.4
Dif.	10.6		10.7		10.6
Na	30.2	6.1	24.1	11.1	13.0
Dif.	11.4		11.3		11.2
K	41.6	6.2	35.4	11.2	24.2
Dif.	5.2		5.3		5.4
Rb	46.8	6.1	40.7	11.1	29.6
Dif.	7.9		8.0		7.7
Cs	54.7	6.0	48.7	11.4	37.3
		3 Molal.			
Li	18.5	6.0	12.5	10.5	2.0
Dif.	10.1		10.2		10.0
Na	28.6	5.9	22.7	10.7	12.0
Dif.	11.2		11.1		11.0
K	39.8	6.0	33.8	10.8	23.0
Dif.	5.3		5.3		5.2
Rb	45.1	6.0	39.1	10.9	28.2
Dif.	7.9		8.0		8.2
Cs	53.0	5.9	47.1	10.7	36.4
		5 Molal.			
Li	17.9	5.7	12.2	10.2	2.0
Dif.	9.6		9.7		9.3
Na	27.5	5.6	21.9	10.6	11.3
		Dif.	11.0		10.8
K	Dif. 16.5		32.9	10.8	22.1
		Dif.	5.2		
Rb	44.0	5.9	38.1		
Dif.	7.9		8.0		
Cs	51.9	5.8	46.1		

When one considers the large variation in the contraction which takes place in the formation of the solid salts from the elements, from 15% with lithium iodide to 56% with caesium chloride, even this rough additive relationship is noteworthy.

[1] Similar data for barium chloride and bromide obtained by Mr. P. B. Goode give values 57.7 and 44.7, respectively, with a difference of 2 (6.5). This value is not far from the average difference between chlorides and bromides of the univalent elements.

TABLE VII.

Molecular Volumes of Solid Salts.

	Cl.	Dif.	Br.	Dif.	I.
Li	20.5	4.6	25.1	7.9	33.0
Dif.	6.5		8.0		7.9
Na	27.0	6.1	33.1	7.8	40.9
Dif.	10.5		10.2		12.3
K	37.5	5.8	43.3	9.9	53.2
Dif.	5.7		6.1		6.6
Rb	43.2	6.2	49.4	10.4	59.8
Dif.	—0.8		—1.5		—2.2
Cs	42.4	5.5	47.9	9.7	57.6
Cs-Li	21.9		22.8		24.6

Since the salts are undoubtedly not all equally dissociated at a given molal concentration, and since the molecular volumes of the solid salts are only approximately additive, it is not to be expected that the values for the sum $(a + b)$ will be strictly additive, except at a dilution so great that dissociation is nearly complete. But at such concentrations experimental values for change in volume during solution become much less accurate.

At 0°, 50° and 70°, and within the same concentration limits, the same additive relationships hold. Figures showing this to be true follow for as many instances as it seems worth while to give.

TABLE VIII.

Infinite Dilution, 0°.

	Cl.	Dif.	Br.	Dif.	I.
Li	22.2	5.9	16.3	10.8	5.5
Dif.	13.1		13.1		13.5
Na	35.3	5.9	29.4	10.4	19.0
Dif.	11.3		10.6		10.5
K	46.6	6.6	40.0	10.5	29.5
Dif.	4.9		5.8		5.9
Rb	51.5	5.7	45.8	10.4	35.4
Dif.	7.8		8.1		7.5
Cs	59.3	5.4	53.9	11.0	42.9

1 Molal, 0°.

	Cl.	Dif.	Br.	Dif.	I.
Li	20.8	5.8	15.0	10.2	4.8
Dif.	12.4		12.5		12.3
Na	33.2	5.7	27.5	10.4	17.1
Dif.	10.9		10.8		10.6
K	44.1	5.8	38.3	10.6	27.7
Dif.	5.2		5.3		5.4
Rb	49.3	5.7	43.6	10.5	33.1
Dif.	7.9		7.9		7.7
Cs	57.2	5.7	51.5	10.7	40.8

3 Molal, 0°.

	Cl.	Dif.	Br.	Dif.	I.
Li	19.3	5.5	13.8	9.9	3.9
Dif.	11.4		11.4		11.0

TABLE VIII (*continued*).

	Cl.	Dif.	Br.	Dif.	I.
Na................	30.7	5.5	25.2	10.3	14.9
Dif.	11.0		10.6		10.5
K................	41.7	5.9	35.8	10.4	25.4
Dif.	5.1		5.3		5.2
Rb................	46.8	5.7	41.1	10.5	30.6
Dif.	8.0		8.2		
Cs................	54.8	5.5	49.3		
		5 Molal, 0°.			
Li................	18.4	5.2	13.2	9.7	3.5
Dif.	10.7		10.5		9.9
Na................	29.1	5.4	23.7	10.3	13.4
		Infinite Dilution, 50°.			
Li................	20.7	6.9	13.8	12.2	1.6
Dif.	9.3		9.8		10.0
Na................	30.0	6.4	23.6	12.0	11.6
Dif.	12.2		11.6		11.8
K................	42.2	7.0	35.2	11.8	23.4
Dif.	5.2		5.6		5.1
Rb................	47.4	6.6	40.8	12.3	28.5
Dif.	7.6		7.9		8.0
Cs................	55.0	6.3	48.7	12.2	36.5
		1 Molal, 50°.			
Li................	19.8	6.6	13.2	11.6	1.6
Dif.	9.3		9.5		9.1
Na................	29.1	6.4	22.7	12.0	10.7
Dif.	11.7		11.6		11.7
K................	40.8	6.5	34.3	11.9	22.4
Dif.	5.1		5.2		5.3
Rb................	45.9	6.4	39.5	11.8	27.7
Dif.	7.9		7.9		7.9
Cs................	53.8	6.4	47.4	11.8	35.6
		3 Molal, 50°.			
Li................	18.7	6.1	12.6	11.4	1.2
Dif.	9.1		9.0		9.1
Na................	27.8	6.2	21.6	11.3	10.3
Dif.	11.5		11.3		11.3
K................	39.3	6.4	32.9	11.3	21.6
Dif.	5.1		5.3		5.2
Rb................	44.4	6.2	38.2	11.4	26.8
Dif.	7.8		8.0		7.9
Cs................	52.2	6.0	46.2	11.5	34.7
		5 Molal, 50°.			
Li................	18.0	5.9	12.1	10.8	1.3
Dif.	8.8		8.9		8.6
Na................	26.8	5.8	21.0	11.1	9.9
		Dif.	11.3		11.1
K.............. Dif.	16.6		32.3	11.3	21.0
		Dif.	5.0		5.1

TABLE VIII (*continued*).

	Cl.	Dif.	Br.	Dif.	I.
Rb	43.4	6.1	37.3	11.2	26.1
Dif.	7.9		8.0		
Cs	51.3	6.0	45.3		
		Infinite Dilution, 70°.			
Li	21.8	7.3	14.5	12.5	2.0
Dif.	33.5		34.0		33.6
Cs	55.3	6.8	48.5	12.9	35.6
		1 Molal, 70°.			
Li	20.4	6.8	13.6	12.1	1.5
Dif.	33.3		33.5		33.3
Cs	53.7	6.6	47.1	12.3	34.8
		3 Molal, 70°.			
Li	19.2	6.5	12.7	11.6	1.1
Dif.	32.9		33.1		33.0
Cs	52.1	6.3	45.8	11.7	34.1
		5 Molal, 70°.			
Li	18.5	6.2	12.3	11.1	1.2
Dif.	32.6		32.8		
Cs	51.1	6.0	45.1		

Upon the same assumption as that made in the earlier paper, that at infinite dilution the sum of $a + b$ for lithium iodide is equally distributed between the lithium and iodide ions, Table IX can be constructed to show the change in volume in the formation of the ions from the elements. The values are expressed in cubic centimeters per gram atom and apply at 25°.

TABLE IX.

Li	Na	K	Rb	Cs	I	Br	Cl
—1.4	—12.4	—24.0	—29.1	—37.2	—1.4	—12.7	—19.1

Values at other temperatures are not very different from these. The only apparent regularity in this table is the increase in the values with increasing atomic volume and compressibility in the case of the metals and with increasing compressibility and hydration in the case of the halogens, the atomic volumes of the halogens being all nearly the same.

It is interesting to note the properties of the pairs of elements which according to the above table produce nearly equal contraction. Lithium in the ionic condition is more hydrated, but has a smaller compressibility than iodine, and its atomic volume is only one-half as large; the sodium ion also is more hydrated than the bromine ion, but its compressibility is less than one-third that of bromine, while the two elements have nearly the same atomic volume; the potassium ion is slightly more hydrated than the chlorine ion, but chlorine is three times as compressible and has only half as large an atomic volume.

Where, in general, solution produces contraction, then, since dissociation and probably hydration increase with increasing dilution, the contraction during solution should increase with the dilution, as is the case with the greater portion of the salts. On the other hand, wherever expansion occurs during solution, one might expect increasing expansion with increasing dilution. This latter effect actually occurs with only two salts of those which produce expansion during solution, lithium iodide and lithium bromide, and even with these salts only at high concentrations and at temperatures of 25° and above. On the other hand there is no case where there is *diminishing contraction* with increasing dilution.

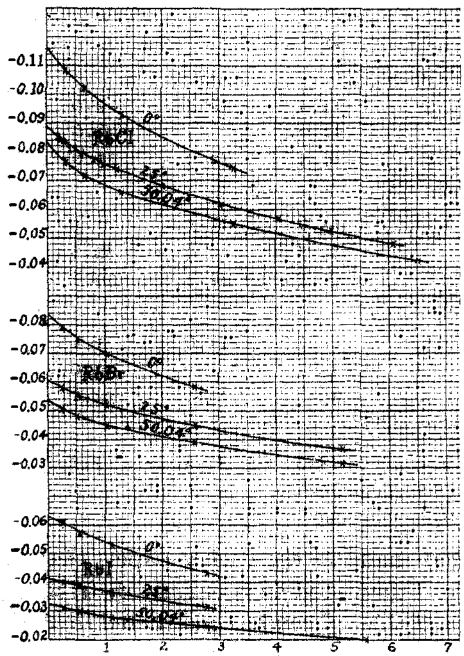

Fig. 8.

With lithium bromide and iodide at lower concentrations the expansion during solution diminishes instead of increasing, but, as was pointed out in the former paper, such an effect might be caused by the compensating influence of an increasing degree of hydration.

Since the formation of hydrates is undoubtedly hindered by rising temperature, this chief cause of contraction during solution should have less effect at higher temperatures. Hence diminution in volume during solution should become less with rising temperature, while expansion should become greater. Practically this is the case with all the salts except lithium chloride up to 50°, and with most of them up to 70°. Furthermore the changes in volume during solution at 50° and at 70° are not very different.

It is curious, however, that in the case of lithium chloride and bromide the contraction is greater at 50° than at 25°, and that at 100° lithium chloride shows even greater contraction than at 0°. Potassium chloride was the only other salt with which measurements were made at 100°, and here also the results showed contraction greater than at 70°.

Since in both instances the 100° curve is not far from parallel with those obtained at lower temperatures, it is not unreasonable to suppose that the origin of this peculiarity is to be sought in some change in the water itself rather than in one affecting either the ions or the molecules. It is on the whole unlikely that so marked a change would affect both the ions and the molecules to a like degree. In this connection it is worth pointing out that several properties of water, for instance, density, specific heat and compressibility, pass through minima with changing temperature. In any event the evidence is too meagre for drawing any certain conclusions as to the cause of this effect. Further work upon change in volume during solution at high temperatures is under way.

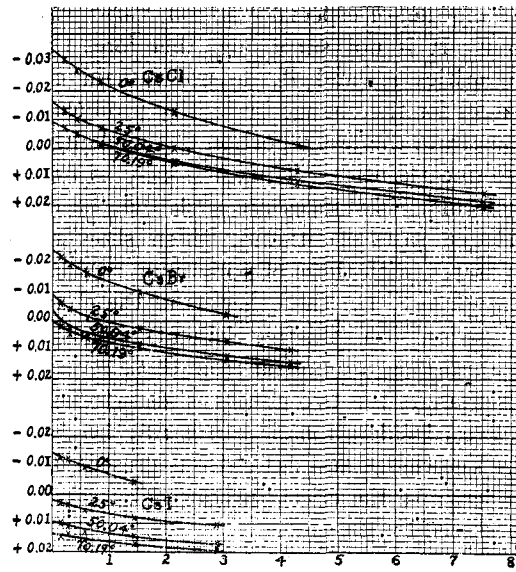

Fig. 9.

At first sight it would seem that one might separate the effects due to the ionized and un-ionized portions, if the degree of dissociation of the salt at different concentrations is known. In fact, an attempt has been made to do this by Heydweiller[1] in recent papers dealing with the properties of solutions of various electrolytes, by the use of the formula:

$$\Delta_s = B_s + (A_s - B_s)i$$

where $\Delta_s = 100\ (s - 1)/m$, the percentage density difference between solution (s) and water (1) per mol, A_s and B_s represent the separate effects of ionized and un-ionized material, respectively, and i the degree of dissociation.

Heydweiller finds that, using the values for the two constants A_s and B_s in the above equation, the calculated increase in density agrees fairly closely with the observed over a range of concentration between four normal and about half normal, although at lower concentrations marked deviations appear. Heydweiller determines the degree of dissociation at any concentration from the relation of the conductivity to the conductivity at infinite dilution. This method of calculation, obviously, is based on two assumptions of questionable validity: First, it is well known that the degree of dissociation is not accurately given by the relation of the conductivity of a solution to the conductivity at infinite dilution; second, it seems hardly possible that the constants in the above equation are really constants over any considerable range of concentra-

[1] *Ann. Physik*, **30**, 873 (1909); **37**, 739 (1912).

tion, because the degree of hydration of either a molecule or an ion surely changes with the concentration, that is, a change in volume produced by a molecule, or especially an ion, varies with the concentration of the solution. It is not surprising, therefore, that Heydweiller's values for the quantities A_s and B_s do not remain constant at high dilutions. The values for the change in density produced by the molecules, because they constitute the lesser portion of the change, are naturally more affected by the uncertainties. Thus it is easy to understand that the values for the molecular substances are such that he classes as similar compounds the halogen salts of lithium, which show marked tendencies to form solid hydrates, with those of potassium, rubidium and cesium, which crystallize anhydrous. On the other hand the change in volume in the production of the ions from the free elements, calculated by Heydweiller[1] upon similar assumptions, are not far from those given upon page 101. This attempt to disentangle the two effects is an extremely interesting one, but from the above considerations it can hardly be considered to be successful. With the knowledge and data at our present disposal, it does not seem possible to separate the effects produced by the molecular substances from those produced by the ions.

We are greatly indebted to the Carnegie Institution of Washington for very generous assistance in this investigation.

Summary.

1. Data are given from which the densities of aqueous solutions of all the halogen salts of the alkali elements at different temperatures may be very exactly calculated.

2. From these data are calculated the changes in volume which take place during the solution of these salts.

3. The explanation of the observed effects, previously proposed upon the basis of Richards's hypothesis of compressible atoms and that of hydration, is supported. This explanation assumes that the following two changes, which take place during solution and dissociation, are the chief causes of the observed effects:

(*a*) When the molecules dissociate, they are freed in large part from compression due to chemical affinity, with considerable expansion (from 15 to 56% of the original volume of the uncombined elements).

(*b*) When the ions and probably the molecules are combined with water both the hydrated substance and the water undergo compression. The latter effect varies regularly with the compressibilities of the substances involved as well as with their affinities for each other.

4. The change in volume in the formation of the solution from the free halogens and alkali metals and water is found to be nearly additive at all concentrations; at low concentrations because the changes involved

[1] *Ann. Physik*, 37, 767 (1912).

are chiefly due to the formation of the ions from the elements, which are independent of the salts involved; at high concentrations because the molecules, being less hydrated and less compressible produce smaller contractions, and because the molecular volumes of the salts are very nearly additive.

5. The effect of rising temperature is found in general to diminish contraction or increase expansion owing to lessened hydration of all the substances concerned. Marked exceptions exist at ordinary temperatures in lithium chloride and bromide, and at high temperatures in potassium chloride also.

6. It is pointed out that no simple method exists for separating the effects due to ionized and un-ionized material because of the varying magnitude of the change for each ion or molecule with changing concentration.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF JOHNS HOPKINS UNIVERSITY.]

THE ACTION OF SALTS WITH WATER OF HYDRATION AND WITHOUT WATER OF HYDRATION ON THE VELOCITY OF SAPONIFICATION OF ESTERS.[1]

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Received November 5, 1915.

Jones and Anderson,[2] in their work on the absorption spectra of solutions, studied the absorption spectra of neodymium chloride in water, in methyl alcohol and in mixtures of these two solvents. They found two sets of absorption spectra corresponding, the one to the aqueous solution and the other to the alcoholic.

In the mixture of these solvents both of these spectra were obtained. Similar results were obtained with neodymium nitrate and praseodymium chloride.

Jones and Strong[3] studied a fairly large number of salts in a large number of solvents, and found a large number of "solvent bands." This raised the question whether combined water has different power to absorb light from free water? This was answered by Jones and Guy,[4] by means of the radiomicrometer. They showed that *combined water* was *far more transparent than pure water.*

This conclusion was confirmed by the work of Jones, Shaeffer and Paulus.[5]

[1] The results of this investigation are recorded in full in *Publ. Carnegie Inst. Wash.*, No. **230**.

[2] *Publ. Carnegie Inst. Wash.*, No. 110; *Am. Chem. J.*, **41**, 163 (1909).

[3] *Ibid.*, No. 130 and **160**; **43**, 37, 224 (1910); **45**, 1 (1910); **47**, 27 (1912); *Physik. Z.*, 10, 449 (1909); *Phil. Mag.*, April, **1910**; *J. chim. phys.*, **8**, 131 (1910).

[4] *Publ. Carnegie Inst. Wash.*, No. **190**; *Ann. physik.*, **43**, 555 (1914).

[5] *Physik. Z.*, **15**, 447 (1914).