The chief results of this research may be summed up as follows:

1. The densities and indices of refraction at 25° of solutions of the chlorides, bromides and iodides of lithium, sodium and potassium have been accurately determined at various concentrations.

2. The increments of density and refractive index for solutions of the above salts are calculated at 25° and are found to decrease slowly with increasing concentration and to be very closely additive at equivalent concentrations, especially at low concentrations.

3. It is pointed out that no refractive constant for one component of a solution, which is calculated upon the assumption that the specific refraction of the other component remains constant in solution and equal to that of the pure substance, is entirely satisfactory, since in general specific refraction, no matter by what formula calculated, changes with even slight changes in conditions.

4. The specific refractions of the salts in question, calculated by the Lorentz and Lorenz formula upon the assumption that the specific refraction of water does not change in solution, are found to be very nearly constant, but to increase very slightly with increasing dilution.

5. The molecular refractions of the nine salts are found to be very nearly additive at all concentrations.

The data given in this paper allow the computation of the change in volume during solution in water of the salts. This question is discussed in detail in the following paper.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

CHANGES IN VOLUME UPON SOLUTION IN WATER OF THE HALOGEN SALTS OF THE ALKALIS.

BY GREGORY PAUL BAXTER.

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It is commonly stated that when salts are dissolved in water the volume of the solution is less than the sum of the volumes of the salt and the water.[1] In some cases the volume of the solution is even less than the volume of the water alone.[2] Furthermore, the contraction is greater the more dilute the solution,[3] as is evident from the well known fact that usually contraction continues to take place as a solution is diluted. It is less well recognized that in a few instances the volume of the solution is greater than the sum of the volumes of the salt and the water,

[1] Nernst, *Theoret. Chem.*, trans., p. 381 (1904); Ostwald, *Lehrbuch*, 1, 782 (1903)

[2] Thomsen, *Therm. Untersuch.*, 1, 45 (1882). MacGregor, *Trans. Roy. Soc. Can.* 1890, 19; 1891, 15. *Trans. Nova Scotia Inst. Nat. Sci.*, 7, 368 (1890). Traube, *Z. anorg. Chem.*, 3, 1 (1892).

[3] Nernst, *Loc. cit.*

although as early as 1873 Favre and Valson pointed out that this is the case with the halogen salts of ammonium.[1] Later Traube[2] showed that expansion takes place with lithium bromide and ammonium nitrate, although not with ammonium iodide. Quite recently, a similar expansion has been observed by Buchanan,[3] who found that in the saturated solutions of the halogen salts of cesium the "molecular volumes" of the salts in solution are greater than those of the solid salts, although the reverse is true with the corresponding salts of potassium and rubidium. Buchanan pointed out that this peculiarity indicates *contraction during crystallization.*

Previous attempts to correlate the sum of the volumes of the salt and the water and the volume of the resulting solution have been somewhat hampered by lack of sufficiently accurate density determinations, both with regard to the salts and their solutions, the chief error in the case of the solutions being due to inaccurate determination of concentration. The data furnished in the preceding paper[4] upon the refractive power of the halogen salts of lithium, sodium, and potassium in aqueous solution, together with recent specific gravity determinations of solids (see Table IV), allow the calculation of the change in volume during the solution of the foregoing salts with considerable certainty, and since these values were determined under essentially the same conditions they are strictly comparable. The interesting feature of the results is that not only the expansion during solution in the case of lithium bromide is confirmed, but also that lithium iodide is found to behave similarly.

In the following tables are given the data illustrating the magnitude of the changes in volume during solution for the fifteen salts of all the alkali metals with the halogens. The values in Table I, for the lithium, sodium, and potassium salts, are taken from the preceding paper. In the case of the rubidium and cesium salts Buchanan's results are employed, and for sake of comparison his experiments with potassium salts are given in Table II. The specific gravities of the solid salts used in the calculations are given in Table IV, except that in Buchanan's experiments his own values for the specific gravities are used. Buchanan's results for the specific gravities of the salts under consideration are probably slightly too low, owing to occlusion of mother liquor by the crystals used in the determinations, although the small differences between his values and those given in Table IV may be due in part, at least, to the fact that the data in Table IV refer to the fused salts:

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[1] *Compt. rend.*, **77**, 802 (1873).

[2] *Loc. cit.*

[3] *Am. J. Sci.*, **21**, 25 (1906).

[4] Baxter, Boylston, Mueller, Black and Goode.

TABLE I.

Salt.	Gram molecular concentration.	Volume of solution. cc.	Volume of water. cc.	Volume of salt. cc.	Change in volume during solution. cc.	Change in volume per gram of salt. cc.	Change in volume per gram molecule of salt. cc.
LiCl....	0.15	250.61	249.94	0.76	—0.09	—0.06	—2.5
	0.17	250.865	250.136	0.848	—0.119	—0.068	—2.9
	0.22	250.865	249.852	1.134	—0.121	—0.052	—2.2
	0.23	250.61	249.54	1.16	—0.09	—0.04	—1.7
	0.23	250.61	249.47	1.18	—0.04	—0.02	—0.8
	0.33	250.865	249.320	1.721	—0.176	—0.0494	—2.09
	0.66	100.405	99.195	1.360	—0.150	—0.0534	—2.26
	0.66	250.865	247.838	3.405	—0.378	—0.0537	—2.28
	1.39	100.432	97.766	2.868	—0.202	—0.0341	—1.45
	1.61	100.432	97.360	3.315	—0.243	—0.0355	—1.51
	2.64	100.432	95.316	5.441	—0.325	—0.0289	—1.23
	3.31	100.432	93.909	6.831	—0.308	—0.0218	—0.93
NaCl...	0.09	1001.75	1000.18	2.47	—0.90	—0.170	—9.9
	0.09	1001.75	1000.15	2.57	—0.98	—0.178	-10.4
	0.17	1001.75	998.77	4.69	—1.71	—0.170	—9.9
	0.18	99.869	99.526	0.499	—0.156	—0.146	—8.5
	0.19	501.20	499.49	2.60	—0.89	—0.160	—9.4
	0.95	99.869	98.103	2.547	—0.821	—0.1481	—8.66
	0.96	99.869	98.086	2.615	—0.832	—0.1488	—8.70
	2.70	38.695	36.610	2.856	—0.771	—0.1262	—7.38
KCl....	0.13	1001.75	998.20	4.77	—1.22	—0.128	—9.6
	0.13	100.45	100.08	0.49	—0.12	—0.12	—9.0
	0.13	250.57	249.65	1.23	—0.31	—0.126	—9.4
	0.13	501.20	499.33	2.52	—0.65	—0.129	—9.6
	0.13	250.57	249.67	1.26	—0.36	—0.143	-10.7
	0.33	100.45	99.50	1.24	—0.29	—0.117	—8.7
	0.33	100.45	99.49	1.26	—0.30	—0.118	—8.8
	0.64	501.20	492.03	11.99	—2.82	—0.118	—8.8
	0.67	100.45	98.62	2.50	—0.67	—0.134	-10.0
	0.67	100.45	98.57	2.50	—0.62	—0.124	—9.3
	0.67	100.45	98.58	2.50	—0.63	—0.126	—9.4
	1.00	100.45	97.54	3.76	—0.85	—0.113	—8.3
	1.00	100.45	97.54	3.77	—0.86	—0.114	—8.4
	1.28	100.45	96.79	4.79	—1.13	—0.118	—8.8
	1.34	100.45	96.53	5.01	—1.09	—0.109	—8.1
	1.35	99.869	95.927	5.032	—1.090	—0.109	—8.1
	2.00	100.45	94.41	7.53	—1.49	—0.099	—7.4
	2.01	100.45	94.47	7.53	—1.55	—0.103	—7.7
	2.67	100.45	92.32	10.03	—1.90	—0.0950	—7.08
	2.68	100.45	92.31	10.06	—1.92	—0.0958	—7.14
	3.30	100.45	90.33	12.38	—2.26	—0.0925	—6.80
	3.34	100.45	90.16	12.54	—2.25	—0.0900	—6.71
LiBr...	0.02	100.25	100.18	0.06	+0.01	+0.05	+4.0
	0.04	100.25	100.16	0.10	—0.01	—0.03	—3.0
	0.05	100.25	100.14	0.11	0.00	0.00	0.0

TABLE I (*continued*).

Salt.	Gram molecular concentration.	Volume of solution, cc.	Volume of water, cc.	Volume of salt. cc.	Change in volume during solution, cc.	Change in volume per gram of salt. cc.	Change in volume per gram molecule of salt. cc.
LiCl....	0.05	100.25	100.12	0.12	+0.01	+0.02	+2.0
	0.09	100.25	100.00	0.24	+0.01	+0.01	+1.0
	0.12	100.25	99.95	0.30	0.00	0.00	0.0
	0.17	99.869	99.460	0.414	—0.005	—0.003	—0.3
	0.20	100.25	99.76	0.49	0.00	0.00	0.0
	0.22	50.17	49.91	0.27	—0.01	—0.01	—1.0
	0.42	50.17	49.65	0.53	—0.01	—0.006	—0.5
	0.42	50.17	49.65	0.53	+0.01	+0.006	+0.5
	0.44	50.17	49.61	0.56	0.00	—0.00	0.0
	0.51	50.17	49.54	0.64	—0.01	—0.005	—0.4
	0.55	50.17	49.48	0.69	0.00	0.000	0.0
	0.74	50.150	49.228	0.936	—0.014	—0.0043	—0.43
	1.92	50.20	47.75	2.42	+0.03	+0.004	+0.3
	2.39	50.15	47.048	3.011	+0.091	+0.0087	+0.76
	4.83	27.167	23.687	3.290	+0.190	+0.0168	+1.46
NaBr...	0.05	100.250	100.130	0.162	—0.042	—0.086	—8.8
	0.09	100.25	100.03	0.30	—0.08	—0.09	—9.0
	0.11	100.250	99.995	0.373	—0.118	—0.104	-10.7
	0.19	100.25	99.76	0.67	—0.18	—0.09	—9.0
	0.21	100.250	99.760	0.709	—0.219	—0.102	-10.5
	0.28	100.250	99.605	0.953	—0.308	—0.107	-11.0
	0.29	100.25	99.68	0.99	—0.28	—0.094	—9.7
	0.46	99.869	98.723	1.558	—0.412	—0.088	—9.1
	0.46	50.150	49.564	0.795	—0.209	—0.088	—9.1
	0.67	50.16	49.33	1.14	—0.31	—0.090	—9.3
	0.74	50.16	49.22	1.26	—0.32	—0.084	—8.6
	0.76	50.146	49.183	1.299	—0.336	—0.0860	—8.85
	0.91	50.146	48.998	1.565	—0.417	—0.0886	—9.12
	1.92	87.35	82.98	5.73	—1.36	—0.0788	—8.11
	6.71	66.64	54.10	15.30	—2.76	—0.0600	—6.18
KBr....	0.03	1001.75	1000.59	1.38	—0.22	—0.058	—6.9
	0.08	501.20	499.67	1.81	—0.28	—0.056	—6.7
	0.12	501.20	499.03	2.63	—0.46	—0.064	—7.6
	0.13	100.301	99.858	0.553	—0.110	—0.073	—8.7
	0.25	100.301	99.427	1.094	—0.220	—0.073	—8.7
	0.32	100.324	99.228	1.375	—0.279	—0.074	—8.8
	0.36	100.301	99.040	1.556	—0.295	—0.069	—8.2
	0.36	99.869	98.596	1.580	—0.307	—0.071	—8.5
	0.37	100.301	98.986	1.618	—0.303	—0.068	—8.1
	0.39	99.869	98.515	1.672	—0.318	—0.069	—8.2
	0.63	100.324	98.086	2.754	—0.516	—0.068	—8.1
	0.70	99.869	97.375	3.034	—0.540	—0.0649	—7.74
	0.79	99.869	97.061	3.431	—0.623	—0.0663	—7.90
	0.87	50.146	48.571	1.903	—0.328	—0.0629	—7.49
	0.98	50.146	48.426	2.122	—0.402	—0.0680	—8.10
	2.06	38.695	35.776	3.464	—0.545	—0.0574	—6.84

TABLE I (*continued*).

Salt.	Gram molecular concentration.	Volume of solution. cc.	Volume of water. cc.	Volume of salt. cc.	Change in volume during solution. cc.	Change in volume per gram of salt. cc.	Change in volume per gram molecule of salt. cc.
LiI.....	0.08	99.869	99.556	0.274	+0.039	+0.035	+4.7
	0.11	99.869	99.468	0.353	+0.048	+0.034	+4.6
	0.11	99.869	99.454	0.360	+0.054	+0.037	+5.0
	0.16	99.869	99.272	0.534	+0.063	+0.0290	+3.9
	0.18	99.869	99.207	0.588	+0.074	+0.0309	+4.1
	0.19	99.869	99.155	0.632	+0.082	+0.0319	+4.3
	0.38	38.695	38.137	0.490	+0.068	+0.0342	+4.6
	1.01	38.695	37.260	1.284	+0.151	+0.0290	+3.88
	1.30	38.695	36.835	1.656	+0.204	+0.0307	+4.11
NaI....	0.04	1001.75	1000.48	1.57	—0.30	—0.052	—7.8
	0.05	1001.75	1000.10	1.95	—0.30	—0.042	—6.3
	0.05	1001.75	1000.12	1.96	—0.33	—0.046	—6.9
	0.05	1001.75	1000.13	2.05	—0.43	—0.057	—8.6
	0.25	99.869	98.942	1.038	—0.111	—0.0292	—4.38
	0.26	99.869	98.911	1.072	—0.114	—0.0288	—4.32
	0.48	99.869	98.131	1.956	—0.218	—0.0308	—4.62
	1.42	38.695	36.656	2.255	—0.216	—0.0262	—3.96
	2.62	38.695	34.876	4.148	—0.329	—0.0216	—3.24
KI.....	0.03	1001.75	1000.64	1.41	—0.30	—0.068	—11.3
	0.06	1001.75	999.31	2.95	—0.51	—0.055	—9.1
	0.07	1001.75	998.35	3.97	—0.57	—0.046	—7.6
	0.14	99.869	99.186	0.768	—0.085	—0.036	—6.0
	0.19	99.869	98.972	1.018	—0.121	—0.0382	—6.34
	0.32	99.869	98.392	1.694	—0.217	—0.0414	—6.88
	0.55	99.869	97.313	2.926	—0.370	—0.0406	—6.74
	1.88	38.695	35.225	3.880	—0.410	—0.0339	—5.63

TABLE II.

Salt.	Gram molecular concentration.	Volume of solution. cc.	Volume of water.[1] cc.	Volume of salt. cc.	Change in volume during solution. cc.	Change in volume per gram of salt. cc.	Change in volume per gram molecule of salt. cc.
KCl.........	4.14	1148.5	1000.0	182.1	—33.6	—0.0947	—7.06
KBr.........	4.67	1223.5	1000.0	254.5	—31.0	—0.0455	—5.41
KI..........	6.19	1442.3	1000.0	487.7	—45.4	—0.0306	—5.07
RbCl........	6.00	1295.7	1000.0	347.3	—51.6	—0.0549	—6.65
RbBr........	5.18	1296.7	1000.0	346.6	—49.9	—0.0449	—7.43
RbI.........	5.55	1482.1	1000.0	510.2	—28.1	—0.0161	—3.42
CsCl.........	7.62	1595.9	1000.0	514.4	+81.5	+0.0398	+6.70
CsBr........	4.22	1255.4	1000.0	253.7	+ 1.7	+0.0015	+0.32
CsI..........	2.86	1240.9	1000.0	204.5	+36.4	+0.0395	+10.25

As has already been pointed out, the chief feature of interest in the foregoing tables is the fact that in the case of five of the salts the volume

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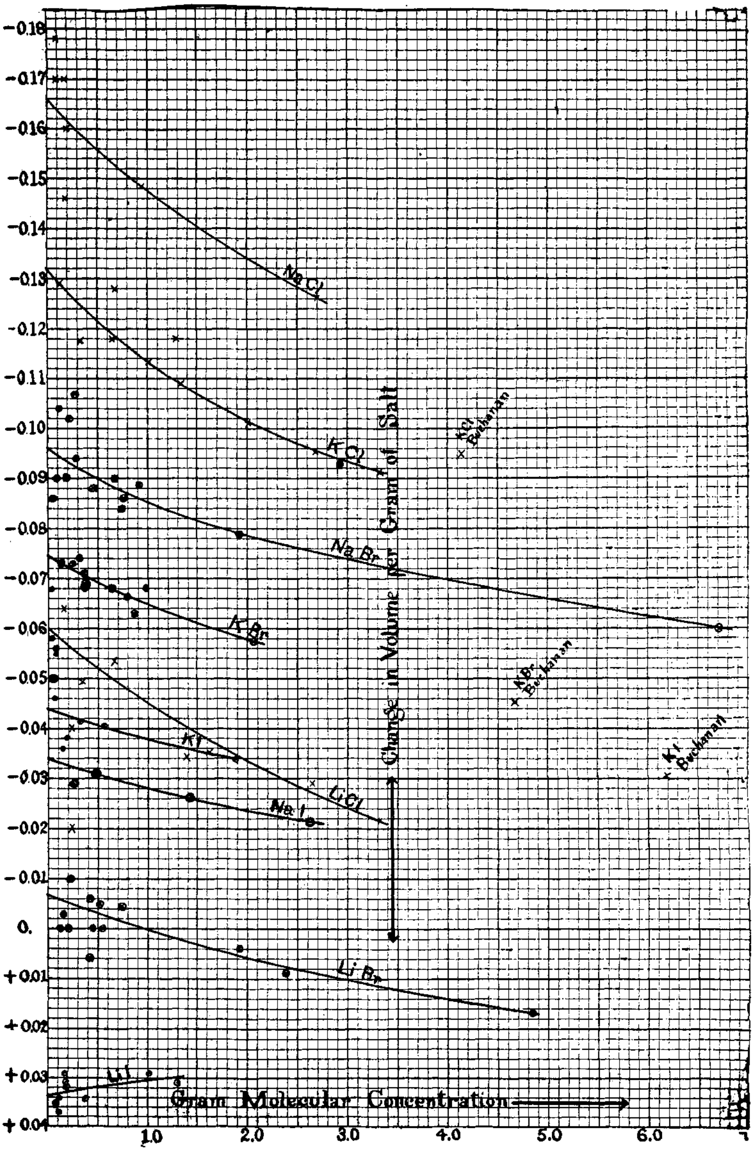
[1] For convenience, Buchanan's results are referred to 1000 cc. of water, although the experiments were carried out with much smaller quantities.

of the solution is greater than the sum of the volumes of the water and the salt, *i. e.*, that *expansion* takes place during solution. It is noticeable that such cases are confined to the salts of lithium and cesium, lithium chloride being the only halogen salt of either of these metals which shows contraction upon solution, and even with this salt the contraction per



gram molecule is considerably less than in the case of any one of the nine other salts which exhibit contraction.

With salts of sodium, potassium, and rubidium and the same halogen, in all three series the contraction per gram molecule varies somewhat irregularly within rather narrow limits.

On the other hand, in the case of salts of the same metal with different halogens, the contraction is always greater with chlorides and with bromides than with iodides.

From inspection of the curves on page 927 it can be seen that the increase in contraction with increasing dilution is greatest with chlorides and least with iodides. In the case of lithium iodide there is increasing *expansion* with dilution if anything.

Many attempts have been made to connect mathematically the densities of solutions with the salt content. Valson,[1] Favre and Valson,[2] Nicol,[3] Bender,[4] Traube,[2] Rogow,[5] Kohlrausch and Hallwachs,[6] and Kohlrausch[7] have shown that in dilute solutions of strong electrolytes the increase in volume of the solvent, due to the solution of one gram molecule of electrolyte, is an additive property, which increases with increasing dilution and is usually less than the molecular volume of the solid salt.

The researches of Charpy,[8] Wade,[9] Barnes and Scott,[10] Forch[11] and Heydweiller[12] have brought forth other interesting relationships concerning the rate of change in density with changing concentration as well as concerning molecular volume in solution.

In considering possible causes for contraction during solution many investigators have assumed the contraction to be confined to the solute, although some have attributed the change in volume to the water alone. In a few cases both solute and solvent have been assumed to change in volume.[13] The first two assumptions are purely arbitrary, however, no facts being known which tend to show that both solute and solvent

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[1] *Compt. rend.*, 73, 441 (1871).

[2] *Loc. cit.*

[3] *Phil. Mag.*, [5] 16, 121 (1883).

[4] *Wied. Ann.*, 20, 560 (1883).

[5] *Z. physik. Chem.*, 11, 657 (1893).

[6] *Wied. Ann.*, 53, 14 (1894).

[7] *Ibid.*, 56, 185 (1895).

[8] *Compt. rend.*, 109, 299 (1899).

[9] *J. Chem. Soc.*, 75, 254 (1899).

[10] *J. Physic. Chem.*, 2, 536 (1899).

[11] *Wied. Ann.*, [4] 12, 591 (1903).

[12] *Verh. d. d. physik. Ges.*, 11, 37 (1909); *Z. physik. Chem.*, 70, 128 (1910).

[13] Favre and Valson, Kohlrausch, Forch, *Loc. cit.* Ostwald, *Lehrbuch*, 1, 784 (1903). Tammann, "Ueber die Beziehung zwischen den inneren Kräften und Eigenschaften der Lösungen," 1907, p. 78.

do not participate in the change in volume. There can be no doubt that the water takes part in the change, since the solution in some cases occupies less volume than the water alone.

Tammann has discussed in detail the properties of solutions with reference to those of the solvent and has assumed, since solutions when subjected to changes of pressure and temperature behave approximately in the same way as the same volume of water at a higher pressure, a compression of the water by the solute owing to increase of internal pressure, termed "binnendruck." It is a matter of considerable uncertainty whether the compression of the water is applied to all the water or to only a portion. Either assumption is capable of explaining the observed regularities. Drude and Nernst's[1] hypothesis of "electrostriction" of the water in the field of the ions is no more specific in its nature. Furthermore, the compression of the salt itself is a factor which cannot be neglected and in the following pages the attempt is made to show that change in volume of the salt probably plays a considerable part in the final result.

Recent investigations by T. W. Richards[2] upon the significance of changing atomic volume as applied to a hypothesis of compressible atoms furnishes a basis for a possible explanation of changes in volume upon solution. This hypothesis involves the assumption of elastic atoms relatively large with reference to the "free space" and, in combination at least, probably in intimate contact. According to the hypothesis the elastic atoms are susceptible to both distortion and compression under the influence of chemical affinity, molecular (or atomic) cohesion, or external pressure.

In the first paper on the subject the following statement occurs apropos of the molecular volumes of hydroxides:[3]

"It is interesting to note that in this table, where the substances are arranged in the order of the contraction which ensues when hydroxyl combines with the metal, they *should also be arranged in the electrochemical order*. That is to say, the solution tension of a metal appears to be associated with the excess of affinity of the metal for hydroxyl over its affinity for itself, and intensity of potential seems to be associated with intensity of atomic compression. The inference to be drawn from this comparison is, of course, that the formation of the metallic ion in water is connected with the affinity of the metal for water—an affinity which manifests itself even when both the 'bonds' of oxygen are filled. Similar attraction for nitrogen or sulphur would explain cases in which the solvent does not contain oxygen.

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[1] *Z. physik. Chem.*, 15, 79 (1894).

[2] *Proc. Am. Acad.*, 37, 3 (1901); 37, 399 (1902); 38, 293 (1902); 39, 581 (1904).

[3] *Ibid.*, 37, 12.

"If this is true, contraction should take place when salts are dissolved in water. This inference is amply verified by facts. In some cases the solution occupies even less space than the water alone, involving a total contraction greater than the volume of the salt itself. The best known of these cases are those of lithic, sodic and baric hydroxides, and cobalt, nickel, zinc and magnesium sulphates, but undoubtedly others exist. In a large majority of cases when an electrolyte is dissolved in water, the sum of the volumes of the salt and of the solvent taken together considerably exceeds the volume of the solution. This contraction is usually ascribed wholly to the dissolved substance in dilute solutions, but it seems to me that the behavior of the salts named above proves the falsity of this method of calculation. *The water as well as the salt must contract when a salt is dissolved.* So many complications are concerned in the act of the solution of an electrolyte that it is difficult to unravel the tangled clues; but the wide deviations exhibited by different substances seem to indicate that there are present overlapping contractions and expansions, the resultant of which is a smaller quantity than some of the individual influences. Such contractions and expansions are just what one would expect to find in a readjustment of affinities."

It is evident from the fact that the solution of salts in water may be accompanied by either an increase or a decrease in volume that at *least two important influences must be at work, one involving expansion, the other contraction.* Experimentally it is possible to observe only the resultant of the combined effects. Although on this account it is difficult to discover the nature and the magnitude of the individual influences, the foregoing hypothesis of compressible atoms suggests the following possible causes of change in volume during solution in the case of electrolytes dissolving in water.

(1) If, when the salt dissolves, partial dissociation takes place, this initial disintegration of the molecule is undoubtedly accompanied by change in volume, since it is well known that the molecular volume of a salt is not equal to the sum of the atomic volumes of its constituents. Richards has pointed out that in the case of the halogen salts of lithium, sodium, and potassium the diminution in volume upon the union of the metal and the halogen is very considerable and is a function of the compressibilities of the free elements and of their affinities for each other.[1] These data are given in Tables III and IV, certain slight changes having been made in Richards' table, owing to the availability of more reliable experimental work. There are added similar data for rubidium and cesium.

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[1] *Proc. Am. Acad.*, 39, 585 (1904).

TABLE III.

Element.	Atomic weight. Ag = 107.88.	Specific gravity.[1]	Atomic volume. cc.	Compressibility[2] megabars × 10^6.	Heat of oxidation. Kilogram calories.	Heat of combination with hydrogen.[4] Kilogram calories.
Li........	6.94	0.534	13.1	8.8	143 (2M + O)[3]	
Na.......	23.00	0.971	23.7	15.4	101 "	
K........	39.10	0.862	45.4	31.5	87 "	
Rb.......	85.45	1.532	55.8	40.0	84 "	
Cs........	132.81	1.87	71.0	61.0	83 "	
Cl........	35.46	1.412	25.0	95.0	—18 (Cl_2O)	22.0
Br.......	79.92	3.121	25.6	51.8		8.4
I	126.92	4.94	25.7	13.0	45 (I_2O_5)	-6.0

TABLE IV.

Salt.	Molecular weight.	Specific gravity[5] of fused salt.	Sum of atomic volumes. cc.	Molecular volume. cc.	Contraction in formation of solid = *a*. cc.	Change in volume[6] during solution = *b*. cc.	*a* + *b*. cc.	Compressibility[7] megabars × 10^6.
LiCl......	42.40	2.07	38.1	20.5	—17.6	— 1.91	—19.5	
LiBr.....	86.86	3.46	38.7	25.2	—13.5	+0.03	—13.5	
LiI.......	133.86	4.06	38.8	33.0	— 5.8	+4.02	— 1.8	
NaCl.....	58.46	2.14	48.7	27.2	—21.5	— 8.64	—30.1	4.1
NaBr.....	102.92	3.08	49.3	34.2	—15.1	— 8.85	—24.0	5.1
NaI......	149.92	3.67	49.4	40.9	— 8.5	— 4.26	—12.8	6.9
KCl......	74.56	2.00	70.4	37.3	—33.1	— 8.47	—41.6	5.0
KBr......	119.02	2.74	71.0	43.5	—27.5	— 7.72	—35.2	6.2
KI.......	166.02	3.12	71.1	53.4	—17.7	— 6.28	—24.0	8.6
RbCl.....	120.91	2.75	80.8	44.0	—36.8	— 6.65	—43.5	
RbBr	165.37	3.28	81.4	50.5	—30.9	— 7.45	—38.4	
RbI......	212.37	3.44	81.5	61.9	—19.6	— 3.40	—23.0	
CsCl......	168.27	3.97	96.0	42.4	—53.6	+ 6.74	—46.9	
CsBr.....	212.73	4.38	96.6	48.6	—48.0	+ 0.43	—47.6	
CsI.......	259.73	4.51	96.7	57.7	—39.0	+10.4	—28.6	

During solution the portion of the salt which is dissociated is freed not only from the compression due to chemical affinity but also from that due to molecular cohesion, for in the solution the ionic cohesion

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

[2] Richards, Stull and Bonnet, *Pub. Car. Inst.*, **76**, 15 (1907); Richards and Stull, *Ibid.*, **7** (1904).

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

[4] Landolt-Börnstein-Meyerhoffer, *Tabellen.*

[5] For the specific gravities of the iodides and the rubidium and cesium salts, see Archibald, *J. Chem. Soc.*, **85**, 776 (1904); Richards and Archibald, *Proc. Am. Acad.*, **38**, 453 and 465 (1903); Baxter and Brink, THIS JOURNAL, **30**, 46 (1907).

[6] The values for the first nine salts refer to molal solutions and are obtained by multiplying values taken from the curves on page 927 by the molecular weight. The values for the rubidium and cesium salts refer to the concentrations of Buchanan's experiments.

[7] Richards and Jones, THIS JOURNAL, **31**, 158 (1909).

must be negligible in comparison with that between the particles of solid or liquid elements. Furthermore, in the case of the halogens at any rate the self-affinity is considerable, as is shown by the diatomic molecules, and in the ionic form the halogen is probably free from the compression due to this self-affinity. Hence the contraction during the formation of the solid salt from the elements is even less than the expansion to be expected upon dissociation.

The fact that *expansion during solution of solids in water is known to occur only with strong electrolytes* supports the idea that in the dissociation of the molecules the atoms are freed from the compression due to chemical combination.

This cause of increase in volume is not the only one which may be suggested. As Richards has pointed out,[1] the charged ions may be subjected to more or less distension through electrical self-repulsion. Furthermore, even in the case of the undissociated portion of the salt slight expansion during solution probably occurs, since the substance is freed at least from the compression due to molecular cohesion. Both of these effects are probably much less important than the one outlined above.

That this expansion during dissociation is far from being the most important factor which influences change in volume during solution is evident from the fact that sodium, potassium, and rubidium salts, as well as lithium chloride, exhibit *contraction* during solution, while in the case of only one of the other five salts, lithium iodide, does the expansion during solution approach the value of the contraction in the formation of the solid salt from its constituent elements (columns 6 and 7, Table IV). It is to be noted that the values for the change in volume during solution in the case of the lithium, sodium, and potassium salts refer to molal solutions in which the salts are about seventy-five per cent. dissociated. In the case of the rubidium and cesium salts the values refer to much more concentrated solutions and are undoubtedly smaller than for less concentrated solutions, at least for the salts which show contraction during solution.

(2) As opposing this tendency toward expansion during solution, it is natural to consider any tendency toward combination between the water and the salt, *i. e.*, either ionic or molecular hydration. While it is reasonable to suppose that hydration in general increases with increasing dilution and diminishes with rising temperature, knowledge of the exact extent of this hydration is at present very limited.[2] The most reliable quantitative measurements of ionic hydration are those by Washburn,[3] who has determined the relation of the average hydration of the

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[1] *Proc. Am. Acad.*, 37, 16 (1901).

[2] For a critical review of the subject of hydration see Washburn, *Technology Quarterly*, 21, 360 (1908).

[3] THIS JOURNAL, 31, 322 (1909).

lithium, sodium and potassium ions to that of the chlorine ion in 1.2 molal solution to be 4.7, 2.0 and 1.3, respectively, at 25°. From the work of Biltz, H. C. Jones, and others, it is probable, however, that the hydration of the cesium ion is the least of those of the alkalies, and that the chlorine ion is more and the iodine ion less hydrated than the bromine ion.

With regard to the hydration of molecules, evidence is still less certain, especially with electrolytes. The possession of crystal water may be considered evidence of the presence of hydrated molecules in solution, and roughly a measure of the extent of the hydration. On the other hand, the absence of crystal water does not preclude the existence of hydrated molecules in solution. In the case of the fifteen salts under consideration, only lithium and sodium salts crystallize with water of crystallization at ordinary temperatures. Judging from the number of molecules of water of crystallization and the stability of the solid hydrates, one might conclude that the hydrates of molecular lithium halides in solution contain more combined water and are more stable than those of sodium, and those of sodium more than those of the other alkali metals. Further generalizations are evidently unwarranted.

The effect of the hydration of the ions upon the total volume of the products will obviously depend not only upon the extent of the hydration and the affinity of the elements for the water, but also upon the compressibility of the metal or halogen on the one hand and that of water on the other. Since the compressibility of water is relatively large, 48×10^{-6} megabars, its compression by combination in hydration is undoubtedly an important factor in changes in volume in aqueous solutions. With regard to the compressibility of water, Richards[1] has already pointed out that there is good reason for believing that in the water molecule the hydrogen is much more compressible than the oxygen. Hence, with an element which has a strong affinity for oxygen a smaller compression of the water is to be expected than with an element of strong affinity for hydrogen.[2]

An approximate idea of the relative affinities of the different elements under consideration for oxygen and hydrogen may be obtained by comparing the heats of combination of the elements with oxygen and hydrogen, as given in Table III. In the case of the metals the affinity for oxygen is greatest with lithium, varying only slightly with the other four elements. The compounds of these metals with hydrogen are so unstable that their affinities for hydrogen must be negligible. In the case of the halogens the affinity for oxygen is much lower than in the case of the metals, and is considerably less with chlorine than with iodine. This is

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[1] *Proc. Am. Acad.*, 39, 595 (1904).

[2] This suggestion was made to me by Prof. Richards.

in accordance with the relative affinities of the halogens for hydrogen, the relation being the reverse of those with reference to oxygen. Thus in general, since the compression by the metallic ion is probably applied to the less compressible oxygen, one might expect *the compression of the water through hydration of the metallic ions to be much less than through the hydration of the halogen ions.* In the case of the halogens *the compression of the water through the hydration of the chlorine ion should be most and through that of the iodine ion least.*

In the case of strong electrolytes the effect of the hydration of molecules in producing change in volume during solution is undoubtedly smaller than that of the hydration of ions. In the first place, even in a four times molal solution nearly fifty per cent. of an alkali halide is dissociated. In the second place, the salts themselves are much less compressible than the elements (see Tables III and IV), so that *the change in volume due to hydration of the molecules may be attributed chiefly to the compression of the water.*

Thus it appears that the opposing tendencies towards expansion and contraction during solution are greater with ions than with molecules, *i. e.*, that *the ions are responsible for the greater part of the changes in volume which take place during solution.*

In connection with the foregoing explanation of change in volume during solution the following statement by Favre and Valson is of interest:

"Lorsq'un sel se dissout, on peut admettre qu'il se produit deux effets de sens inverse, (1) un effet de contraction du dissolvant sous l'influence du sel, (2) un effet d'augmentation de volume du sel, par suite de la dissociation plus ou moins avancée de ses elements constituants. Le premier effet est, dans le généralité des cas, plus considerable que le second, de sorte que le résultat final est ordinairement une contraction."

Upon the assumption that the change in volume upon solution in water of one of the salts in question is chiefly due to the *difference* between the expansion due to dissociation and the contraction due to hydration, it is a difficult matter in any particular case to predict whether the resultant will be a negative or positive quantity. One might expect, however, that the observed contraction or expansion would not be very large in any case. This is in fact true.

In comparing the salts of the different metals we find that the contractions during the formation of the solid salts from the elements show a very considerable continuous increase from lithium to cesium in the five sets of metallic salts, the difference between rubidium and cesium salts being especially large. It is probable, then, that corresponding expansions take place during dissociation.

Although the metallic ions differ considerably in the extent to which they are hydrated, since, as has been already pointed out, the effect of the metallic ions in compressing the water molecules is probably applied chiefly to the oxygen which is the less compressible portion of the water, only slight differences among the metallic ions are to be expected as far as the compression of the water is concerned. The compressibilities of the different metals are undoubtedly of far greater importance than the extent of the hydration or the affinities for oxygen in determining the contraction due to hydration. These compressibilities increase rather rapidly with increasing atomic volume, lithium being a very slightly compressible substance, but cesium being seven times as compressible. Thus the greater hydration of the lithium ion is compensated by its lesser compressibility, while the lesser hydration of the cesium ion is compensated by its greater compressibility.

It is not at all surprizing, therefore, to find the lithium and cesium salts exhibiting either expansion during solution or very slight contraction, the lithium salts chiefly because of the small compressibility of lithium, and the cesium salts because of the large contraction during the formation of the solid salts from the elements, and the small hydration.

With regard to the comparison of the chlorides, bromides, and iodides, the contraction during the formation of the solid salts is in every case greatest with chlorides and smallest with iodides. Although no certain evidence is available concerning the relative hydration of the halogen ions, it is highly probable that the chlorine ion is most and the iodine ion least hydrated. This, together with the high heat of combination of chlorine and hydrogen and the negative heat of combination of iodine with hydrogen, leads one to expect much greater compression of the hydrated water molecules in the case of chlorine than in the case of iodine, while the low compressibility of iodine would tend still farther to cause the contraction during the hydration of the iodine ion to be less than that of the other halogens. Bromine is intermediate in its properties between chlorine and iodine. Hence, in spite of the smaller contraction during the formation of the solid iodides, a smaller contraction or a larger expansion during solution of iodides than of chlorides may be reasonably expected, as is actually the case.

A still more rational comparison of the different salts is obtained by finding the algebraic sum of (*a*) the change in volume during the formation of the solid salt from the solid or liquid elements and (*b*) the change in volume during solution. This sum, which is indicated in the eighth column of Table IV, although it makes no allowance for incomplete dissociation, may be considered a measure of the *contraction produced in the formation of the ions from the free elements.* These figures do not refer to the same concentrations with the rubidium and cesium salts as with the others, still the values may be legitimately used for purposes of comparison.

The sum is the smallest in the case of the lithium salts and largest with cesium salts, while it is smallest with iodides and largest with chlorides, cesium chloride and bromide being only the exceptions. Even here the discrepancy is very small and easily accounted for by the high concentration at which the contraction during solution for cesium chloride was determined; that is, of the metals which have the greatest affinity for oxygen and least for hydrogen and which therefore can be expected to compress the water less than do the halogens, those with the smallest compressibility give the smallest values for this sum; while of the halogens, which have a relatively large affinity for hydrogen and which therefore may be expected to compress the water to a greater extent, chlorine, with the greatest affinity for hydrogen, the highest hydration, and the greatest compressibility gives the largest value for the sum of the contractions.

In the case of lithium iodide where the causes for contraction are least, the observed expansion during solution is nearly seventy per cent. of the contraction during the formation of the solid salt from the elements, a rather striking coincidence in connection with the fact that the salt at the concentration in question is between seventy and seventy-five per cent. dissociated. On the other hand, cesium chloride and bromide yield maximum values, as is to be expected.

If the sum, $a + b$, represents the contraction in the formation of the ions from the elements, it should be an additive property with different salts. Table V contains the values of this sum in cubic centimeters per gram molecule for the salts of lithium, sodium, and potassium at molal concentration, these salts all being very nearly seventy-five per cent. dissociated under these conditions. Table VI contains the corresponding values for zero concentration, obtained by prolonging the curves on page 927. Since the values in Table VI apply to complete dissociation they are of greater interest than those in Table V. The rubidium and cesium salts are not included because the single values for the change in volume during solution were obtained at different concentrations, all of which were much higher than molal:

TABLE V.

	Cl	Dif.	Br	Dif.	I
Li..................	19.5	6.0	13.5	11.7	1.8
Dif...........	10.6		10.5		11.0
Na..................	30.1	6.1	24.0	11.2	12.8
Dif...........	11.5		11.2		11.2
K..................	41.6	6.4	35.2	11.2	24.0

TABLE VI.

	Cl	Dif.	Br	Dif.	I
Li	20.1	6.0	14.1	12.8	1.3
Dif.	11.1		10.9		12.3
Na	31.2	6.2	25.0	11.4	13.6
Dif.	11.7		11.4		11.3
K	42.9	6.5	36.4	11.5	24.9

In both tables the additive relations are as close as could be expected when the variety of data upon which the values depend is considered.

Obviously, the foregoing data do not afford a means of calculating the change in volume in the formation of any one ion from the free element. However, the lithium and iodine ions taken together show almost no change in volume in their formation from the free elements. It is possible that this result is due to partial compensation by *expansion* in the formation of one ion and *contraction* in the formation of the other. Of these two elements the lithium is the less compressible, but its ion is more hydrated than the iodine ion. Furthermore, lithium iodide contains eighteen times as much iodine as lithium by weight. All things considered, one cannot be far wrong in assuming that the change in volume is equally distributed between the lithium and iodine ions. Upon this basis the following table has been constructed to show the change in volume in the formation of six ions from the elements at infinit dilution. The values are expressed in cubic centimeters per gram atom:

TABLE VII.

Li	0.7	Cl	18.8
Na	12.1	Br	12.6
K	23.8	I	0.7

It is interesting to note, as Ostwald has already pointed out,[1] that the heat evolved in the formation of an ion from the free element is a constant. This fact is well illustrated by the additive relationships in the algebraic sum of the heat of formation and the heat of solution of salts. The two latter values for the lithium, sodium, and potassium halides are given in Table VIII, and the sums of the two in Table IX:

TABLE VIII.

Salt.	Heat of formation, kg. cal.	Heat of solution, kg. cal.
LiCl	93.8	+ 8.4
LiBr	80.0	+11.4
LiI	61.2	+14.9
NaCl	97.7	— 1.2
NaBr	85.7	— 0.2
NaI	69.1	+ 1.3
KCl	105.6	— 4.4
KBr	95.3	— 5.1
KI	80.1	— 5.1

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[1] *Grundriss der Allgemeinen Chemie*, 280 (1899).

TABLE IX.

	Cl	Dif.	Br	Dif.	I
Li	102.2	10.8	91.4	15.3	76.1
Dif.	5.7		5.9		5.7
Na	96.5	11.0	85.5	15.1	70.4
Dif.	4.7		4.7		4.6
K	101.2	11.0	90.2	15.2	75.0

(3) Blanchard[1] has called attention to the fact that, if, as is commonly believed, liquid water consists in part of polymerized molecules $(H_2O)_x$, the formation of hydrates in solution will alter the equilibrium between the simple molecules and the polymers. Since there is evidence that the change from the polymerized molecules to the simple molecules is accompanied by contraction, if in hydration the simple water molecules combine with the hydrated substance, so that a portion of the polymerized molecules dissociate into simple molecules, it is obvious that in this way also hydration would produce contraction during solution. On the other hand, if in hydration the polymerized molecules are ever combined with the hydrated substance, it is probable that such a change would produce expansion, owing to the formation of new polymers at the expense of the simple molecules.

It is not only uncertain to what extent these phenomena take place during the solution of a salt, but it is also uncertain to what extent water is polymerized at ordinary temperatures. The formation of the polymerized water molecules is certainly retarded by rising temperature. If the first assumption is correct, *i. e.*, if in hydration the simple water molecules combine with the hydrated ion, then the contraction during solution would be greatest with the ions which are most extensively hydrated. This is, however, not the case, for while the chloride ion produces more contraction than the less hydrated bromide ion, and the iodide ion, which is probably least hydrated, produces least contraction, the lithium ion, which is the most hydrated of all the metallic ions, produces far less contraction, than the sodium, potassium and rubidium ions, although slightly more than the cesium ion. The facts fit the case no better if the assumption is made that hydration is combination with polymerized water. Hence this factor, although it may be of influence, is undoubtedly of less importance than the two which have been discussed.

If the resultant effect of dissociation is to produce contraction, then, since dissociation and probably hydration increase with the dilution, the contraction per gram molecule of salt should increase with the dilution, as is the case with seven of the nine salts for which the change with the dilution was investigated. With lithium iodide, on the other hand,

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[1] THIS JOURNAL, 26, 1318 (1904).

the resultant is expansion, hence the expansion should increase with the dilution. This seems actually to be the case to a slight extent, although with lithium bromide, where the increase in volume is very slight at all concentrations, the reverse is apparently true. The latter fact may be due to the compensating effect of the increased hydration which accompanies dilution.

The formation of hydrates in aqueous solution is undoubtedly hindered by rising temperature, while the dissociation changes only slightly. Hence the contraction due to hydration would be less, while the expansion due to dissociation would remain nearly constant, since the temperature coefficient of expansion of solids is usually small. Consequently any resultant diminution in volume during solution ought to decrease with rising temperature, while a resultant increase in volume should still further increase. This is in accordance with the fact pointed out by Traube[1] that "molecular solution volume" increases with rising temperature to a maximum between 50° and 70°.

The foregoing explanation of the causes of changes in volume during solution is proposed as a tentative one, to be further tested and amplified. It is obvious that at present it would have been impossible, upon the basis of the known properties of the elements and compounds in question, to predict with certainty whether the resultant effect in any case would be expansion or contraction, although some idea might be obtained as to whether the resultant effect would be large or small. Undoubtedly other influences than those which have been proposed affect the changes in volume during solution. From so limited a range of material to arrive at a complete and accurate knowledge of the phenomena involved could hardly be expected, and no claim is made that such a result has been reached. The purpose of this paper is to call attention to the following facts which certainly cannot be disregarded in any consideration of the subject.

(1) No adequate explanation of the causes of the changes in volume which actually take place during the solution of electrolytes in water has been proposed.

(2) The existing data show beyond question that the phenomena which take place are complex. Since these phenomena include both contraction and expansion, at least two important influences must be at work.

(3) Upon the basis of Richards's hypothesis of compressible atoms and that of hydration, an explanation of the observed effects with the class of alkali halides has been devised. This explanation assumes that at any rate the following two changes take place during solution and dissociation:

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[1] *Z. anorg. Chem.*, **8**, 55 (1895).

(*a*) The salt is freed in large part from compression due to chemical affinity and to molecular cohesion.

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

(4) It is shown that the change in volume in the formation of the ions from the elements, as measured by the sum of the change in volume in the formation of the solid salt and the change in volume during solution, is an additive property.

(5) The part which the polymerization of water plays in the change is uncertain. Probably this effect varies in importance with varying temperature. It is also probable that at the temperature of the experiments cited, the effect is small, since the observed effects are not in accord with those to be expected if the contraction is due wholly to changing polymerization.

It is obvious that the data furnished at the beginning of this paper allow the calculation of the densities of aqueous solutions of many of the salts considered up to moderately high concentrations.

The study of change in volume during solution will be continued in this laboratory by the examination of other salts and other solvents, and by the determination of the effect of varying temperature on the magnitude of the observed effect.

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THE DISTRIBUTION OF AMMONIA BETWEEN WATER AND CHLOROFORM.

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The distribution of ammonia between water and chloroform has been studied by several investigators. The results have been employed to determin the concentration of free ammonia in an aqueous solution, which contains also some compound of ammonia, such as the blue cuprammonia compounds and the phosphates of ammonium. Until recently the distribution was determined only for dilute solutions, where the concentration of ammonia in the water layer was not greater than normal.

Hantzsch and Sebaldt[1] found that the ratio of the concentrations of ammonia in water and chloroform is 25.1 at 25°, the mean of five determinations in which the concentration in the water layer varies from 0.00275 to 0.04425 normal. At 2° this ratio is 38.53. Dawson and McCrae[2] give the following values for the distribution ratio: 26.3 at 20°, 24.9 at

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[1] *Z. physik. Chem.*, 30, 258 (1899).

[2] *J. Chem., Soc.*, 77, 1239 (1900).