

and the Lorentz¹ and Lorenz² formulas. Values for the density of water are taken from the tables of Landolt-Börnstein-Meyerhoffer.

Temperature.	$\frac{n-1}{d}$.	$\frac{n^2-1}{n^2+2} \frac{1}{d}$.
20°.....	0.333941	0.206256
25°.....	0.333818	0.206209
30°.....	0.333694	0.206167

The specific refraction is not constant in either case, diminishing regularly with increasing temperature.³ The temperature coefficient is smaller in proportion to the magnitude of the specific refraction in the case of the Lorentz and Lorenz formula. The difference between two successive values of the specific refraction correspond to a difference of 0.00007 in the index of refraction in the case of the Lorentz and Lorenz formula, and of 0.00012 in the case of the Gladstone and Dale formula, while the values for the index of refraction found in this investigation are probably correct within 0.00002.

As the result of this research the index of refraction of water for sodium light at three temperatures is found to be:

	Referred to air at the same temperature.	Referred to vacuum.
20°.....	1.33299	1.33335
25°.....	1.33248	1.33284
30°.....	1.33190	1.33225

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THE REFRACTIVE POWER OF THE HALOGEN SALTS OF LITHIUM, SODIUM AND POTASSIUM IN AQUEOUS SOLUTION.

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The refractive power of aqueous solutions of electrolytes has been the subject of numerous researches by many investigators,⁴ and attention has been called to several kinds of regularities. One sort concerns the change in index of refraction of the solution with changing concentration. Another concerns the more or less close application of the Law of Mixtures to the specific refractions of the components of the solution and that of the solution. Still a third regularity has very recently been pointed out by Chéneveau and concerns the change in the index of refraction of the solvent alone as it is diluted with solute.

¹ *Wied. Ann.*, 9, 642.

² *Ibid.*, 11, 77 (1880).

³ Concerning the change in specific refraction with the temperature in the case of organic substances see Falk, *THIS JOURNAL*, 31, 86 (1909).

⁴ For a very complete bibliography of the subject see Chéneveau, *Ann. chim. phys.*, 8th Series, 12, 384 (1907).

With regard to the first sort of regularity, it is well recognized that the index of refraction of a solution of an electrolyte does not increase at the same rate as either the percentage composition or the concentration. This is due, in part at least, to the fact that when a salt is dissolved in water the contraction or expansion during solution per unit quantity of salt varies with the concentration of the solution. It is pointed out in a following paper that there is good reason for believing that this varying expansion or contraction during solution is closely connected with electrolytic dissociation, and hydration. In any case, in comparing the indices of refraction of solutions of different substances, it is most reasonable to select solutions of the same degree of dissociation.

Bender¹ first showed that with dilute solutions of electrolytes, where the degree of dissociation is large, the increments of refractive index with changing concentration, if referred to molecular quantities of salt, show distinct additive relationships. This is of course to be expected if the property is ionic rather than molecular. The additive relationships would be most satisfactory at infinit dilution, but the difficulty in obtaining sufficiently accurate measurements makes the comparison less satisfactory with very dilute solutions.

The second sort of regularity, which serves to connect index of refraction and density, concerns the specific refractions of the solutions of electrolytes and of their components. Of the various expressions for specific refraction in common use, the best known and the most satisfactory from a general standpoint are those of Gladstone and Dale,² and Lorentz³ and Lorenz,⁴ $\frac{n-1}{d}$ and $\frac{n^2-1}{n^2+2} \frac{1}{d}$, respectively. The second of these two is in general more nearly a constant under varying conditions. It is to be noted, however, that neither expression remains exactly a constant with changing temperature⁵ and that *at present there is no wholly satisfactory general expression connecting change of index of refraction with changing density*. Hence any relationship which depends upon specific or molecular refraction is more or less uncertain.

The Law of Mixtures has been found first by Biot and Arago to hold for the specific refractions of solutions and their components, *i. e.*, the following equation holds very closely although not exactly true:

$$k_e x + k_w (100 - x) = k_s 100,$$

where k_e , k_w and k_s represent the specific refractions of solute, solvent

¹ *Wied. Ann.*, **39**, 89 (1890). See also Valson, *Jahresb. Chem.*, **1873**, 135.

² *Phil. Trans.*, **1858**, 887.

³ *Wied. Ann.*, **9**, 642 (1880).

⁴ *Ibid.*, **11**, 70 (1880).

⁵ See especially Falk, *THIS JOURNAL*, **31**, 86 (1909); also Baxter, Burgess and Daudt, preceding paper.

and the solution, respectively, and x represents the per cent. of solute.

Upon the assumption that the specific refraction of the solvent in the solution does not change with changing concentration and is equal to that of pure solvent at the same temperature, the specific refraction of the solute can be calculated from that of the solution. The results so obtained for the specific refraction of an electrolyte are not absolutely constant with changing concentration, the differences being usually ascribed to the salt itself. To ascribe all the differences to the salt alone is, however, a somewhat questionable method of procedure, since during the solution and dissociation of an electrolyte deep-seated changes in both solute and solvent undoubtedly take place. Even upon the above assumption the change in the specific refraction of the electrolyte with changing concentration is not very large, and interesting additive relationships have been obtained by comparison of the molecular refractions of different electrolytes, the latter values being obtained by multiplying the specific refractions by the molecular weights. It is interesting to note that the molecular refractions of electrolytes in aqueous solution, when compared with the corresponding values calculated from the index of refraction and the density of the solid, where the latter is either amorphous or isotropic, show in most cases considerable differences.

Chéneveau's¹ method of determining the change in the index of refraction of the water by the electrolyte also depends upon the assumption of a constant specific refraction of water, and offers no special advantages over the Law of Mixtures.

Although the experimental work upon which the previous considerations have been based has in isolated cases been very carefully carried out, in the majority of instances not only is there no assurance that such is the case but there is evidence that certain precautions necessary for very accurate work were omitted. Consequently some uncertainty exists as to the exactness with which the various relationships hold even for the simpler substances. The physical measurements of index of refraction and density are comparatively easy to make with a high degree of accuracy. On the other hand, since frequently little care seems to have been taken to ensure freedom of the substances employed from probable impurities, especially from moisture, many determinations of concentration are open to suspicion. The object of the present investigation was to repeat with considerable care some of the earlier experimental work. For the sake of comparison, the salts examined include a few which have already been very carefully investigated.

The halogen compounds of the alkalis were chosen for examination because of certain distinct advantages which they seemed to offer. In the first place, the molecular structure of these salts seems to be as simple

¹ *Loc. cit.*

as any, and is surely similar. Hence constitutive irregularities such as are manifested by isomeric organic derivatives are undoubtedly at a minimum. In the second place, these salts are all highly dissociated in aqueous solution, and to essentially the same extent at equivalent concentrations. The proportion of the salt in the ionic condition being consequently high, even at considerable concentrations, the excess of the solution over water in refractive power is due largely to the combined effects of cations and anions. Constitutive influences within the molecule being able to affect only a portion of the total quantity of electrolyte, additive relationships are to be expected to hold as closely in this series of electrolytes as in any.

One of the chief differences between the salts in question lies in the fact that, although *hydrolysis* is surely very slight at ordinary temperatures, *hydration* both of ions and of molecules undoubtedly exists, and to various degrees. Washburn,¹ for instance, has shown that the relative hydrations of the lithium, sodium, and potassium ions referred to the chlorine ion as unity, are 4.3, 2.0, and 1.3 in normal solution at 25°. Furthermore, there is good reason for believing that the chlorine ion is more and the iodine ion less hydrated than the bromine ion.² With regard to the hydration of the molecules, the situation is less certain. But if crystal water may be considered a measure of the extent of molecular hydration, lithium salts are most and potassium least hydrated.

Purification of Materials.

Hydrochloric Acid.—The hydrochloric acid used in the preparation of all the chlorides was the commercial chemically pure article, once distilled.

Hydrobromic Acid.—In the case of the hydrobromic acid used in the preparation of the bromides, more elaborate precautions were taken to eliminate traces of chlorine and iodine usually contained in hydrobromic acid made from commercial bromine, since mere crystallization of bromides does not free them at all rapidly from chlorides and iodides. The removal of chlorine was secured by distilling the bromine three times from a solution of a bromide. In each distillation the bromide was made from a portion of the product of the previous distillation.³ Iodine was eliminated by boiling with an excess of free bromine a solution of a bromide made from the product. The purified bromine was either used directly, after distillation, or was converted into hydrobromic acid with hydrogen sulfide and water. The solution of hydrobromic acid was

¹ THIS JOURNAL, 31, 322 (1909).

² For a critical review of the subject of hydration see Washburn, *Technology Quarterly*, 21, 360 (1909).

³ Richards and Wells, *Proc. Am. Acad.*, 41, 440 (1906); Baxter, *Ibid.*, 42, 202 (1906).

freed from sulfur and bromide of sulfur by filtration and the traces of sulfuric acid formed during the action of the bromine on the hydrogen sulfide were eliminated by precipitation in moderately dilute solution with recrystallized barium hydroxide. The acid was then twice distilled, the second distillation being with a quartz condenser.

Hydriodic Acid.—Hydriodic acid was prepared by methods very similar to those used in the purification of the hydrobromic acid.¹ The greater part of the chlorine and bromine was removed from commercial iodine by initial distillation from solution in aqueous potassium iodide. Then the product was twice reduced to hydriodic acid by hydrogen sulfide and water, and the solution of hydriodic acid, after prolonged boiling to remove hydrocyanic acid resulting from impurity of cyanogen in the original iodine,² was partially oxidized to iodine with a slight excess of recrystallized potassium permanganate. The resulting iodine was finally again reduced with hydrogen sulfide, the suspended sulfur was removed from the hydriodic acid solution by filtration, and the hydriodic acid was twice distilled, once with a still and condenser made entirely of glass, and once with a quartz condenser. Although the acid was colored strongly with free iodine, in the crystallization and fusion of the salts made from the acid the iodine was completely removed.

Lithium Chloride.—In the purification of the lithium salts commercial lithium carbonate was the starting point of all the pure material. It was found advantageous first to wash the carbonate by decantation with water, since a considerable portion of the more soluble carbonates could be extracted in this way. In the preparation of lithium chloride the carbonate was next dissolved in hydrochloric acid and reprecipitated with an excess of ammonium carbonate and ammonia. After thorough washing with water the carbonate was again dissolved in hydrochloric acid and the salt was several times recrystallized from a solution strongly acid with hydrochloric acid. The product was free from all but spectroscopic traces of sodium.

Lithium Bromide and Iodide.—In the preparation of lithium bromide and iodide the washed carbonate was first dissolved in nitric acid and the lithium nitrate was three times crystallized to eliminate chlorides as well as metallic impurities. The third crop of crystals was essentially free from sodium. Lithium carbonate was then precipitated from the purified nitrate by means of ammonium carbonate and the lithium carbonate washed until the wash waters were free from nitrate. Finally the carbonate was dissolved in either hydrobromic or hydriodic acid and the bromide and iodide were recrystallized at least three times.

Since the precipitation of lithium carbonate by ammonium carbonate

¹ Baxter, *Proc. Am. Acad.*, 40, 419 (1904).

² Richards and Singer, *Am. Chem. J.*, 27, 205 (1902).

always involves a very considerable loss of material, owing to the solubility of lithium carbonate in solutions of ammonium salts, other methods of purification were attempted. Of these, one of the most effective was the solution of the carbonate in a solution of carbonic acid and subsequent precipitation by boiling, although it is best suited for the treatment of small quantities of material.

Sodium Chloride.—Sodium chloride was purified by twice precipitating the salt from aqueous solution by means of hydrochloric acid gas.

Sodium Bromide and Iodide.—Sodium bromide and iodide were prepared by dissolving the purified carbonate in pure hydrobromic and hydriodic acids, respectively. The carbonate itself had been three times recrystallized to free it from other alkali impurities and salts of sodium.¹ Finally the bromide and iodide were three times recrystallized.

Potassium Chloride.—Potassium chloride was purified in the same fashion as in the case of sodium chloride, by double precipitation with hydrochloric acid.

Potassium Bromide.—For the preparation of potassium bromide, potassium oxalate was three times recrystallized, until free from chloride, and was converted into the bromide by the cautious addition of a slight excess of bromine.² The potassium bromide was finally several times crystallized.

Potassium Iodide.—Potassium iodide was prepared by the action of pure hydriodic acid on potassium bicarbonate which had been freed from sodium by crystallization from aqueous solution.³ The salt was then purified further by crystallization.

In the preparation of all these salts platinum vessels were largely employed, especially in the later stages of the purifications. Crystals were separated from mother liquor by centrifugal drainage with a centrifugal machine provided with platinum baskets and receivers. All the water was doubly distilled, once from alkaline permanganate and once from very dilute sulfuric acid, with the use of block tin condensers in both distillations. When tested spectroscopically the salts gave indications of great purity. Their solutions were perfectly clear. There seemed every reason to believe that the quality of the material was more than sufficient for the purpose.

As has been strongly emphasized by Richards,⁴ one of the most important precautions in preparing a definite quantity of salt for exact work is that of fusing the substance in order to eliminate last traces of moisture. This precaution was observed in all cases.

¹ Richards and Wells, *THIS JOURNAL*, 27, 471 (1905).

² Richards and Mueller, *Ibid.*, 29, 664 (1907).

³ Baxter and Brink, *Ibid.*, 30, 50 (1908).

⁴ *Z. physik Chem.*, 46, 189 (1903).

In the case of sodium and potassium chlorides, which show no tendency to become basic when fused even in moist air, the fusion was carried out in platinum crucibles or dishes, and the salt was weighed out from ordinary weighing bottles to which the salts had been transferred immediately after fusion. Although Richards and Wells¹ and Richards and Stähler² have shown that sodium and potassium chlorides containing traces of hydrochloric acid, when fused in platinum vessels attack the platinum slightly, the impurity introduced in this way must have been very small, since no perceptible amount of platinum could be detected in either the fused salt or in its aqueous solution.

Lithium chloride, on the other hand, possesses the above disadvantage of becoming basic when fused in air, while in addition it is very hygroscopic and correspondingly difficult to weigh. Hence this salt was first fused in a platinum boat in a current of dry nitrogen and hydrochloric acid gases,³ and the boat was weighed in a glass weighing bottle to which it had been transferred without exposure to moist air,⁴ after the hydrochloric acid gas had been displaced by dry nitrogen and this in turn by dry air. The nitrogen had been prepared by the method of Wanklyn by passing air charged with an excess of ammonia over hot copper and removing the excess of ammonia with sulfuric acid, first dilute, then concentrated. In a recent private communication, Dr. R. C. Wells has called our attention to the fact that nitrogen made in this way usually contains appreciable amounts of hydrogen, resulting from the catalytic decomposition of the excess of ammonia in contact with the hot copper. This hydrogen could have had no injurious effect upon either the lithium chloride or the bromides and iodides of all three alkalis, which also were fused in an atmosphere containing nitrogen.

The three bromides were prepared for weighing in much the same way that the lithium chloride was prepared, by fusion in a current of pure dry nitrogen and hydrobromic acid gases.⁵ After the fusion of the salt, the hydrobromic acid gas was displaced by nitrogen and the nitrogen in turn by dry air, before the boat was transferred to the weighing bottle in which it was weighed. The fused bromides were perfectly clear and yielded exactly neutral aqueous solutions.

In the case of the iodides, fusion was carried out in a current of pure dry nitrogen. Since lithium iodide, when fused under these conditions becomes somewhat basic, a small proportion of pure ammonium iodide

¹ THIS JOURNAL, 27, 463 (1905).

² *Ibid.*, 29, 630 (1907).

³ For a description of the apparatus and the purification of the gases see Baxter and Hines, THIS JOURNAL, 27, 226 (1905).

⁴ Richards and Parker, *Proc. Am. Acad.*, 32, 59 (1896).

⁵ For a description of the apparatus for the preparation and purification of the gases, see Baxter, *Proc. Am. Acad.*, 39, 246 (1903).

was added to the salt before fusion, and the greater part of the water of crystallization was carefully expelled before the volatilization of the ammonium iodide. In this way the alkalinity of the fused salt, although only in one case entirely eliminated, was reduced to a quantity corresponding to less than two-tenths of a milligram of lithium hydroxide in every case, and usually to less than one-tenth of a milligram. Each solution of lithium iodide was tested for ammonium salts with Nessler's solution, with negative results in all cases.

The potassium and sodium iodides, when fused in nitrogen, gave neutral solutions.

After the salt had been dried and weighed, the boat and salt were placed in a stout flask and the salt was dissolved in the minimum amount of water. The solution was then quantitatively transferred to a graduated flask. When very small flasks were employed it was sometimes necessary to evaporate slightly the rinsings of the solution flask. This evaporation was carried out on a steam bath in a platinum dish carefully protected from dust and fumes. Next the flask was filled nearly to the graduation with freshly distilled water at the desired temperature and the solution was thoroughly shaken in order to avoid subsequent change of volume in mixing. Then the flask was immersed in a water thermostat maintained at 25° and was allowed to remain in the thermostat for from two to six hours, according to the size of the flask, until constant temperature was reached. The volume of the solution was adjusted exactly to the graduation while the flask remained in the thermostat. Finally the solution was very thoroughly mixed by shaking, and the flask with contents, after being carefully dried with a clean cloth and allowed to come nearly to the temperature of the balance room, was weighed.

The flasks were of various sizes, from 35 cc. to 1000 cc., the smaller flasks being employed for the more concentrated, the larger for the less concentrated solutions. The greater accuracy necessary in determining the composition and density of the less concentrated solutions was thus more easily attained. The necks of the flasks were considerably constricted at the point of graduation, in order to make possible more accurate adjustment of the volume of the solution. The flasks were always weighed by substitution, the smaller flasks upon a balance sensitive to one-tenth of a milligram, the larger upon one sensitive to two milligrams. The true volumes of the flasks at 25° were determined by weighing them filled with pure water, the volume of the apparent gram of water being assumed to be 1.00400 cc. at 25° .

In some instances solutions were prepared by dilution to definite volume of a weighed amount of a stronger solution, and in the case of a few of the most concentrated solutions the salt was not weighed before

dissolving, but the composition of the solution was determined by analysis for halogen by precipitation of the silver halide. These exceptions are noted in the tables of results.

The salts themselves were weighed on a very sensitive Troemner balance with weights standardized in the fashion described by Richards.¹

All weights, both of salts and of solutions, were corrected to the vacuum standard, the following quantities being added for each gram of salt:

LiCl.....	+0.00044	LiBr.....	+0.00021	LiI.....	+0.00015
NaCl.....	+0.00042	NaBr.....	+0.00025	NaI.....	+0.00019
KCl.....	+0.00046	KBr.....	+0.00029	KI.....	+0.00024

The measurements of the indices of refraction of the solutions were made with an improved form of Pulfrich refractometer² manufactured by Zeiss of Jena. This instrument is provided with a vernier enabling the observer to read the angle of emergence of the ray of grazing incidence with an accuracy of 0.5'. The correction of the scale was found by determining the reading for pure water and comparing this reading with that interpolated for the index of refraction of water from the tables furnished with the instrument, the index of refraction of water for sodium light at 25° being assumed to be 1.33248.³ The difference between the reading actually observed and that interpolated from the table was used as a correction for the scale. The accuracy of the index of refraction for observations made in this way is about four units in the fifth decimal place. The instrument is further provided with a micrometer attachment by means of which differences of less than five degrees between the angles of emergence for two liquids can be determined with an accuracy of 0.1'. The readings of the micrometer were found to correspond exactly with graduations of the divided circle in the neighborhood of the reading for pure water. In the examination of the more dilute solutions this micrometer was employed, the difference between the reading for pure water and that for the solution being subtracted from the interpolated reading for water. An accuracy as great as two in the fifth decimal place of the index of refraction was thus obtained. With most solutions for which the readings of the refractometer differed from that of water by less than five degrees the latter method was employed. Although the tables furnished with the instrument apply at 20° both of the above methods of comparison with water obviate the necessity of applying a temperature correction. The temperature correction for the prism of the instrument is, however, only 0.000034 per degree.

Both the cell and the prism of the refractometer were provided with

¹ THIS JOURNAL, 22, 144 (1900).

² *Z. physik. Chem.*, 18, 294 (1895).

³ Baxter, Burgess and Daudt, see preceding paper.

devices for maintaining constant temperature by means of water circulation, a surrounding jacket in the case of the prism and a hollow silver plunger in the case of the cell. Water flowed from a large constant level reservoir through a twelve-meter coil of small lead pipe in a thermostat, and thence through a short insulated tube to the water jacket of the refractometer. Even with cold water flowing through the lead coil the temperature of the thermostat remained constant within five one-hundredths of a degree. After the current of water had flowed through the jackets of the refractometer for a few moments no important difference in temperature could be detected by means of thermometers, one of which was placed in the thermostat and the other in the plunger dipping into the cell of the refractometer. Since a difference in temperature of one-tenth of a degree is necessary to produce a change in the index of refraction of water of one unit in the fifth decimal place, the adjustment of temperature was evidently sufficiently exact.

Both thermometers were carefully compared with one standardized by the Physikalisch-Technisches Reichsanstalt.

Observations with all the solutions were made with sodium light. For the present purpose this light is essentially homogeneous, since the difference in index of refraction of water for the two yellow rays of sodium light is only two in the fifth decimal place.

After the introduction of each solution into the dried cell of the refractometer and the immediate closing of the cell by means of the plunger, which was made to fit tightly around the rim of the cell by means of a rubber ring in order to avoid evaporation of the solution, the temperature of the solution was allowed to come to constancy at 25°. Next the reading of the instrument was taken. The solution in the cell was then several times replaced with a fresh sample by means of a pipet, readings being taken in each case as soon as the temperature became constant. These readings seldom varied as much as 0.3'. The index of refraction corresponding to the average of the readings with each solution is given in the tables.

The weight of salt, the weight of the solution and the volume of the solution being known, the per cent. of salt and the specific gravity of the solution referred to water at 4° were calculated. Upon the assumption that the specific refractions of the salt and the water are additive, the specific and molecular refractions of the salt were computed by equations I and II, respectively:

$$\text{I.} \quad k = \frac{1}{\rho} \left(\frac{(n_s^2 - 1)}{(n_s^2 + 2)} \frac{100}{d_s} - \frac{(n_w^2 - 1)}{(n_w^2 + 2)} \frac{(100 - p)}{d_w} \right)$$

$$\text{II.} \quad Mk = \frac{M}{\rho} \left(\frac{(n_s^2 - 1)}{(n_s^2 + 2)} \frac{100}{d_s} - \frac{(n_w^2 - 1)}{(n_w^2 + 2)} \frac{(100 - p)}{d_w} \right)$$

in which

- k = specific refraction of the salt in solution;
 M = molecular weight of the salt;
 p = per cent. of salt;
 n_s = index of refraction of the solution at 25°;
 n_w = index of refraction of water at 25°;
 d_s = density of the solution at 25°;
 d_w = density of water at 25°.

In calculating molecular weights, values referred to silver 107.88 are employed as follows:

Li.....	6.94	Na.....	23.00	K.....	39.10
Cl.....	35.46	Br.....	79.92	I.....	126.92

As stated before, the refractive index of water is assumed to be 1.33248 at 25°. It is to be noted, however, that the method of standardizing the refractometer by comparison with pure water makes the final result for the molecular refraction of the salt independent of a small error in the refractive index of water. The density of water at 25° is assumed to be 0.997071. Since this value was used in the standardizing of the graduated flasks, the calculated molecular refraction of the salt is essentially independent of a small error in this value also.

In the following tables the values for index of refraction are referred to air. They may be referred to vacuum in the usual way by multiplying by the refractive index of air referred to vacuum, the latter value being 1.000265 at 25° and normal pressure. Since in each experiment the reading for pure water was always taken shortly before the reading for the solutions the effect of variation in the density of the air upon the index of refraction of air referred to a vacuum has no effect upon the corrected index of refraction of the solution and hence upon the molecular refraction. Since, however, the effect upon the calculated specific refraction of the salt of correcting the indices of refraction of water and the solution to vacuum is very slight, as the following table shows,

Salt.	Concentration. Per cent.	Specific refraction uncorrected.	Specific refraction corrected to vacuum.
NaBr.....	1	0.1235	0.1235
	17	0.12444	0.12448
	46	0.12368	0.12374
LiCl.....	13	0.20448	0.20456

this correction is omitted in the calculations of the refractive constants.

The following tables give for each salt and each solution investigated, w_s , the weight of salt in grams in vacuum; w_p , the weight of solution in grams in vacuum; p , the per cent. of salt in solution; m , the gram molec-

ular concentration of salt per liter; d , the density of the solution; n , the index of refraction of the solution for sodium light; k , the specific refraction of the salt; and Mk , the molecular refraction of the salt.

It is to be noted that the specific and molecular refractions are much more highly sensitive to experimental differences in the case of dilute solutions than in the case of concentrated solutions. For instance, with a one per cent. solution of sodium bromide a difference of 0.00001 in the refractive index makes a difference of 0.3 per cent. in the molecular refraction of the salt, and a difference in the density of 0.0001 produces a difference of 1.4 per cent. in the molecular refraction. On the other hand, with a seventeen per cent. solution similar differences in the measurements produce differences in the molecular refraction of only 0.03 and 0.08 per cent., respectively. An error of one-tenth of one per cent. in the concentration of the solution produces an error of 0.07 per cent. in the molecular refraction no matter what the actual concentration.

Unless otherwise stated, the experimental work was performed by A. C. Boylston.

TABLE I.—LITHIUM CHLORIDE.

M = 42.40.

w_s .	w_l .	p .	m .	d .	n .	k .	Mk .
1.5684	250.78	0.6254	0.1477	1.00068	1.33388	0.2093	8.88 ¹
1.7524	251.155	0.6977	0.1648	1.00116	1.33405	0.2115	8.97
2.3459	251.466	0.9329	0.2206	1.00240	1.33456	0.2134	9.05
2.4061	251.22	0.9578	0.2265	1.00243	1.33446	0.2066	8.76 ¹
2.4333	251.17	0.9688	0.2292	1.00271	1.33460	0.2088	8.86 ¹
3.5588	252.148	1.4114	0.3347	1.00511	1.33555	0.2106	8.93
2.8123	101.716	2.7648	0.6608	1.01308	1.33833	0.2052	8.70 ¹
7.0410	254.153	2.7703	0.6621	1.01311	1.33842	0.2068	8.77
5.9308	103.411	5.7352	1.393	1.02966	1.34465	0.2073	8.79
6.8558	103.931	6.5965	1.610	1.03484	1.34653	0.2071	8.78
11.2518	106.289	10.5860	2.643	1.05832	1.35494	0.2049	8.69
14.1275	107.762	13.1099	3.315	1.07299	1.36024	0.2045	8.67

TABLE II.—SODIUM CHLORIDE.

M = 58.46.

w_s .	w_l .	p .	m .	d .	n .	k .	Mk .
5.2938	1002.54	0.5280	0.0904	1.00079	1.33342	0.1605	9.38
5.5077	1002.73	0.5493	0.0940	1.00098	1.33341	0.1545	9.03
10.0384	1005.88	0.9980	0.1715	1.00413	1.33417	0.1558	9.11
1.0674	100.301	1.0618	0.1825	1.00432	1.33433	0.1628	9.52
5.5737	503.59	1.1068	0.1903	1.00477	1.33438	0.1592	9.31
5.5357	103.352	5.3562	0.9486	1.03488	1.34169	0.1584	9.26
5.5969	103.396	5.4131	0.9591	1.03532	1.34179	0.1582	9.23
6.1128	42.616	14.344	2.704	1.10146	1.35747	0.1582	9.23

¹ Experiment by P. B. Goode, the remainder by N. H. Black.

TABLE III.—POTASSIUM CHLORIDE.

M = 74.56

<i>w_s</i>	<i>w_l</i>	<i>p</i>	<i>m</i>	<i>d</i>	<i>n</i>	<i>k</i>	<i>M_k</i>
9.5104	1004.79	0.9466	0.1274	1.00303	1.33376	0.1544	11.51 ¹
0.9790	100.76	0.9716	0.1307	1.0031	1.33380	0.1550	11.56
2.4558	251.38	0.9769	0.1315	1.0032	1.33380	0.1520	11.34
5.0204	502.89	0.9983	0.1344	1.00337	1.33382	0.1514	11.29 ¹
2.5179	251.46	1.0013	0.1348	1.0036	1.33388	0.1516	11.31
2.4705	101.68	2.4297	0.3299	1.0122	1.33577	0.1539	11.48
2.5042	101.70	2.4623	0.3344	1.0124	1.33581	0.1539	11.48
23.9109	514.50	4.6474	0.6398	1.02654	1.33871	0.1518	11.33 ¹
4.9785	103.31	4.8150	0.6648	1.0285	1.33896	0.1500	11.19
4.9898	103.27	4.8318	0.6663	1.0281	1.33896	0.1505	11.22
4.9926	103.28	4.8340	0.6667	1.0282	1.33896	0.1500	11.19
7.4973	104.75	7.1573	1.0012	1.0428	1.34215	0.1522	11.35
7.5119	104.77	7.1699	1.0031	1.0430	1.34215	0.1518	11.32
9.5598	105.96	9.0221	1.277	1.0549	1.34463	0.1523	11.36
10.0038	106.25	9.4153	1.340	1.0577	1.34517	0.1517	11.31
10.0394	105.685	9.5004	1.349	1.05814	1.34528	0.1520	11.34 ¹
15.017	109.15	13.758	2.005	1.0865	1.35122	0.1527	11.39
15.022	109.21	13.755	2.006	1.0872	1.35122	0.1517	11.31
20.003	112.05	17.852	2.671	1.1155	1.35678	0.1514	11.29
20.063	112.10	17.858	2.679	1.1160	1.35687	0.1510	11.27
24.701	114.77	21.522	3.299	1.1426	1.36202	0.1508	11.25
25.018	114.92	21.770	3.341	1.1441	1.36238	0.1513	11.28

TABLE IV.—LITHIUM BROMIDE.

M = 86.86.

<i>w_s</i>	<i>w_l</i>	<i>p</i>	<i>m</i>	<i>d</i>	<i>n</i>	<i>k</i>	<i>M_k</i>
0.1982	100.09	0.1980	0.0228	0.9984	1.33273	0.1370	11.90 ²
0.3335	100.20	0.3328	0.0383	0.9995	1.33300	0.1418	12.32 ²
0.3898	100.24	0.3889	0.0449	0.9999	1.33307	0.1412	12.27
0.4324	100.26	0.4313	0.0496	1.0001	1.33309	0.1409	12.24 ²
0.8179	100.53	0.8136	0.0939	1.0028	1.33369	0.1440	12.51 ²
1.0314	100.69	1.0244	0.1184	1.0044	1.33401	0.1427	12.40
1.4443	100.613	1.4355	0.1665	1.00745	1.33466	0.1427	12.40
1.6999	101.17	1.6802	0.1952	1.0092	1.33499	0.1419	12.32
0.9492	50.71	1.8718	0.2179	1.0108	1.33530	0.1400	12.16
1.8296	51.34	3.5637	0.4198	1.0233	1.33788	0.1407	12.22
1.8442	51.343	3.5919	0.4232	1.0234	1.33793	0.1416	12.30
1.9285	51.40	3.7527	0.4427	1.0245	1.33825	0.1430	12.42
2.2189	51.61	4.2994	0.5092	1.0287	1.33905	0.1417	12.31
2.3906	51.72	4.6222	0.5486	1.0309	1.33954	0.1427	12.40
3.2410	52.325	6.1940	0.7441	1.04335	1.34200	0.1408	12.23
8.3797	55.99	14.966	1.922	1.1153	1.35662	0.1405	12.20
10.4304	57.340	18.190	2.395	1.14337	1.36254	0.1415	12.29
11.397	35.015	32.55	4.829	1.2889	1.39194	0.1407	12.22 ³

¹ Experiment by A. C. Boylston, the remainder by E. Mueller.² Diluted from a more concentrated solution.³ Analyzed by precipitation of the bromine as silver bromide.

TABLE V.—SODIUM BROMIDE.

M = 102.92.

<i>w_s</i>	<i>w_l</i>	<i>p</i>	<i>m</i>	<i>d</i>	<i>n</i>	<i>k</i>	<i>M_k</i>
0.4873	100.324	0.4857	0.0472	1.00074	1.33311	0.1233	12.69
0.9171	100.66	0.9110	0.0888	1.0041	1.33370	0.1227	12.62 ¹
1.1254	100.828	1.1162	0.1090	1.0058	1.33402	0.1235	12.71 ¹
2.0110	101.48	1.9817	0.1949	1.0123	1.33522	0.1262	12.98 ¹
2.1383	101.607	2.1044	0.2072	1.01354	1.33535	0.1234	12.70 ¹
2.8718	102.186	2.8104	0.2784	1.01931	1.33639	0.1226	12.61 ¹
2.9840	102.23	2.9218	0.2895	1.0198	1.33649	0.1246	12.82
4.6970	103.133	4.5543	0.4570	1.03268	1.33883	0.1255	12.91
2.3960	51.815	4.6241	0.4642	1.03320	1.33890	0.1254	12.90
3.4325	52.62	6.5288	0.6655	1.0490	1.34159	0.1241	12.77
3.8110	52.89	7.2055	0.7382	1.0544	1.34257	0.1247	12.83
3.9149	52.954	7.3936	0.7587	1.05600	1.34291	0.1252	12.88
4.7177	53.572	8.8063	0.9142	1.06832	1.34501	0.1244	12.80
		17.261	1.920	1.14479	1.35822	0.1245	12.81 ²
		46.06	6.716	1.5005	1.41841	0.1237	12.73 ²

TABLE VI.—POTASSIUM BROMIDE.

M = 119.02.

<i>w_s</i>	<i>w_l</i>	<i>p</i>	<i>m</i>	<i>d</i>	<i>n</i>	<i>k</i>	<i>M_k</i>
3.7914	1001.45	0.3786	0.0318	0.99971	1.33292	0.1277	15.22
4.9685	503.18	0.9874	0.0832	1.00396	1.33370	0.1277	15.22
7.2169	504.80	1.4297	0.1210	1.00718	1.33408	0.1237	14.73
1.5140	101.079	0.4978	0.1268	1.00776	1.33425	0.1259	14.99 ¹
2.9991	102.135	2.9364	0.2512	1.01829	1.33596	0.1247	14.84
3.7684	102.705	3.6692	0.3155	1.02373	1.33684	0.1251	14.89
4.2634	103.013	4.1387	0.3572	1.02704	1.33743	0.1260	15.00 ¹
4.3275	102.635	4.2164	0.3640	1.02770	1.33749	0.1251	14.89
4.4345	103.131	4.2999	0.3714	1.02821	1.33763	0.1261	15.01
4.5802	102.809	4.4552	0.3852	1.02941	1.33777	0.1254	14.92 ¹
7.5466	105.346	7.1636	0.6318	1.05006	1.34115	0.1254	14.92
8.3119	105.405	7.8856	0.6990	1.05543	1.34200	0.1255	14.94 ¹
9.4012	106.178	8.8542	0.7907	1.06317	1.34327	0.1254	14.92
5.2158	53.645	9.7228	0.8736	1.06977	1.34435	0.1253	14.92
5.8142	54.098	10.7475	0.9799	1.07881	1.34575	0.1247	14.84
9.4922	45.164	21.017	2.061	1.16718	1.35984	0.1251	14.89

TABLE VII.—LITHIUM IODIDE.

M = 133.86.

<i>w_s</i>	<i>w_l</i>	<i>p</i>	<i>m</i>	<i>d</i>	<i>n</i>	<i>k</i>	<i>M_k</i>
1.1125	100.377	1.1083	0.0832	1.33424	1.00509	0.1463	19.59
1.4318	100.610	1.4231	0.1070	1.33468	1.00742	0.1433	19.18
1.4602	100.623	1.4512	0.1092	1.33473	1.00755	0.1445	19.35
2.1668	101.149	2.1422	0.1621	1.33580	1.01282	0.1422	19.04
2.3885	101.305	2.3577	0.1785	1.33620	1.01438	0.1441	19.29
2.5650	101.434	2.5287	0.1917	1.33641	1.01567	0.1426	19.09
1.9882	40.013	4.9689	0.3838	1.34033	1.03405	0.1432	19.17
5.2155	42.367	12.3103	1.007	1.35311	1.09490	0.1417	18.97
6.7241	43.451	15.4751	1.298	1.35908	1.12291	0.1419	18.99

¹ Diluted from a more concentrated solution.² Analyzed by precipitation of the bromine as silver bromide.

TABLE VIII.—SODIUM IODIDE.

M = 149.92.

<i>w_s</i>	<i>w_l</i>	<i>p</i>	<i>m</i>	<i>n</i>	<i>d</i>	<i>k</i>	<i>M_k</i>
5.7423	1003.29	0.5723	0.0382	1.33333	1.00154	0.1289	19.32 ¹
7.1559	1004.33	0.7125	0.0476	1.33352	1.00258	0.1291	19.36
7.1678	1004.36	0.7137	0.0477	1.33353	1.00261	0.1289	19.32
7.5042	1004.70	0.7469	0.0499	1.33362	1.00294	0.1299	19.47
3.8022	102.454	3.7111	0.2540	1.33793	1.02588	0.1302	19.52
3.9599	102.581	3.8603	0.2645	1.33817	1.02716	0.1300	19.49
7.1698	105.014	6.8272	0.4789	1.34278	1.05152	0.1300	19.48
8.2630	44.812	18.4384	1.425	1.36281	1.15808	0.1295	19.42
15.2028	49.977	30.418	2.621	1.38783	1.29156	0.1292	19.36

TABLE IX.—POTASSIUM IODIDE.

M = 166.02.

<i>w_s</i>	<i>w_l</i>	<i>p</i>	<i>m</i>	<i>d</i>	<i>n</i>	<i>k</i>	<i>M_k</i>
4.3878	1002.10	0.4379	0.0264	1.33306	1.00045	0.1263	20.97
9.2024	1005.58	0.9151	0.0553	1.33367	1.00382	0.1274	21.15
12.3546	1007.77	1.2259	0.0742	1.33409	1.00601	0.1299	21.57
2.3910	101.286	2.3607	0.1442	1.33554	1.01419	0.1304	21.64
3.1698	101.852	3.1122	0.1912	1.33658	1.01986	0.1305	21.67
5.2754	103.379	5.1029	0.3181	1.33927	1.03515	0.1295	21.50
9.1138	106.142	8.5864	0.5497	1.34422	1.06282	0.1295	21.50
12.0873	47.209	25.604	1.881	1.37194	1.2200	0.1289	21.40

From the data recorded in the foregoing tables various values of interest may be computed.

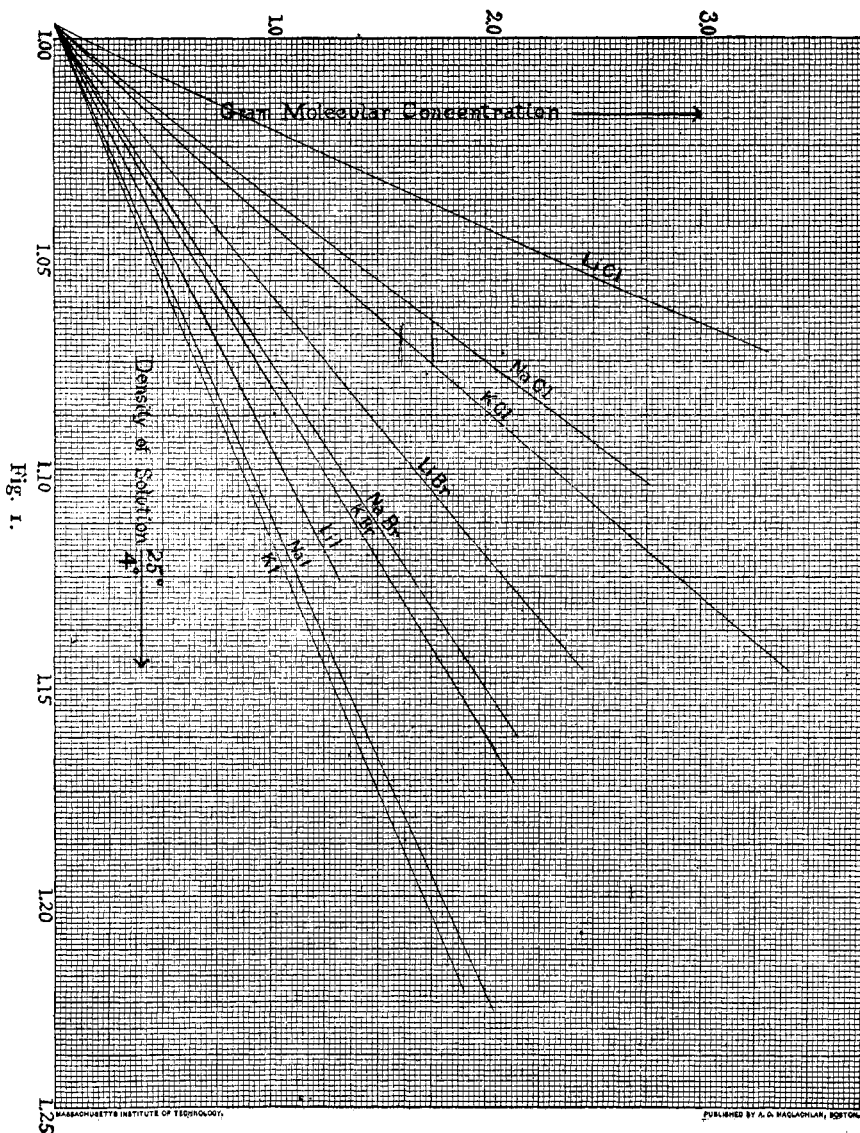
The increase in density of the solutions with increasing concentration is nearly, but not quite, proportional to the quantity of salt in unit volume. In Table X are given the quotients of the differences between the densities of the solution and of water divided by the molal concentrations:

TABLE X.

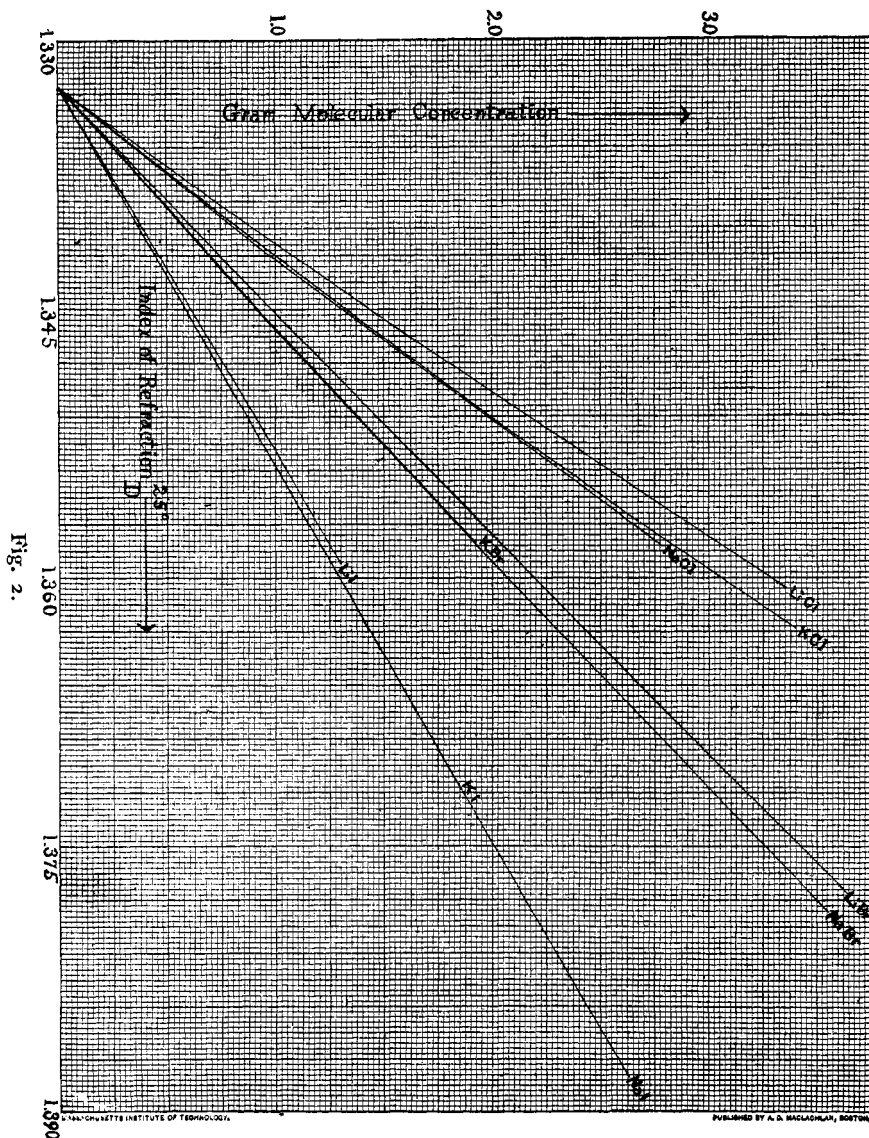
<i>m</i>	LiCl.	NaCl.	KCl.	LiBr.	NaBr.	KBr.	LiI.	NaI.	KI.
0.05				0.060	0.078	0.083		0.117	0.123
0.10		0.0414		0.061	0.079	0.083	0.0964		
0.15	0.0246		0.047	0.0625		0.0843	0.0972		0.1187
0.2	0.0242	0.0405		0.0624	0.0787	0.0845	0.0970		0.1191
0.3	0.0240		0.0460		0.0790	0.0841	0.0964	0.1136	0.1196
0.5				0.0620	0.0779	0.0840		0.1137	0.1196
0.8	0.0242		0.0467	0.0622	0.0778	0.0834			
1.0		0.0399	0.0456		0.0780	0.0834	0.0972		
1.3	0.0236		0.0453				0.0969		
1.5	0.0235							0.1130	
1.8									0.1185
2.0			0.0448	0.0615	0.0769	0.0826			
2.5	0.0232	0.0386	0.0444	0.0611				0.1123	
3.5	0.0229		0.0441						
4.8				0.0604					
6.7					0.0750				

¹ Diluted from a more concentrated solution.

These increments decrease slowly with increasing concentration except in the case of lithium iodide. Hence the curves on page 917 representing change in index of refraction with changing concentration are slightly convex with respect to the vertical axis. Furthermore, even at 2 molal concentration, where dissociation has taken place to the extent of about sixty per cent., the values in Table X show distinct additive relationships between the different salts. At lower concentrations



the additive relations are still more striking, *i. e.*, for a given ion the increment is constant, although the effect of the molecules is evidently not far from additive. In Table XI are given the increments for the



different salts¹ in 1 molal solution, the values² being taken from curves plotted with the results in Table X. It is to be noted that the differences as well as the increments change with the concentration:

TABLE XI.

	Cl	Dif.	Br.	Dif.	I.
Li.....	0.0237	0.0382	0.0619	0.0351	0.0970
Dif.....	0.0162		0.0157		0.0163
Na.....	0.0399	0.0377	0.0776	0.0357	0.1133
Dif.....	0.0056		0.0057		0.0057
K.....	0.0455	0.0378	0.0833	0.0357	0.1190

These additive relationships were first pointed out by Valson¹ and have been frequently investigated by others. The calculations have been made here because the solutions were prepared at a somewhat higher

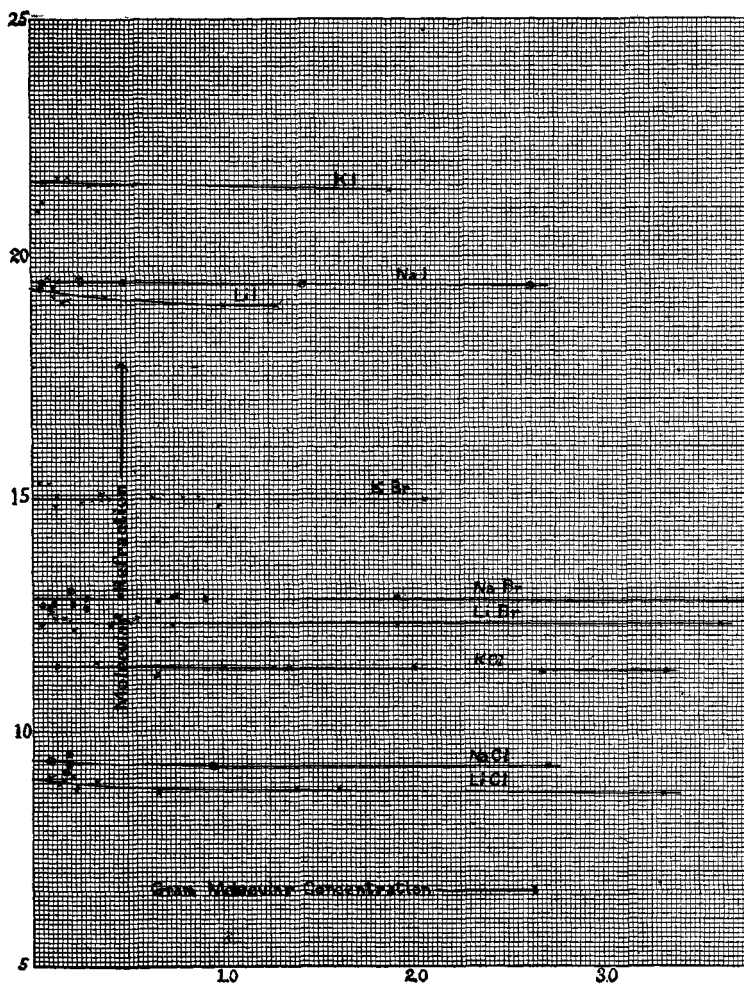


Fig. 3.

¹ *Compt. rend.*, 73, 441 (1871).

temperature than has been commonly employed and because of the care with which the solutions were made up.

The cause of the decrease in the increments with increasing concentration is the increasing contraction which takes place during the solution of most salts in water, lithium bromide and iodide being exceptions to this rule and showing expansion during solution. This question of contraction and expansion during the solution of the alkali halides is discussed in a following paper.

In Table XII are given similar increments for change in the refractive index, obtained by dividing the differences between the refractive indices of the solution and of water by the molal concentration. As in the case of the density increments these values decrease with increasing concentration, although more slowly than the latter. Hence the curves on page 917 are slightly convex with respect to the vertical axis:

TABLE XII.

<i>m.</i>	LiCl.	NaCl.	KCl.	LiBr.	NaBr.	KBr.	LiI.	NaI.	KI.
0.05				0.0125	0.0134	0.0138		0.0222	0.0217
0.10		0.0102		0.0129	0.0138	0.0140	0.0208		
0.15	0.0095		0.0101	0.0131		0.0140	0.0205		0.0212
0.2	0.0091	0.0100		0.0129	0.0139	0.01385	0.02066		0.02144
0.3	0.0092		0.00997		0.0140	0.01380	0.02046	0.02148	0.02133
0.5	0.00892			0.01292	0.01380	0.01372		0.02150	0.02136
0.8			0.00973	0.01279	0.01370	0.01361			
1.0		0.00971	0.00965		0.01370	0.01354	0.02049		
1.3	0.00874		0.00949				0.02049		
1.5	0.00873							0.02129	
1.8									0.02098
2.0			0.00935	0.01256	0.01340	0.01327			
2.5	0.00850	0.00924	0.00910	0.01254				0.02111	
3.5	0.00838		0.00896						
4.8				0.01231					
6.7					0.01280				

As has already been pointed out by Bender and others, these increments exhibit additive relationships, which are more striking at low than at high concentrations, indicating that the ionic but not the molecular increments are nearly constant. Values, taken from curves, for 1 molal solutions are given in the following table. Here also the differences between the increments for corresponding salts are not constant with changing concentration:

TABLE XIII.

	Cl.	Dif.	Br.	Dif.	I.
Li.....	0.00885	0.00390	0.01275	0.00774	0.02049
Dif.....	0.00086		0.00090		0.00088
Na.....	0.00971	0.00394	0.01365	0.00772	0.02137
Dif.....	0.00006		0.00011		0.00017
K.....	0.00965	0.00389	0.01354	0.00766	0.02120

The most noticeable feature of these results is the fact that the increments for potassium salts are uniformly lower than those for sodium salts, although lithium salts give the smallest increments. This peculiarity is undoubtedly closely connected with the contraction which takes place during the solution of the sodium and potassium salts, the contraction per gram molecule being *greater* with sodium than with potassium salts except with the iodides where the reverse is true. Lithium salts show smaller contractions than either sodium or potassium salts, the bromide and iodide in fact showing expansion during solution.

The specific and hence the molecular refractions of the different salts (see Tables I to IX) are nearly constant with varying concentration, although a very slight gradual increase in these constants with diminishing concentration is noticeable in all cases. In the case of lithium chloride and iodide this increase seems to be somewhat more marked at low concentrations. So marked an increase at so low concentration could hardly be due to increased dissociation in the case of electrolytes of so large a tendency to dissociate. Furthermore, if due to this cause, it is to be expected with all the salts examined. If caused by an unusually high degree of hydration, a similar effect is to be expected with lithium bromide where no such effect apparently exists. It is to be remembered that with the more dilute solutions the refractive constants are obtained by difference between two relatively large quantities, and consequently are less to be relied upon than the values obtained from the more concentrated solutions. Hence it is not at all impossible that the larger increase in the case of lithium chloride and iodide is due merely to experimental irregularities.

In comparing the molecular refractions of the different salts, in order to avoid as far as possible the effect of different degrees of dissociation, hydration or any other influences, it is well to select values for molecular refraction at equivalent concentrations, since then the above effects may be expected to be as nearly as possible the same in all cases. In the following table are given values taken from the curves of molecular refraction given on page 918, at unimolecular concentration:

TABLE XIV.

	Cl.	Dif.	Br.	Dif.	I.	Av.
Li.....	8.75	3.54	12.29	6.71	19.00	
Dif.....	0.50		0.51		0.43	0.48
Na.....	9.25	3.55	12.80	6.63	19.43	
Dif.....	2.10		2.11		2.05	2.09
K.....	11.35	3.56	14.91	6.57	21.48	
Av.....		3.55		6.64		

The additive relationships indicated by this table are as regular as could be reasonably expected.

Obviously the foregoing table affords no means of determining directly the atomic refractions of the six elements involved. However, it is possible to obtain a value for the atomic refraction of hydrogen from measurements of the index of refraction and density of this substance in the gaseous state, the index of refraction of the gas for sodium light being 1.000138 referred to vacuum at 0° and 760 mm., and the density 0.000896 under the same conditions.¹ The atomic refraction of hydrogen found in this way is 1.03. It may be added that Conrady² found the average atomic refraction of hydrogen in organic substances to be 1.05, a value in close agreement with the above. Although there is no positive evidence that the atomic refraction of hydrogen in the ionic state is identical with that of the gas or of the element in organic combinations, on account of the low value of this constant the error caused by such an assumption is probably small.

The molecular refraction of hydrochloric acid has recently been found in this laboratory³ to be 8.53 at unimolal concentration at 25°. The difference between the value for hydrochloric acid and that for hydrogen, 7.50, may be assumed to represent the atomic refraction of chlorine. From the latter value the following tables of atomic refractions may be constructed:

TABLE XV.

H	=	1.03
Cl	=	7.50
Br	=	7.50 + 3.55 = 11.05
I	=	11.05 + 6.63 = 17.68
Li	=	1.25, 1.24, 1.32. Av. 1.27
Na	=	1.75, 1.75, 1.75. Av. 1.75
K	=	3.85, 3.86, 3.80. Av. 3.84

The values for chlorine, bromine and iodine are all considerably higher than the values for the same elements computed by Conrady⁴ from results with organic compounds, 6.00, 8.93 and 14.12, respectively, while the indices of refraction and densities of chlorine and bromine gases yield the values 5.78 and 8.45.

It is evident from this table that the atomic refractions of the alkali metals in solution are relatively much smaller than those of the halogens, as was to be expected from an examination of the curves showing change in index of refraction with changing concentration. Furthermore, in the two series of similar elements, as Gladstone and Kanonnikoff have already pointed out, atomic refraction increases with increasing atomic weight. No further generalizations can safely be made from so limited a number of atomic refractions.

¹ Landolt-Börnstein-Meyerhoffer.

² *Z. physik. Chem.*, 3, 210 (1889).

³ This investigation, by Mr. Frederick Barry, is not yet published.

⁴ *Loc. cit.*

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.

CAMBRIDGE, MASS.

[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.

Received April 13, 1911.

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.*