centage of total salt) of the intermediate ion might even increase on dilution. The explanation here advanced is in agreement with the essential constancy of the migration ratios of other related salts, such as cadmium bromide, to much higher concentration, since cadmium iodide is recognized as furnishing an extreme typical case of complex formation.

To sum up, the behavior of ternary salts can be explained within the experimental error of the available data as being due to the pressure of intermediate ions, and also of complex ions in the more concentrated solutions.

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CERTAIN PHYSICAL PROPERTIES OF THE ALKALI NITRATES AND CHLORIDES.

BY F. L. HAIGH.

Received July 15, 1912.

The elements belonging to any group in the periodic classification exhibit, as is well known, chemical and physical properties which, in a general way, are simple functions of the atomic weights. Thus, if the numerical values for a given property be taken, they will show, as a rule, a more or less regular increase—or decrease, as the case may be—with increasing atomic weights of the elements. The same general statement may be said to apply to a series of compounds of the elements in such a group. This relation may be easily represented graphically by plotting the atomic weights as abscissas and the given properties as ordinates. When this is done it will at once be clear that the above generalization is only a rough approximation, since the points so plotted will seldom, if ever, lie exactly in a straight line or on a regular curve.

The present investigation is a study of several physical properties of two salts of the entire series of alkali metals, including lithium, sodium, potassium, rubidium, cesium and the radical ammonium, the object in view being the determination of the exact quantitative relations which exist between the properties considered and the atomic weights of the metals. For this purpose the nitrates and chlorides have been chosen. The following physical properties have been considered:

1. Specific gravity of solids.
2. Melting points.
3. Heat of solution.
4. Solubility.
5. Specific gravity of solutions.
6. Expansion of solutions.
7. Index of refraction of solutions.

For the more common salts these properties have all been quite thoroughly studied by previous investigators, and the results are available in the literature. The data are not complete, however, especially for the rubidium and cesium salts, and a large part of the work here described consisted in obtaining the values for these salts. A few determinations were carried out on the sodium and potassium salts as a means of checking the methods used and to give an idea of the accuracy of the results. In some instances, notably where the properties of solutions were being considered, it was impossible to obtain strictly comparable data from the literature, and the determinations were, therefore, carried out for the entire series without regard to previous work. The several properties will be considered in the order given above, and in conclusion the results will be discussed briefly.

The accuracy of the values obtained for the physical properties of any substance depends in a large measure on the purity of the material used. In the present investigation all the salts employed were of a high grade of purity. A brief account of the methods used in their preparation seems desirable, however.

Lithium Nitrate, Lithium Chloride.—These salts were prepared from pure lithium carbonate (Kahlbaum's). The carbonate was dissolved in the required acid and reprecipitated with ammonium carbonate. The precipitate was washed, dried, and ignited to remove ammonium salts, dissolved in the pure acid, and the solution evaporated to dryness. Since these salts absorb water readily they were always dried just before use.

Ammonium Nitrate, Ammonium Chloride, Sodium Nitrate, Potassium Nitrate.—The purest salts that could be obtained from the laboratory stock were recrystallized.

Sodium Chloride.—This salt was purified by precipitation with hydrochloric acid.

Potassium Chloride.—This salt was prepared by dissolving pure potassium chloride (Kahlbaum's) in distilled water and reprecipitating with alcohol.

The Rubidium Salts.—These were prepared from material which was purified by precipitation as the double rubidium lead chloride by passing chlorine gas into a solution of rubidium chloride containing suspended lead chloride. Rubidium nitrate and chloride were obtained from this compound by the usual methods. Spectroscopic tests showed not the slightest trace of potassium or cesium. The nitrate was further purified by recrystallization, and the chloride by precipitation with alcohol.

The Cesium Salts.—These were prepared from material which was purified by precipitation as the double cesium antimony chloride. Cesium nitrate and chloride were obtained from this compound by the usual methods. These salts showed no potassium or rubidium with the spectroscope.

Specific Gravity of Solids.

The specific gravity of most of the salts under consideration has been determined before. The results obtained by the older investigators need not be considered here in detail. They will be found in Dammer's "Handbuch der Anorganischen Chemie," and Landolt-Börnstein's "Physikalisch-Chemische Tabellen." Some of the values appear to be quite inaccurate. In the table at the end of this section will be found a summary of some of the more recent determinations.

The method used for the determinations made in the course of this work was investigated by Mr. C. R. Downs, of this laboratory, who determined the specific gravity of several of the alkali sulfates. The author is indebted to him for the preliminary work and certain modifications in the details of procedure. As finally adopted the method in detail was as follows: The pyknometer used had a capacity of about 25 cc., and was of the usual bottle form, but was fitted with a cap to cover the perforated stopper. This cap rested on the outer beveled edge of the neck and the joint was made tight by grinding with corborundum powder. Carbon tetrachloride was prepared by drying the commercial article with calcium chloride and distilling. About 20–25 grams of the pure salt, which had been ground, put through a 50 mesh sieve, and thoroughly dried, were placed in a small Erlenmeyer flask and covered to the depth of about three-fourths of an inch with carbon tetrachloride. The flask was then attached to a reflux condenser and the contents boiled on the steam bath for at least half an hour. After cooling, the greater part of the clear liquid was decanted through a dry filter into another flask. The solid was shaken with the remaining liquid forming a thick suspension, and poured as completely as possible into the pyknometer through a small funnel. Enough of the clear liquid was added to fill it. The pyknometer was immersed in a thermostat at 20° for at least 20 minutes. The stopper was then inserted tightly, the joint wiped dry with a bit of filter paper, and the cap put in place. The pyknometer was removed from the bath, set into cold water for two or three minutes, wiped quickly with a soft cloth, placed upon the balance and counterbalanced with the approximate weights. After allowing it to stand thus for a few minutes to acquire the temperature of the room the exact weight was taken. It was found in the preliminary work that without the cap the pyknometer lost weight rapidly owing to evaporation of the carbon tetrachloride, but this was effectually prevented by the cap. As a check on this weight, the pyknometer was refilled with the liquid, and after the same treatment in the thermostat, was weighed again. A mean of these two weights (sometimes three or four weights were taken) was used in making the calculations. The contents of the pyknometer were then removed as completely as possible by rinsing with carbon tetrachloride into a small tared evaporating dish. The liquid was evaporated on the steam bath, and the salt dried in an oven or ignited, depending on the salt used, and its weight determined. The weight of the pyknometer filled with carbon tetrachloride solution alone was determined in duplicate in the manner already described. The specific gravity of the carbon tetrachloride solution was obtained with an Ostwald pyknometer of about 10 cc. capacity. In the case of ammonium chloride it was necessary to use a lighter liquid, since the specific gravity of this salt is less than that of carbon tetrachloride. Benzene was chosen for this purpose, and was prepared by drying the commercial article over metallic sodium and distilling. The method, however, was identically as described for the other salts. The solubility of the salts in carbon tetrachloride was determined by evaporating 10–15 grams of the solution, but in every case the residue was less than 0.0005 gram, and was, therefore, negligible. All weighings were corrected for displaced air, using the method given by Treadwell-Hall.[1] The specific gravity of the salt 20°/4° was calculated in the usual way. In the following table the first column gives the formula of the salt; the second column (*w*) gives the weight of salt used; the third (*l*) the weight of liquid displaced; the fourth (*s*) the specific gravity of the liquid 20°/4°; while columns five and six give, respectively, the values calculated from each set of data, and the mean values for each salt.

Salt.	*w*.	*l*.	*s*.	Sp. gr. 20°/4°.	Mean.
$LiNO_3$	21.7606	14.6613	1.5930	2.3659	2.3658
	21.1012	14.2095	1.5930	2.3656	
$RbNO_3$	23.6599	12.1157	1.5932	3.1113	3.1119
	24.2192	12.3957	1.5930	3.1125	
$CsNO_3$	24.9901	10.9270	1.5931	3.6434	3.6432
	24.8594	10.8706	1.5930	3.6430	
LiCl	17.3205	13.3423	1.5930	2.0680	2.0678
	20.3421	15.6749	1.5931	2.0676	
NH_4Cl	19.6184	11.2991	0.87850	1.5253	1.5256
	20.7644	11.6086	0.87846	1.5259	
RbCl	17.4164	10.0497	1.5930	2.7607	2.7621
	17.5563	10.1209	1.5930	2.7634	
CsCl	20.5832	8.2227	1.5930	3.9788	3.9875
	20.4957	8.1895	1.5931	3.9871	

The table which follows is a summary of the values given by some of the more recent investigators, together with our own results. From these we have selected what appear to be the most trustworthy values for the entire series, and from these the molecular volumes have been calculated. Fig. 1 shows the relation of the specific gravities of the salts to the atomic weights of the contained alkali metals, and Fig. 2 the relation of the molecular volumes to the atomic weights of the metals. For comparison

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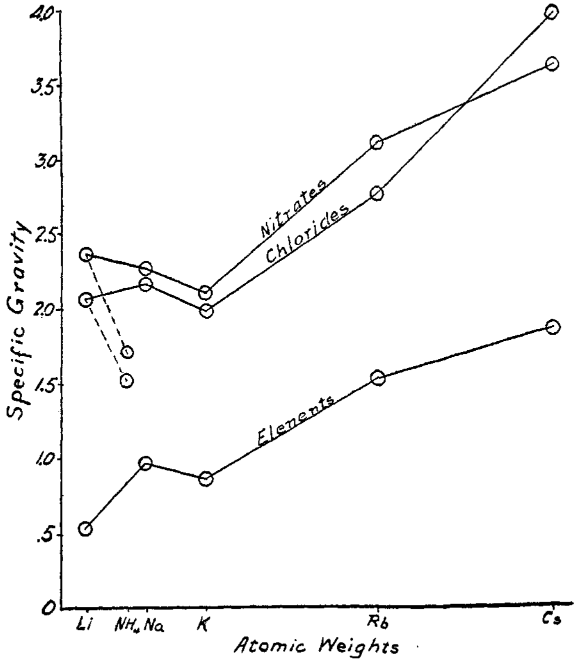
[1] *Analytical Chem.*, 2, 14 (1911).


4.0
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Specific Gravity
Nitrates
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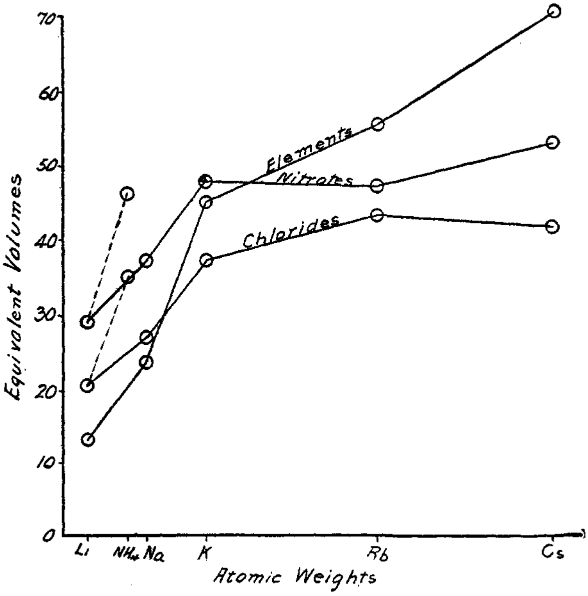
Li
NH₄
Na
K
Rb
Cs
Atomic Weights

Fig. 1.


70
60
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40
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10
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Equivalent Volumes
Elements
Nitrates
Chlorides
Li
NH₄
Na
K
Rb
Cs
Atomic Weights

Fig. 2.

these properties of the metals themselves have also been plotted, using the values given in Abegg's "Handbuch der Anorganischen Chemie," which are as follows:

Metals.	Sp. gr. 20°/4°.	Atomic volumes.
Li	0.534	13.1
Na	0.9712	23.7
K	0.8621	45.36
Rb	1.532	55.8
Cs	1.87	71.0

SUMMARY OF SPECIFIC GRAVITY OF SOLIDS.

Salt.	Haigh.	Other investigators.			Selected values.	Molecular volumes.
$LiNO_3$	2.366	2.4(?)[1]			2.366	29.1
NH_4NO_3	...	1.725[1]			1.725	46.4
$NaNO_3$	...	2.265[1]	2.267[2]		2.266	37.5
KNO_3	...	2.109[1]			2.109	48.0
$RbNO_3$	3.112	3.131[1]			3.112	47.4
$CsNO_3$	3.643	3.687[3]			3.643	53.5
LiCl	2.068	...			2.068	20.5
NH_4Cl	1.526	1.532[2]			1.526	35.1
NaCl	...	2.167[1]	2.174[2]		2.170	27.0
KCl	...	1.989[1]	1.994[2]	1.951[4]	1.991	37.5
RbCl	2.762	2.706[4]			2.762	43.7
CsCl	3.987	3.972[3]	3.982[4]		3.987	42.3

Melting Points.

An examination of the literature shows that the melting points of all the alkali nitrates and chlorides are known with a considerable degree of accuracy with the possible exception of rubidium nitrate, whose melting point seems not to have been determined before. We have, therefore, determined the melting point of this salt, and also that of cesium nitrate, as previous determinations of the latter do not agree closely. A nitrogen filled mercury thermometer registering to 550° was used, and a slight modification of the method in general use for taking the melting points of organic compounds was adopted. A bath of fused sodium and potassium nitrates and sodium nitrite in about equal quantities was prepared in a small flask, and the thermometer suspended so that the bulb dipped almost to the bottom of the flask. A few small crystals of the salt were placed in a capillary melting point tube, and the operation of determining the melting point was carried out in the usual way. To standardize the thermometer the melting points of sodium nitrate, potassium nitrate, and zinc were used. The figures of Stern[5] were accepted for the

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[1] Retgers, *Z. physik. Chem.*, **3**, 289 (1889); **4**, 597 (1889); **6**, 193 (1890).

[2] Krickmeyer, *Ibid.*, **21**, 53 (1896).

[3] Richards and Archibald, *Proc. Am. Acad.*, **38**, 413 (1903); *Z. anorg. Chem.*, **34**, 353 (1903).

[4] Buchanan, *Proc. Chem. Soc.*, **21**, 122 (1905).

[5] *Z. physik. Chem.*, **65**, 667 (1909).

first two, *viz.*, $NaNO_3$ = 306.8°, KNO_3 = 334.5°. The thermometer was found to read 4.5° too low at the melting point of sodium nitrate, and 6.5°–7° too low at the melting point of potassium nitrate. The melting point of zinc could not be determined in this way as the formation of the oxide interfered with the observation. Fifty or sixty grams of pure zinc were put in a crucible, covered with powdered charcoal, and melted. The thermometer bulb was protected by a thin glass tube and immersed to the same depth as it had been in the fused salts bath, and the zinc allowed to cool. The temperature which remained constant longest was taken as the melting point; 419° C. was accepted as the true melting point. The thermometer was found to read 12° too low at this point. When these corrections were plotted as ordinates against the thermometer readings as abscissas they were found to lie almost exactly in a straight line. It was, therefore, assumed that at intermediate points the correction also lay on this line, and this has been used as the basis for the corrections applied to the melting points determined.

Rubidium nitrate was recrystallized from a rather large volume of water, dried, and the melting point taken in the manner described.

Corrected melting point: (1) 312.5°–314°, (2) 312°–314°. This material was twice more recrystallized and then melted sharply: (1) 312°–313°, (2) 313°.

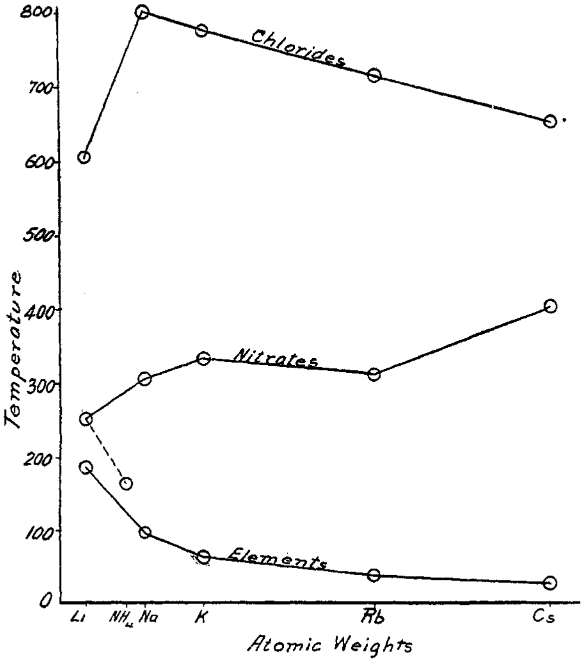

Fig. 3.

Cesium nitrate, recrystallized, melted at 405.5°–407°; again recrystallized, melted sharply at 407°.

Practically all of the older determinations of melting points are inaccurate, owing to the difficulties attending the measurement of high temperatures. It is only quite recently that the melting points of such substances as gold, zinc, etc., which are frequently used for standardizing thermometers have been definitly fixed within narrow limits of error. For this reason only a few of the more recent determinations are given in the following table. The final column is made up of the values which seem to be the most trustworthy:

SUMMARY OF MELTING POINTS.

Salt.	Melting points as given by various investigators.					Selected values.
$LiNO_3$	253[1]					253°
NH_4NO_3	165[2]					165°
$NaNO_3$	308[1]	306.8[3]				306.8°
KNO_3	337[1]	334.5[3]				334.5°
$RbNO_3$	313[4]					313°
$CsNO_3$	414[5]	405[6]	407[4]			407°
$LiCl$	602[7]	605–607[8]				607°
NH_4Cl	(sublimes)					..
$NaCl$	810[8]	803[9]	804.1[10]	801[11]	800[12]	801°
KCl	778[8]	775[9]	772.3[10]			775°
$RbCl$	712–713[8]					713°
$CsCl$	631[7]	647[6]				647°

Heat of Solution.

So far as the writer is aware, the heats of solution of rubidium and cesium nitrates have not been previously investigated. To complete the series these were determined. It also seemed advisable to repeat the determinations for rubidium and cesium chlorides and for lithium nitrate and chloride. As a check on the method, determinations were carried out on some of the sodium and potassium salts. The calorimeter used was of the usual pattern, and consisted of an outer double walled water jacket of copper, a second vessel of tin-foil supported by corks, and the inner vessel which was of silver. A wooden ring formed the top and sup-

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[1] Carveth, *J. Physic. Chem.*, **2**, 209 (1898).

[2] Pickering, *J. Chem. Soc.*, **36**, 200 (1879).

[3] Stern, *loc. cit.*

[4] Haigh.

[5] Richards and Archibald, *loc. cit.*

[6] Foote and Levy, unpublished work.

[7] Carnelley, *J. Chem. Soc.*, **29**, 489 (1876); **1**, 281 (1878); **37**, 125 (1880).

[8] Hüttner and Tamman, *Z. anorg. Chem.*, **43**, 224 (1905).

[9] Arndt, *Z. Elektrochem.*, **12**, 337 (1906).

[10] Plato, *Z. physik. Chem.*, **55**, 721 (1906); **58**, 350 (1907).

[11] White, *Am. J. Sci.*, **28**, 453 (1909).

[12] Burgess, "Measurement of High Temperatures," Burgess-Le Chatelier.

ported the silver cup. The cover was a disk of wood with holes for the thermometer, stirrer, and funnel through which the salt was introduced. The stirring apparatus was a small brass rod carrying three screw paddles driven by a water motor. The heat capacity of the calorimeter vessel, stirrer and thermometer bulb was 13.9 calories. The differential thermometer had been carefully compared by Professor Foote with an accurately standardized one belonging to Professor Mixter. The total correction for an interval of 5° was +0.023°. It was compared with the same standard again by the writer toward the end of the work and the same scale of corrections found to hold throughout. The calorimeter held about 500 grams of water. An amount of the salt was used which would give a dilution of one molecule of salt to 400 molecules of water. The temperature of the calorimeter water was about 20–22° in all the determinations. The salts were ground very fine, and, with the exception of the lithium salts, were put through a 100-mesh sieve. The time required for complete solution was never more than three minutes. The operation

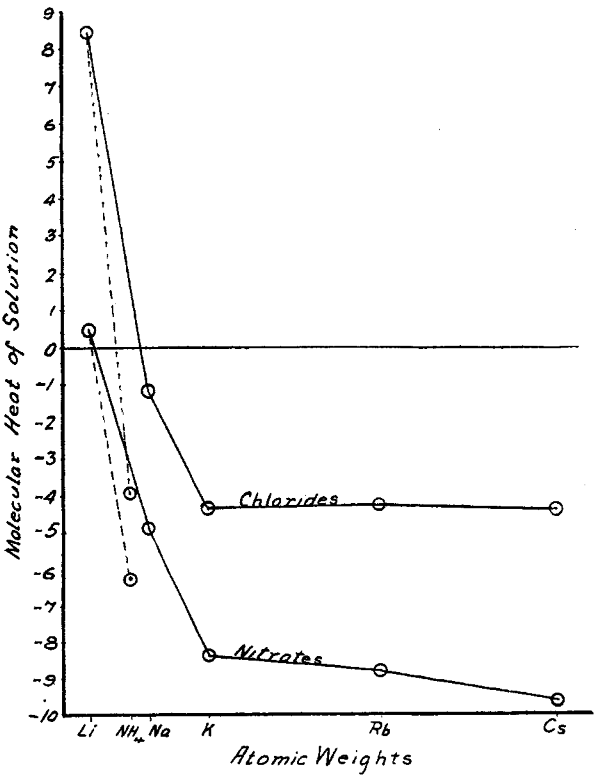

Fig. 4.

of determining the heat of solution needs no description, being carried out in the usual way.

The following table is a summary of the data obtained and the results: The first column gives the formula of the salt; the second, the weight of salt used; the third, the weight of water plus the heat equivalent of the calorimeter; the fourth, the corrected rise or fall in temperature of the water in the calorimeter; and columns five and six, respectively, the heat of solution calculated from each set of data, and the mean values for each salt.

Salt.	Wt. of salt.	Wt. water + 13.9.	$t_2 - t_1$.	Heat of sol. calories.	Mean.
$LiNO_3$	4.1403	519.7	+0.050°	+0.433	
	4.0917	517.1	+0.047°	+0.410	+0.439
	4.0883	517.5	+0.054°	+0.472	
$NaNO_3$	5.900	518.1	—0.660°	—4.969	
	5.900	520.1	—0.655°	—4.913	—4.942
	5.900	520.3	—0.659°	—4.945	
KNO_3	7.000	522.9	—1.096°	—8.284	
	7.000	522.5	—1.102°	—8.324	—8.315
	7.000	523.4	—1.102°	—8.337	
$RbNO_3$	10.400	526.3	—1.180°	—8.804	
	10.400	527.9	—1.172°	—8.771	—8.780
	10.400	523.5	—1.181°	—8.765	
$CsNO_3$	13.500	515.1	—1.297°	—9.646	—9.603
	13.500	519.6	—1.280°	—9.603	
	13.500	517.1	—1.284°	—9.586	
	13.500	514.9	—1.288°	—9.576	
LiCl	2.9308	513.9	+1.138°	+8.476	
	2.9911	513.9	+1.161°	+8.473	+8.474
	3.0038	513.9	+1.166°	+8.474	
KCl	5.1761	513.9	—0.583°	—4.318	—4.321
	5.1761	513.9	—0.584°	—4.325	
RbCl	8.388	513.9	—0.568°	—4.207	
	8.388	513.9	—0.572°	—4.237	—4.227
	8.388	513.9	—0.572°	—4.237	
CsCl	11.680	513.9	—0.578°	—4.281	
	11.680	513.9	—0.583°	—4.318	—4.293
	11.680	513.9	—0.578°	—4.281	

The following table is a summary of the results of previous investigators together with our own, from which what appear to be the most trustworthy values have been selected for the entire series. In most cases the mean of several values has been taken for the "selected value," the underlined figures being used for this purpose:

SUMMARY OF HEAT OF SOLUTION.

Salt.	Haigh.	Other investigators.					Selected values.
$LiNO_3$	+0.439	+0.296[2]					+0.439
NH_4NO_3	...	—6.20[1]	—6.322[2]				—6.261
$NaNO_3$	—4.942	—4.66[1]	—5.032[2]				—4.878
KNO_3	—8.315	—8.29[1]	—8.516[2]	—8.376[4]			—8.374
$RbNO_3$	—8.780	...					—8.780
$CsNO_3$	—9.603	...					—9.603
LiCl	+8.474	+8.440[2]	+8.4[5]	+8.37[6]			+8.421
NH_4Cl	...	—4.00[6]	—3.880[2]				—3.940
NaCl	...	—1.08[1]	—1.18[2]	—1.164[4]	—1.26[6]		—1.175
KCl	—4.321	—4.19[1]	—4.440[2]	—4.427[3]	—4.403[4]	—4.40[6]	—4.363
RbCl	—4.227	—4.50[6]					—4.227
CsCl	—4.293	—4.68[6]					—4.293

Solubility.

The solubility of all the salts under consideration has been extensively investigated, and the results are well summarized in Abegg's "Handbuch der Anorganischen Chemie." For this reason very few solubility determinations have been carried out in this work. The results on rubidium and cesium nitrates showed certain unexpected peculiarities, however, in that the solubility of rubidium nitrate is greater than that of potassium nitrate, while the solubility of cesium nitrate is less. We have, therefore, duplicated the determinations at 25°. The solubility of these salts, as well as the chlorides of cesium and rubidium, was investigated by Berkeley.[7]

The method used in determining the solubility was as follows: Several grams of the salt were put in each of two small bottles, and a few cc. of distilled water added. One bottle was set into hot water until as much as possible of the salt was dissolved. The bottles were then tightly stoppered, the necks dipped in melted paraffin, and placed in the thermostat at 25°, where they were rotated for several hours. In this way equilibrium was approached from both the unsaturated and the supersaturated solutions. A small sample of the solution was then drawn off into a weighed specimen tube through a filter of glass wool. The tube was quickly stoppered, and weighed; the solution was transferred to a small tared evaporating dish, evaporated to dryness, and the weight of the salt determined. From the weight of the solution and the weight of the dry

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[1] Berthelot, *Ann. chim. phys.*, [5] **4**, 74 (1875).

[2] Thomsen, *J. prakt. Chem.*, [2] **16**, 323 (1877); [2] **17**, 165 (1878).

[3] Rechenberg, *Ibid.*, **19**, 143 (1879).

[4] Pickering, *J. Chem. Soc.*, **51**, 290 (1887).

[5] Lemoine, *Compt. rend.*, **125**, 603 (1897).

[6] De Forcrand, *Ibid.*, **143**, 98 (1906); **152**, 27 (1911)

[7] *Trans. Roy. Soc.*, (*A*) **302**, 207 (1904).

salt the solubility was calculated in grams of salt per 100 grams of water. The results are given in the following table:

SOLUBILITY.

	$NaNO_3$.	KNO_3.	$RbNO_3$.	$CsNO_3$.
Equilibrium reached from unsaturated	92.19	38.51	66.83	26.94
Equilibrium reached from supersaturated	92.09	38.46	66.88	26.95

These figures are in good agreement with the values given by Abegg. Taking the mean of the values given by him for 20° and 30°, which closely approximate the solubility at 25°, the following figures are obtained:

$NaNO_3$.	KNO_3.	$RbNO_3$.	$CsNO_3$.
92.1	38.72	67.8	28.4

To show the real relation existing between the solubilities of the salts and the atomic weights of the contained metals, the figures given by Abegg have been converted to molecular solubilities. Figs. 5 and 6 show the solu-

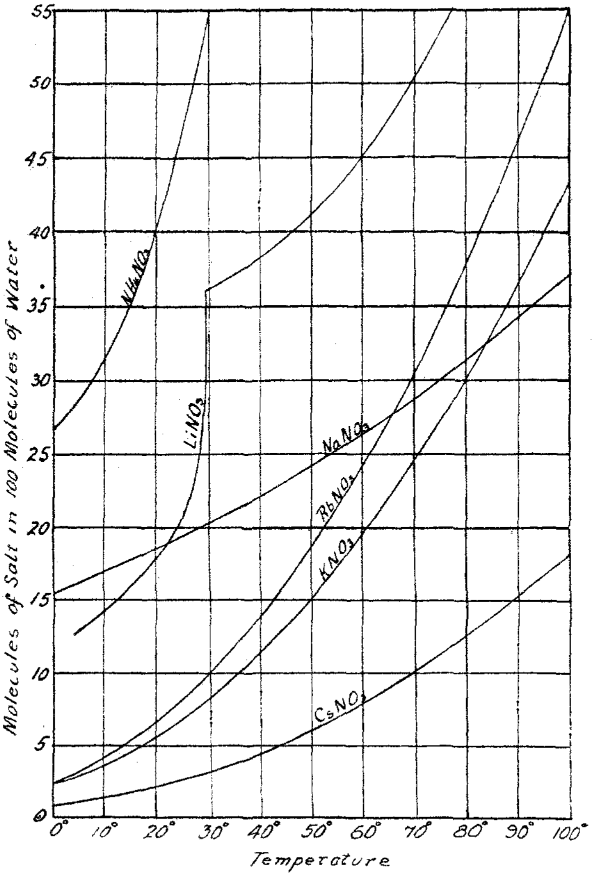

Fig. 5.

bility curves from 0°–100° in gram molecules of salt per 100 gram molecules of water. These results will be discussed later.

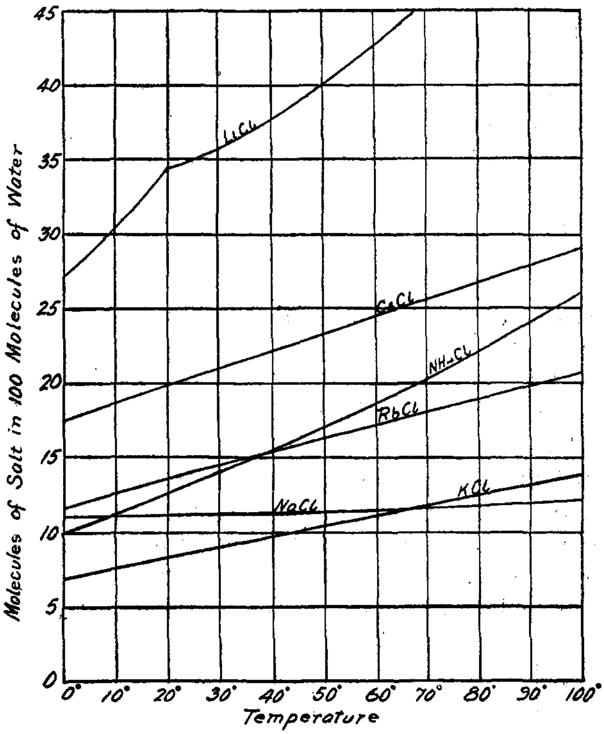

Fig. 6.

Specific Gravity of Solutions.

The specific gravity of solutions is a property which has received frequent attention from previous investigators. The available data are not complete, however, for the series of salts under consideration. For the purpose of comparison it is also essential that only chemically equivalent solutions should be considered, and there is not much uniformity in this respect among the results of different investigators. It seemed advisable, therefore, to choose a strictly defined, uniform concentration of solution, and carry out the measurements for the entire series without regard to previous work. This has been done for the normal and half normal solutions of the nitrates, and for the normal solutions of the chlorides. The normal solution was considered as one which contained one gram equivalent weight of salt in one liter of solution at 20°.

For making up the solutions a small necked, 100 cc. flask was used. It was calibrated by weighing into it 99.823 ± 0.005 gram of water, bringing it to 20° in the thermostat, and marking the level. Exactly one-tenth of a gram equivalent weight of the salt was placed in this flask, distilled water added nearly to the mark, and the flask shaken gently until the salt was completely dissolved. The flask was then placed in the thermostat at 20° for at least 20 minutes, when it was filled exactly to the mark, and shaken until the solution was thoroughly mixed. The specific gravity was determined in duplicate with two Ostwald pyknometers of the usual form, numbered No. 1 and No. 2. To determin their volume at 20° they were filled with recently boiled distilled water, and placed in the thermostat at 20° for 10 minutes. The water was then drawn down to the mark, the pyknometers removed from the thermostat, wiped quickly, and weighed. Subtracting the weight of the empty pyknometer gave the weight of water, which, after correcting for displaced air, was multiplied by the factor 1.001773, giving the volume at 20°. The mean of a number of closely agreeing weights gave No. 1 = 10.3387 cc. and No. 2 = 9.5513 cc. The clean, dry pyknometers were filled with the salt solution, given the same treatment in the thermostat as described above, and the weight determined. The specific gravity was then calculated in the usual way. The results obtained with the two pyknometers agreed very closely throughout, thus serving as an excellent check on the accuracy of the method. The greatest difference obtained in any case was 0.0001, and as a rule it was much less.

The following table is a complete summary of the results. Fig. 7 shows

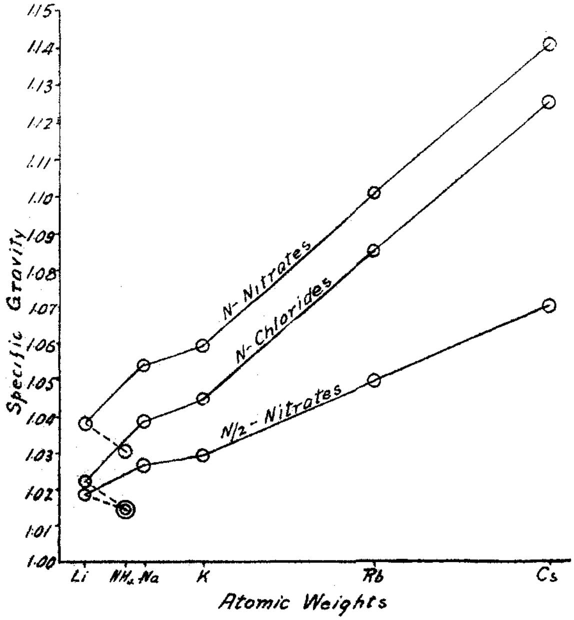

Fig. 7.

the relation of the specific gravities to the atomic weights of the alkali metals. These results will be discussed later.

SPECIFIC GRAVITY 20°/4°.

Normal Solutions.

No.	$LiNO_3$.	NH_4NO_3.	$NaNO_3$.	KNO_3.	$RbNO_3$.	$CsNO_3$.
1	1.03806	1.03040	1.05390	1.05957	1.10081	1.14090
2	1.03800	1.03047	1.05382	1.05951	1.10086	1.14091

No.	LiCl.	NH_4Cl.	NaCl.	KCl.	RbCl.	CsCl.
1	1.02238	1.01454	1.03866	1.04440	1.08537	1.12577
2	1.02237	1.01454	1.03866	1.04446	1.08544	1.12586

Half Normal Solutions.

No.	$LiNO_3$.	NH_4NO_3.	$NaNO_3$.	KNO_3.	$RbNO_3$.	$CsNO_3$.
1	1.01833	1.01449	1.02646	1.02929	1.04994	1.06998
2	1.01827	1.01452	1.02646	1.02936	1.04984	1.07004

Expansion of Solutions.

Although much work has been done on the temperature coefficient of expansion of solutions, the data for the series of salts under consideration are incomplete, and for reasons already mentioned under "*Specific Gravity of Solutions*" it seemed advisable to carry out the determinations for the whole series. This was done for the normal solutions of nitrates and chlorides. The method, briefly stated, consisted in measuring the specific gravity, or specific volume, of the solutions at temperature intervals of 10°, from 0°–50° inclusive, and from these results calculating the expansion. The normal solutions were made up exactly as described under "*Specific Gravity of Solutions.*" After being made up to standard volume the flask containing the solution, with the stopper loosely inserted, was heated on the steam bath for a few minutes to expel dissolved air. This treatment was necessary to prevent bubbles from forming in the pyknometers at the higher temperatures. That evaporation of water during this treatment was negligible was shown experimentally in several cases by the fact that the specific gravity of the solution at 20° before and after the heating was identical, within the limits of error. The specific volumes at the various temperatures were determined with the two Ostwald pyknometers used for measuring the specific gravity. For temperatures other than 20° the volumes were calculated from the volume at 20°, using the coefficient of cubical expansion of glass, *viz.*, 0.00003. The bath for 0° was of finely chopped ice and water, and for the other temperatures a large thermostat was used. The thermometer registered tenths of degrees, and was compared with one of known accuracy. The temperature was always maintained within 0.05° of the desired temperature for at least 10 minutes before drawing the solution in the pyknometer down to the mark. Since 0.1° represents less than 0.0005 gram in the weight of the pyknometer, even in the neighborhood of 50° where expansion is most rapid, the error due to temperature variation is very small. Since the solutions were standardized at 20° the volume at this temperature was taken as the unit volume. The specific volume at each temperature was divided by the specific volume at 20°, giving the volume at the given temperature compared to the volume at 20° as unity. Subtracting one from this number gives the actual expansion or contraction per cubic centimeter, and to avoid small decimals, this number has been multiplied by 10^4. In other words, the values obtained represent the actual change in volume, expressed in cubic centimeters, of ten liters of the solution when the temperature changes from 20° to the temperature considered. Expressed as a formula this becomes

$$\Delta V = \left(\frac{V_t}{V_{20^\circ}} - 1\right).10^4,$$

where V_{20° is the specific volume at 20°, V_t is the specific volume at the temperature t, and ΔV is the expansion of ten liters of the solution.

The following table is a summary of the values obtained. The determinations for ammonium nitrate were duplicated throughout, using separately prepared solutions, to give an idea of the errors. The other values represent the average of duplicate determinations made on one solution with two pyknometers.

SUMMARY OF EXPANSION OF NORMAL SOLUTIONS.

	$LiNO_3$.	NH_4NO_3(1).	NH_4NO_3(2).	$NaNO_3$.	KNO_3.	$RbNO_3$.	$CsNO_3$.
20°–0°	—42.1	—43.1	—43.1	—52.4	—48.2	—49.5	..
20°–10°	—25.3	—25.7	—26.5	—31.0	—28.3	—29.0	..
20°	0	0	0	0	0	0	0
20°–30°	33.4	34.4	33.6	38.4	35.5	36.0	36.1
20°–40°	73.1	72.1	71.7	82.9	78.8	78.9	79.5
20°–50°	118.6	120.2	120.6	132.0	127.2	127.4	127.7
	LiCl.	NH_4Cl.		NaCl.	KCl.	RbCl.	CsCl.
20°–0°	—27.1	—31.0	....	—42.0	—38.5	—38.7	—38.9
20°–10°	—18.0	—19.7	....	—25.4	—23.5	—23.7	—23.2
20°	0	0	....	0	0	0	0
20°–30°	27.0	28.0	....	32.7	31.6	31.1	31.4
20°–40°	61.1	62.8	....	71.4	69.5	69.4	69.3
20°–50°	101.2	105.3	....	116.2	113.0	113.0	112.4

In Fig. 8 these values have been plotted against the atomic weights of the contained alkali metals.

Index of Refraction of Solutions.

The index of refraction of salt solutions is a property which has been frequently investigated, but as with other properties, comparative data for the complete series were not available. To make certain that all results should be strictly comparable, determinations were carried out for the complete series of normal nitrates and chlorides and half normal nitrates, using the same solutions for this purpose which were used in the work on specific gravity of solutions. A Pulfrich refractometer was used. It was standardized against recently boiled distilled water, the index of which has been repeatedly determined. Taking the mean of a large number of determinations given in Landolt-Börnstein's "Physikalisch-Chemische Tabellen," the index of water at 20° is 1.33295, and at 30°, 1.33194. From the tables accompanying the instrument the angles corresponding to these indices should be 20° = 65°47′, and 30° = 65°59′. The difference is 12′ for a temperature interval of 10° or 1.2′ per degree.

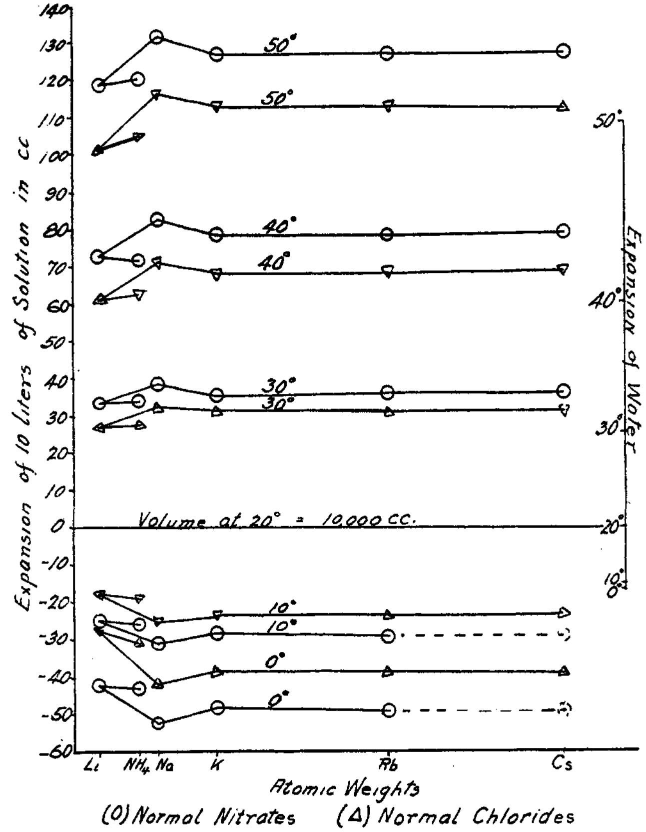

Fig. 8.

During the work on the nitrates, the index of refraction of water was determined several times at various temperatures between 20° and 25°, and the mean correction for the instrument found to be +46′. Before using the instrument for the chlorides it was taken apart and cleaned, after which the index of water was again determined and the correction found to be +55′. The procedure was as follows: A good sodium light was obtained by using a sodium carbonate bead held by a platinum wire loop in the flame of a Bunsen burner. The glass cup of the refractometer was nearly filled with the solution, and a thermometer suspended so that the bulb was immersed in it. The distance of the light was adjusted so that a very sharp division between the light and dark fields was obtained in the microscope. The cross-hairs were then brought to the edge of the shadow, and the angle read. This was repeated several times, the temperature being noted at each reading. The angle could be read to the nearest minute, and it was found that it could be determined with great accuracy, the several readings for a given temperature usually being identical and never varying more than 1′. As the temperature in the dark room varied considerably it was necessary to make a correction for temperature, which, as mentioned above, was 1.2′ per degree. All readings were corrected to 20°. The constant correction for the instrument was then made, and the index of refraction found by the use of the tables accompanying the instrument.

The results are summarized in the following table. Fig. 9 shows the relation of the index of refraction of the solutions to the atomic weights of the alkali metals.

SUMMARY OF INDEX OF REFRACTION OF SOLUTIONS.

Normal Solutions.

	Corrected angle.	Index.
$LiNO_3$	64° 8′	1.34123
NH_4NO_3	63° 53′	1.34251
$NaNO_3$	64° 2′	1.34174
KNO_3	64° 1′	1.34182
$RbNO_3$	63° 51′	1.34268
$CsNO_3$	63° 25′	1.34492
$LiCl$	64° 2′	1.34174
NH_4Cl	63° 46′	1.34311
$NaCl$	63° 50′	1.34277
KCl	63° 52′	1.34260
$RbCl$	63° 43′	1.34337
$CsCl$	63° 16′	1.34571

Half Normal Solutions.

	Corrected angle.	Index.
$LiNO_3$	64° 57′	1.33648
NH_4NO_3	64° 49′	1.33776
$NaNO_3$	64° 52′	1.33751
KNO_3	64° 53′	1.33743
$RbNO_3$	64° 48′	1.33785
$CsNO_3$	64° 34′	1.33902

Discussion of Results.

From a consideration of the foregoing results, as shown in tables and diagrams, it appears impossible to make any single generalization in regard to the properties of the salts of the alkali metals. As is to be expected the properties are, roughly, functions of the atomic weights, but even here the exceptions are perhaps nearly as numerous as the regularities. Certain general tendencies should be noted, however. When the properties are plotted against the atomic weights, a break in the direction of the curve usually occurs at potassium. The elements lithium, sodium and potassium seemingly form one series, and potassium, rubidium and cesium another. It is also to be observed that, as a rule, the properties of the series potassium, rubidium cesium appear to change more regularly than those of the series lithium, sodium, potassium. But here again in several cases unexpected irregularities occur.

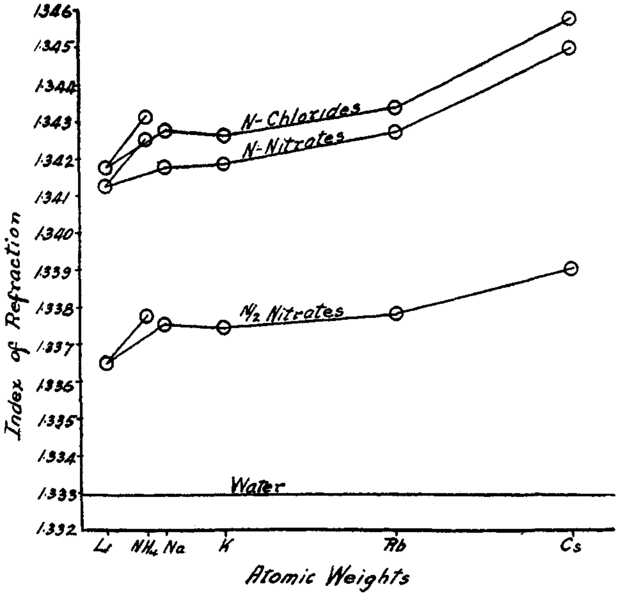

Fig. 9.

The most striking example of this irregularity in the potassium-cesium series is in the case of the nitrates. The melting point of rubidium nitrate is lower than that of potassium nitrate, while the melting point of cesium nitrate is higher. The solubility of rubidium nitrate is greater than that of potassium nitrate, while that of cesium nitrate is less. It is a fact of qualitative significance that the same relationship would hold with the above properties if we were dealing with a mechanical mixture of potassium and cesium nitrates in place of rubidium nitrate. The melting point of such a mixture would be lower than either pure potassium or cesium nitrate, and its solubility would be greater. The molecular volume of rubidium nitrate is also slightly less than that of either potassium or cesium nitrate. Thus, in three of. the seven properties examined rubidium nitrate is not a mean between potassium and cesium nitrates, but gives a value which is either a maximum or a minimum. Irregularities of this kind are not so numerous in the chlorides. With the exception of the molecular volumes, the properties of rubidium chloride approximate a mean between those of the potassium and cesium salts, and even in the case mentioned it would appear that cesium is the irregular member of the series.

It was mentioned above that, in general, the lithium-potassium series is less regular than the potassium-cesium series. It will be seen, however, that in certain cases, notably the equivalent volumes and the heats of solution, the sodium salts quite closely approximate a mean between the lithium and potassium salts. But in the majority of cases the value for the sodium salt approaches more nearly that of the potassium salt than the mean.

The values for the ammonium salts seem to be quite irregular. Tutton,[1] speaking of the sulfates, says that the morphology and optics indicate the peculiar nature of the ammonium radical, but that its molecular constants exhibit it in its proper place, which is immediately after rubidium. It does assume approximately this position in the molecular volume of its salts, and in the index of refraction of equivalent solutions, but in all other properties investigated no particular relationship to rub'dium seems apparent.

It must be remembered that where the properties involving solids are concerned, the values would necessarily change if the substance assumed a different crystallin form. Since the salts in any one series are not necessarily isomorphous, the values for the properties given are not strictly comparable, but they are the best values for comparison that can be obtained.

Considering the results somewhat more in detail, a number of points should be noted. The several properties will be taken up in the same order in which they have been previously considered.

Specific Gravity of Solids.—The results for this property need little comment. The curves (Fig. 1) for the two salts show a general resemblance in form to the curve for the specific gravities of the elements themselves. The curves for the molecular volumes (Fig. 2) are more suggestive. Here again the general resemblance to the curve for the elements is seen. The irregularities of cesium chloride and rubidium nitrate have been mentioned. It is a curious anomaly that while the equivalent volumes of the lithium and sodium salts are greater than the atomic volumes of those elements, the equivalent volumes of the rubidium and cesium salts are actually less than the atomic volumes of the elements (when in the free state) which they contain.

Melting Points.—The peculiar behavior of rubidium nitrate in this regard has been mentioned. It is readily seen from the diagram (Fig. 3)

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[1] *J. Chem. Soc.*, 83, 1049 (1903).

that no generalization is evident in regard to melting points. The curves show little resemblance to each other or to the curve for the metals themselves.

Heat of Solution.—The curves (Fig. 4) resemble each other quite closely. From lithium to potassium they fall very sharply, and from potassium to cesium the curve is nearly horizontal. The values for ammonium lie between sodium and potassium. The heat of solution, as Washburn[1] has pointed out, "is doubtless a composit quantity, including as it does, the heats of disgregation, of ionization, etc., as well as the heat of hydration." The heat of hydration is undoubtedly positive, so that the values for potassium to cesium, which are below those of lithium and sodium, probably indicate a lesser degree of hydration, a conclusion which is in harmony with results obtained from freezing point determinations and other physical properties. The fact that potassium, rubidium, and cesium salts have heats of solution which are nearly equal, makes it not unlikely that the degree of hydration of these dissolved salts is nearly the same.

Solubility.—Aside from the fact, which was mentioned above, that rubidium nitrate is more soluble than either potassium or cesium nitrate, the solubility curves of these three salts resemble each other quite closely in form. The same is true of potassium, rubidium and cesium chlorides. The solubility of rubidium chloride is approximately a mean between potassium and cesium chlorides. Sodium and lithium show little regularity or relationship to the other elements. The form of the curves for the ammonium salts resembles, in general, that of the potassium-cesium group, but its position in the series with regard to the other metals varies with the anion present.

Specific Gravity of Solutions.—From the table and the diagram (Fig. 7) it will be seen that the specific gravity of equivalent solutions at 20° increases quite regularly with increasing atomic weight of the alkali metals. Sodium gives results slightly higher than would be expected, while those for ammonium are considerably lower. Rubidium is here almost the exact mean of potassium and cesium. The values for the half-normal solutions exceed by a small amount the mean between the specific gravity of the normal solutions and that of pure water.

It is of interest to ascertain how closely Valson's Law of Moduli applies to the entire series of alkali nitrates and chlorides. Subtracting the specific gravity of the chlorides from the corresponding nitrates, the following results are obtained.

	Li.	NH_4.	Na.	K.	Rb.	Cs.
NO_3	1.03803	1.03043	1.05386	1.05954	1.10083	1.14090
Cl	1.02237	1.01454	1.03866	1.04443	1.08540	1.12581
Moduli	0.01566	0.01589	0.01520	0.01511	0.01543	0.01509

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[1] *Technology Quarterly*, **21**, 412 (1908).

The variation is from 0.0151–0.0159, or about 5.2%. Subtracting the specific gravity of the ammonium salts from the specific gravity of the corresponding salts of the other metals, the following results are obtained:

	Cl.	NO_3.
Li	1.02237	1.03803
NH_4	1.01454	1.03043
Moduli	0.00783	0.00760
Na	1.03866	1.05386
NH_4	1.01454	1.03043
Moduli	0.02412	0.02343
K	1.04443	1.05954
NH_4	1.01454	1.03043
Moduli	0.02989	0.02911

	Cl.	NO_3.
Rb	1.08540	1.10083
NH_4	1.01454	1.03043
Moduli	0.07086	0.07040
Cs	1.12581	1.14090
NH_4	1.01454	1.03043
Moduli	0.11127	0.11047

The greatest difference here is in the case of sodium, where it amounts to about 2.5%. Taking the mean values of the above results, the moduli for the several salts are as follows (ammonium chloride is taken as unity):

Positive radicals.
NH_4 = 0.0000
Li = 0.0077
Na = 0.0238
K = 0.0295
Rb = 0.0706
Cs = 0.1100

Negative radicals.
Cl = 0.0000
NO_3 = 0.0154

To find the (approximate) specific gravity of any normal solution at 20°, the moduli for the negative and positive radicals of the salt are added to the specific gravity of normal ammonium chloride solution, *viz.*, 1.0145.

Expansion of Solutions.—An interesting relationship was disclosed by the results for the expansion of normal solutions. It appears that the temperature coefficient of expansion for the normal solutions of a given salt of potassium, rubidium, and cesium are identical within the limits of error of the method. The expansion of the sodium salt solutions is slightly more rapid, and that of the lithium and ammonium salts, considerably less. The parallelism between the nitrates and chlorides is only approximate, lithium nitrate, for example, expanding somewhat more rapidly in comparison to the other nitrates than lithium chloride in comparison to the other chlorides. The determinations for cesium nitrate could not be carried out at 0° and 10°, owing to the limited solubility of that salt at those temperatures. The work of previous investigators has indicated that cesium salts are, as a rule, somewhat less hydrated in solution than potassium salts, while rubidium occupies an intermediate position.[1] Our

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[1] Washburn, *Loc. cit.*

results on expansion seem to indicate that any change in hydration accompanying a temperature change is similar for the chlorides, and also for the nitrates, of these three metals. Whether or not this relation extends to other salts than the nitrates and chlorides is, of course, a matter of conjecture.

Index of Refraction of Solutions.—The curves (Fig. 9) showing this property for the normal solutions of the nitrates and chlorides are nearly parallel. This is, of course, to be expected, assuming ionization, for the same reason that the curves for the specific gravity of the same solutions are nearly parallel. The indices for the half normal solutions are approximately the mean between the indices of the corresponding normal solutions and the index of pure water. Rubidium is slightly below the mean of potassium and cesium, and sodium is practically identical with potassium in every case. The position of ammonium in this instance, as was mentioned above, is close to rubidium.

In conclusion, the writer desires to express his thanks to Professor H. W. Foote, under whose direction the above investigation has been carried out, and whose suggestions and criticism have been invaluable.

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ON THE DECOMPOSITION OF METHYLENE IODIDE AND ITS BEARING ON THE CONSTITUTION OF STEEL.

BY EDWARD D. CAMPBELL AND HENRY S. RAWDON.

Received July 1, 1912.

In a recent article, "Decomposition of Bromoform,"[1] George J. Sargent, working under the direction of W. D. Bancroft of Cornell University, has endeavored to demonstrate experimentally that the hypothesis proposed by one of the authors to account for the constitution of the carbides of iron, is unnecessary. Briefly this hypothesis is—that iron may form a number of carbides of the general formula C_nFe_{3n}, instead of a single carbide, CFe_3, as is usually assumed; that when the carbides of iron are dissolved in diluted hydrochloric or sulfuric acid, the first product of solution is the analogous olefin C_nH_{2n}, together with ferrous chloride or sulfate and hydrogen, and that as products of secondary reaction between the "nascent" olefins and nascent hydrogen there will result the corresponding paraffins $C_nH_{(2n+2)}$, together with more or less liquid or solid products formed by the polymerization of unsaturated hydrocarbons of relatively high molecular weight.

It is a little unfortunate that Sargent seems to have so little familiarity with the literature bearing on the constitution of steel, as a little deeper knowledge of that subject might have rendered the publication of his

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[1] *J. Physic. Chem.*, 16, 407.