THE SEPARATION OF LITHIUM FROM THE OTHER ALKALI METALS.

BY SAMUEL PALKIN.

Numerous methods for the separation of lithium from the other alkali metals have been proposed, and in a paper by Skinner and Collins[1] these methods are carefully reviewed. Inasmuch as the errors and difficulties involved in each case have been so clearly pointed out by the above mentioned investigators, no attempt will be made in this paper to review fully the literature on the subject, except to mention those instances where the work has a direct bearing on the principles involved in the method herein proposed.

In brief, it may be stated that the methods depending on organic solvents for the extraction of lithium are of two classes: (1) Those in which the dried mixed chlorides are treated with the solvent. The Rammelsberg[2] (ether-alcohol) method, the Kahlenberg-Krauskopf[3] (pyridine) method and the Winkler[4] (isobutyl alcohol) method are of this class. (2) Those in which the sodium and potassium chlorides are precipitated from solution by the organic solvent. This is the case with the Gooch[5] (amyl alcohol) method.

The salient objections to the methods of the first class, as pointed out in the paper of Skinner and Collins, are (1) tendency to occlusion, therefore incomplete extraction of the lithium; (2) possibility of solution of some of the sodium and potassium chlorides in the lithium solvent; (3) formation of lithium hydroxide on drying the chlorides (the hydroxide being insoluble in the organic medium).

The objections to the methods of the second class, which hitherto has been limited to that of Gooch, are as follows: (1) The amyl alcohol dissolves some of the other salts (sodium and potassium chlorides) and a correction must therefore be applied. The separation is consequently not absolute. (2) The unpleasant odor and disagreeable physiological action of its vapors make it quite objectionable to work with.

The method proposed in this paper, like the Rammelsberg[6] method, makes use of alcohol and ether but in a totally different manner. Instead of *dissolving* out the lithium chloride, the sodium and potassium chlorides are progressively *precipitated* from a water solution. The es-

[1] U. S. Dept. Agr., Bur. Chem., *Bull.* 153 (1912).

[2] *Pogg. Ann.*, 66, 79 (1845).

[3] THIS JOURNAL, 30, 1104 (1908).

[4] *Z. anal. Chem.*, 52, 628–40 (1913).

[5] *Am. Chem. J.*, 9, 33–51 (1887).

[6] *Loc. cit.*

sentials of the method are as follows: The dried mixed chlorides are dissolved in a definite minimum amount of water acidified with HCl, and the major portion of the sodium and potassium chlorides is precipitated by the addition of absolute alcohol followed by ether. The mixture is then filtered, the filtrate evaporated and the residue taken up in absolute alcohol containing a drop of HCl. The residual amount of sodium and potassium chlorides, which under the conditions prescribed rarely exceeds 0.006 g., is then precipitated completely by addition of ether. It will therefore be seen that the objections to the existing methods, as enumerated above, are eliminated in the proposed method.

Experimental.

In order to determine the relative solubility of sodium and potassium chlorides in mixtures of alcohol and ether containing water and hydrochloric acid, a large number of experiments were performed, with a view of obtaining the optimum proportions for the precipitation of these salts. The few following experiments will serve as illustrations:

TABLE I.
Relative Solubilities of Sodium and Potassium Chlorides.

	1.	2.	3.	4.	5.	7.	8.
NaCl (g.)	0.1500	0.1500	0.1500	0.1500	0.0500	....	0.1000
KCl (g.)	0.1500	0.1500	0.1500	0.1500	0.0500	0.1000	....
H_2O (cc.)	6	6	0	0	0	0	0
Conc. HCl (cc.)	2	2	0.3	0.3	0.3	0.3	0.3
Abs. alcohol (cc.)	80[1]	80	60	60	60	60	60
Ether[2]	240	240	300	300	300	300	300
Salt recovered (g.)	0.2702	0.2904	0.2992	0.2993	0.0995	0.0995	0.0996
Salt dissolved (g.)	0.0298	0.0096	0.0008	0.0007	0.0005	0.0005	0.0004
Salt dissolved g. per 100 cc. solvent	0.0091	0.003	0.0002—	0.0002—	0.00011	0.0001+	0.0001+

The experiments on the separate salts, sodium chloride and potassium chloride, respectively, show that only about 0.0005 g. remains in solution in a volume of 360 cc. of liquid. Since only about one-sixth of this volume is used in the final precipitation, the loss is negligible. Experiments on the mixed sodium and potassium chlorides show only a very slightly greater amount dissolved (less than 0.0008 g. per 360 cc.), which is negligible for the volumes used in the actual determinations. Numerous subsequent experiments (Table IV), where separation of lithium from the other alkali metals have been carried out, show quite clearly that the weights of sodium and potassium chlorides recovered are, within experimental errors, practically those used.

[1] In Expt. 1 95% alcohol was used. The remaining ones were carried out with absolute alcohol.

[2] The ether used in these and following experiments was U. S. P., sp. gr. 0.716–0.717 at 25°.

The presence of a large excess of hydrochloric acid was found unnecessary. A slight acidity, however, was found quite essential for the complete aggregation and precipitation of the sodium and potassium chlorides, as illustrated by the following experiments:

TABLE II.
Effect of HCl on Precipitation of Sodium and Potassium Chlorides.

	1.	2.	3.[1]	4.	5.
Mixed salt NaCl and KCl............	Excess	Excess	Excess	Excess	Excess
Water..............................	0	0	0	0	0
Conc. HCl (cc.).....................	0	0.05	0	0.10	0.30
Abs. alcohol (cc.)....................	20	20	20	20	60
Ether (cc.).........................	100	100	100	100	300
Salts dissolved per 100 cc. of liquid....	0.0012	Not weigh-able	..	0.0003	0.0006
Condition of filtrate.................	Turbid	Clear	Turbid	Clear	Clear

The lithium chloride used was prepared from lithium carbonate by treatment with hydrochloric acid. The lithium carbonate available was found to contain a considerable amount of sodium and potassium salts. The purification of the chloride from the other alkali metals was carried out by the method of separation described in this paper and the resulting residue from the alcohol-ether solution evaporated, gently ignited and powdered. This powder was then tested for purity in the following manner: (a) 1 g. dissolved completely without residue in 20 cc. C. P. pyridine on heating. The pyridine had been previously purified by distillation over KOH, the fraction boiling at 115+° being used. (b) 1 g. dissolved completely in 10 cc. absolute alcohol + 1 drop concentrated HCl + 50 cc. ether. No precipitate formed after two hours.

A number of experiments were performed to test the extent of solubility of lithium chloride in varying mixtures of alcohol and ether containing hydrochloric acid. It was found that approximately 10.5 g. were dissolved by 580 cc. of a mixture of one part absolute alcohol and three parts ether at room temperature (about 24°), and that 1 g. of lithium chloride dissolved quite readily in 10 cc. absolute alcohol + 1 drop concentrated HCl, and remained in solution when five times its volume (50 cc.) of ether was added.

Experiments in Table III show the amounts of sodium and potassium chlorides retained in solution after the first precipitation, under the conditions given in the proposed method. The maximum quantity seems to be about 0.006 g. The exact quantity, however, is quite immaterial, as it is all removed in the second or final precipitation. Table IV shows results obtained with mixtures of all three salts, sodium, potassium and

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[1] 0.1 cc. HCl was added to No. 3 and allowed to stand $^1/_2$ hour and the solution became clear.

lithium chlorides. The sodium and potassium chlorides were prepared by precipitating each from a saturated solution with concentrated hydrochloric acid and heating the precipitate to dull redness. A mixture was prepared consisting of 50% sodium chloride and 50% potassium chloride.

TABLE III.—RESULTS ON ONE PRECIPITATION.

	1.	2.	3.	4.	5.	6.
NaCl + KCl used (g.)	0.4950	0.4900	0.4500	0.4000	0.3000	0.0500
NaCl + KCl found	0.4898	0.4856	0.4460	0.3944	0.2958	0.0440
Li_2SO_4 found	0.0110	0.0181	0.0683	0.1332	Spattered	
Li_2SO_4 calc	0.0064	0.0127	0.0637	0.1274		

	7.	8.	9.	10.	11.	12.	13.
NaCl + KCl used (g.)	0.8500	0.8500	1.0000	1.0000	0.7500	1.0000	0.7500
NaCl + KCl found	0.8466	0.8469	0.9957	0.9930	0.7426	0.9985	0.7494
Li_2SO_4 found	Recorded in Table IV.						

TABLE IV.—RESULTS OBTAINED BY APPLICATION OF PROPOSED METHOD.

	1.	2.	3.	4.	5.	6.	7.
NaCl, KCl used (g.)	0.2500	0.4950	0.4900	0.4500	0.4000	0.0100	0.4900
NaCl, KCl found	0.2499	0.4954	0.4906	0.4500	0.3997	0.0101	0.4897
Li_2SO_4	0.3177	0.0071	dish crkd.	0.0640	0.1258	0.6236	0.0126
LiCl equiv	0.2452	0.0054		0.0494	0.0971	0.4812	0.0097
LiCl calc	0.2451	0.0049	0.0098	0.0490	0.0980	0.4806	0.0098

	8.	9.	10.	11.	12.	13.	14.
NaCl, KCl used (g.)	0.4000	0.3000	0.0100	0.2500	0.4000	1.0000[1] NaCl	0.7500[2] NaCl
NaCl, KCl found	0.3994	0.3002	0.0102	0.2500	0.4004	1.0004	0.7496
Li_2SO_4	0.1269	0.2547	0.6367	Spattered		0.0064	0.1538
LiCl equiv	0.0979	0.1966	0.4914	..	..	0.0049	0.1187
LiCl calc	0.0980	0.1961	0.4902	..	..	0.0047	0.1182

	15.	16.	17.	18.	19.	20.	21.
NaCl, KCl used (g.)	1.0000[3] KCl	0.7500[4] KCl	0.4000	0.3750	0.8500	0.5000	0.5000
NaCl, KCl found	0.9996	0.7497	0.3996	0.3752	0.8501	0.5006	0.5000
Li_2SO_4	0.0065	0.1534	..	..	..	..	..
LiCl equiv	0.0050	0.1184	0.0941	0.1183	0.1200	..	0.0012
LiCl calc	0.0047	0.1182	0.0944	$\left.\begin{array}{l}0.1182 \\ 0.1175\end{array}\right\}$	..	..	0.0009
AgCl = LiCl	..	..	0.3182	0.4002	0.4055	Spilled	0.0040

	22.	23.	24.	25.	26.	27.
NaCl, KCl used (g.)	0.5000	0.5000	0.8500	1.0000	0.0100	0.2500
NaCl, KCl found	Crucible spilled	0.5002	0.8504	1.0000	0.0095	0.2496
Li_2SO_4	..	..	..	..	0.0129	0.3173
LiCl equiv	0.0021	0.0050	0.1203	0.0049	0.0100	0.2449
LiCl calc	0.0018	0.0045	..	..	0.0098	0.2452
AgCl = LiCl	0.0072	0.0174	0.4058	0.0165		

[1] NaCl only.   [2] NaCl only.   [3] KCl only.   [4] KCl only.

TABLE V.

		E. K. Nelson.		H. E. Buchbinder.		E. C. Merrill.	
		Taken, g.	Found, g.	Taken, g.	Found, g.	Taken, g.	Found, g.
1............	KCl, NaCl	0.4941	0.4939	0.5000	0.4993	0.2504	0.2502
	LiCl	0.0047	0.0053	0.0039	0.0046	0.2452	0.2466
2............	KCl, NaCl	0.3538	0.3539	0.2000	0.1999	0.0065	0.0063
	LiCl	0.1180	0.1177	0.1968	0.1965	0.4910	0.4897
3............	KCl, NaCl	0.0614	0.0623	0.0100	0.0104	..	..
	LiCl	0.3540	0.3534	0.3936	0.3930	..	..

The lithium chloride (purified as described previously) was used in the form of an alcoholic solution in nearly all the experiments, except in those few cases where large quantities of lithium were necessary, when the quantities were weighed. The alcoholic solutions were made up to volume (about 2.5 g. in 500 cc.) at definite temperature (about 24°) and aliquot portions were measured by a pipet at the same temperature, both for the blank determinations and actual experiments, delivered into Erlenmeyer flasks or tall beakers and evaporated to dryness on the steam bath. Weighed quantities of the other salts were then added. The results in Table IV are self-explanatory. The lithium was weighed in most cases as the sulfate, although in a number of instances it was determined by the "optional method for lithium" as described in the proposed method, that is, by precipitating the halogen as a silver salt after titrating the excess of HCl with 0.1 N alkali and calculating the lithium chloride therefrom.

Some difficulty was experienced in converting large quantities of lithium chloride into Li_2SO_4 and bringing it to a constant weight. A high temperature was necessary. With large quantities of lithium there was some tendency to spatter.

An experiment was made to determine the amount of sodium and potassium chlorides dissolved by the ether-alcohol mixture used in washing. A Gooch crucible containing about 0.5 g. of the mixed salts was ignited, cooled and weighed. This was then washed with 120 cc. of the ether-alcohol mixture (1 part 95% alcohol and 4 parts ether) as directed in the proposed method. The crucible on drying, igniting and weighing showed no change in weight. No residue was found on evaporation of the filtrate.

The method was submitted to three coöperators, Messrs. E. K. Nelson, H. E. Buchbinder and E. C. Merrill, of the Bureau of Chemistry. Definite amounts of lithium were taken in the form of solution, the lithium content of which was previously determined. The mixed sodium and potassium chlorides were, in each case, weighed out by the coöperators. The following results were obtained by them, the lithium being weighed as sulfate.

The Proposed Method.

The total alkali chlorides are dissolved in a minimum amount of cold water in a tall 200 cc. beaker.   About 1.5 cc. will be more than sufficient for 0.5 g. of the salts.   One drop of concentrated HCl is added and *gradually* 20 cc. absolute alcohol—the alcohol being dropped into the center of the beaker (not on the sides) while rotating.   The sodium and potassium chlorides should be precipitated in a perfectly uniform granular condition.   In a similar manner while rotating the beaker, 60 cc. ether are added and the mixture is allowed to stand about 5 minutes, or until the precipitate is well agglomerated and the supernatant liquid almost clear.   The beaker is rotated occasionally.

The mixture is then filtered through a weighed Gooch crucible into an Erlenmeyer flask, using a bell-jar arrangement.   The beaker is thoroughly washed with a mixture of 1 part alcohol and 4 to 5 parts ether.   A rubber tipped rod is necessary for this purpose.   The precipitate in the Gooch crucible is also well washed and the crucible set aside.   The funnel is well washed in order to remove any lithium therefrom into the flask containing the filtrate.

The filtrate is evaporated to dryness on the steam bath (using a current of air).   The residue is taken up with 10 cc. of *absolute alcohol*, warming if necessary, so that practically everything passes into solution.   If a slight film remains on the bottom of the flask and sides, it is removed by rubbing with a rubber-tipped glass rod.   While rotating the flask, 50 cc. ether are added.   *One drop* of concentrated HCl is added, the flask rotated and allowed to stand for one-half hour.   It is well to rotate the flask at frequent intervals.   When the fine precipitate has agglomerated (only a very small amount is usually precipitated), it is filtered through the same crucible as used in the first precipitation, into a tall beaker.   The residue is washed with ether-alcohol mixture, using the same precautions as outlined in the first precipitation.   After drying in an oven, the crucible is gently ignited, cooled and weighed.

The ether-alcohol solution of lithium is evaporated on the steam bath. The residue is taken up in a little water and a slight excess of sulfuric acid added.   The solution is then carefully transferred to a weighed porcelain or platinum dish.   The solution is evaporated as far as possible on the steam bath and the residue is then very gently ignited over a flame.   By placing the dish on a triangle over an asbestos gauze and using a low flame, the solution can be evaporated without spattering.

The residue is then carefully ignited over a full flame.   When charring has occurred, it is well to repeat the ignition with sulfuric acid.   The factor used for conversion of lithium sulfate to lithium chloride was 0.7718.[1]

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[1] With the 1916 atomic weights this factor becomes 0.7713, which does not however materially influence the results.

Optional Method for Lithium.

The solution of the lithium in the ether-alcohol is evaporated to dryness on a steam bath and finally dried in an oven at 110° C. for 15–20 minutes. The residue is taken up in 5–10 cc. alcohol, warming if necessary. This solution is diluted with about 50 cc. of water. If a slight sediment remains, the liquid is filtered through a Gooch crucible and washed with water. A few drops of phenolphthalein are added to the filtrate (the reaction should be acid) and the liquid titrated with tenth-normal alkali. The chlorides are precipitated as the silver salt and from the weight of the latter there is subtracted the amount corresponding to the hydrochloric acid determined in the titration. The factor used for converting AgCl into LiCl was 0.2958.

Where the total quantity of mixed chlorides is greater than 0.5 g., proportionately larger quantities of solvents are necessary in the first precipitation. The second precipitation is carried out in exactly the same manner as for 0.5 g. of salts indicated in the method. More accurate results have been obtained, however, with quantities of total chlorides not exceeding 0.5 g.

WASHINGTON, D. C.

THE PURIFICATION AND ATOMIC WEIGHT OF YTTRIUM.
[SECOND PAPER.]
BY B. SMITH HOPKINS AND CLARENCE W. BALKE.

A preliminary paper on this subject by Egan and Balke appeared in THIS JOURNAL in April, 1913, in which the sources of material, the preliminary processes of purification and the trial determinations of the atomic weight were discussed. Since the publication of this paper, the work has progressed steadily and the purpose of the present communication is to report progress on the problem.

Historical.

The atomic weight of yttrium has been determined by a large number of investigators. The results obtained previous to 1873 are of little value since the material used certainly contained considerable quantities of rare earths other than yttrium. Some of these early investigators, however, obtained numbers which are surprisingly close to the accepted value.

In 1873 Cleve and Höglund[1] published a memoir in which six determinations of the ratio Y_2O_3 to $Y_2(SO_4)_3$ are recorded, the mean value obtained being 89.58. The material used in this series was known to contain a small amount of terbium, which the authors attempted in vain to remove

[1] K. Svenska Vet. Akad. Handlingar, Bb. 1, No. 8 (1873).