ART. XIV.—*The separation of Magnesium Chloride from the Chlorides of Sodium and Potassium by means of Amyl Alcohol;* by R. B. RIGGS.

THIS separation depends on the insolubility of the chlorides of sodium and potassium and the solubility of magnesium chloride in amyl alcohol. That the alkaline chlorides are insoluble in this reagent has already been shown by Gooch in his paper* on the separation of sodium and potassium from lithium by the action of amyl alcohol on their chlorides. In the same paper attention is also called to the solubility of anhydrous magnesium chloride. The difficulty, if there be any, lies in dehydrating this chloride. Attempts to dehydrate magnesium chloride by direct heat result in a more or less complete decomposition. This is also found to be the case where the salt, in a solution containing no free acid, is rendered anhydrous by means of boiling amyl alcohol. The amount decomposed, in this latter case, is however relatively small. The decomposition products are the oxide and hydrochloric acid. It is therefore necessary either to introduce conditions which will prevent such decomposition or to find a means of redissolving any oxide that may be formed. The use of hydrochloric acid gas was deemed impracticable. To use the acid solution was regarded as objectionable† because, in so doing, water, the very substance to be driven out, would be brought into the solution. Experiments were made in which, after the water of the magnesium chloride solution had been nearly or quite expelled by boiling with amyl alcohol, a few drops of benzyl chloride were added and the dehydration completed. The salt dissolved without leaving a residue. So little benzyl chloride was used that it did not seem probable that its use could materially affect the solubility of the chlorides of potassium and sodium. Working on this supposition a series of separations were made the results of which are given below.

Standardized solutions of the several salts were used. The solution of magnesium chloride was prepared from the carbonate, which had been twice precipitated from moderately strong solutions of the chloride. The chloride thus made was free from alkalies and wholly soluble in amyl alcohol. The strength of this solution was found by treating weighed por-

* Am. Chem. Jour., vol. ix. p. 33.

† This objection was afterwards found to be groundless.

tions with sulphuric acid in excess, evaporating, igniting and weighing as sulphate.*

The potassium chloride was obtained from the chlorate. The chloride of sodium was prepared from sodium hydrate (obtained from sodium) and further purified by precipitation by hydrochloric acid.

Both solutions were standardized by evaporating weighed portions to dryness, drying at about 300° C. and weighing.

The solutions, thus standardized, were found to contain respectively 0·5293 grm. NaCl, 0·5412 grm. KCl and the equivalent of 0·4146 grm. MgO to the 100 grams.

Three series of separations, containing severally mixtures of magnesium chloride and one or the other or both of the alkaline chlorides, were made. The solutions were evaporated nearly to dryness. The residue, if any, was taken up with the smallest possible quantity of water and a few drops of hydrochloric acid. 30–40^{cc} of amyl alcohol were then added and the water was expelled by bringing the alcohol to the boiling (128°–130° C.) Eight or ten drops of benzyl chloride were added and the solution was evaporated to about 10^{cc}. A perforated crucible, an asbestus felt and pressure were used in filtering. The filtrate was transferred to a weighed platinum dish and the alcohol driven off by evaporation on a water bath. As soon as the solution became viscous water was added and the evaporation repeated. The residue was finally taken up with water and sulphuric acid was added in slight excess. This solution was evaporated to dryness and the residue ignited and weighed as sulphate. The amyl alcohol precipitate was dissolved and transferred to a weighed platinum dish, evaporated to dryness and heated in an air bath at a temperature of about 300° C. and weighed.

The solubility corrections, as determined by Gooch,† were introduced, viz: For every 10^{cc} of amyl alcohol solution, exclusive of washings, 0·00051 grm. was added to the weight of the insoluble chlorides in case the residue was potassium chloride, 0·00041 grm. in case it was sodium chloride and 0·00092 grm. in case both were present. Equivalent amounts were taken from the weight of the magnesium sulphate.

The results of these separations, including determinations in many cases of the amounts of magnesia carried by the chloride precipitates, are here given.

*Several determinations as phosphate were made which, though agreeing together, gave somewhat lower results than were obtained by weighing the magnesium as sulphate. This may be due to impurities in the chloride or, as is more probable, it may be owing to the slight solubility of the phosphate

† Am. Chem. Jour., vol. ix, p. 48.

	Weight of KCl taken. grm.	Weight of KCl found. grm.	Corr. weight of KCl found. grm.	Error in corr. weight of KCl found. grm.	Weight of MgO found in KCl. grm.
(1)	0·1076	0·1075	0·1079	0·0003 +	0·0002
(2)	0·1084	0·1080	0·1083	0·0001 —	trace
(3)	0·1083	0·1079	0·1083	0·0000	0·0001
(4)	0·1077	0·1071	0·1076	0·0001 —	0·0001
(5)	0·1082	0·1075	0·1080	0·0002 —	0·0002
(6)	0·1085	0·1079	0·1083	0·0002 —	not det.
(7)	0·1628	0·1613	0·1622	0·0006 —	0·0004
(8)	0·1630	0·1614	0·1622	0·0008 —	0·0003
(9)	0·0109	0·0106	0·0110	0·0001 +	not det.
(10)	0·0116	0·0114	0·0118	0·0002 +	0·0001

	Weight of MgO taken. grm.	Weight of $MgSO_4$ found. grm.	Corr. weight of $MgSO_4$ found. grm.	Corr. weight of MgO_4 found. grm.	Error in corr. weight of MgO found. grm.
(1)	0·0092	0·0278	0·0274	0·0091	0·0001 —
(2)	0·0094	0·0275	0·0272	0·0091	0·0003 —
(3)	0·0417	0·1249	0·1245	0·0415	0·0002 —
(4)	0·0421	0·1264	0·1259	0·0420	0·0001 —
(5)	0·0828	0·2482	0·2476	0·0825	0·0003 —
(6)	0·0835	0·2509	0·2503	0·0834	0·0001 —
(7)	0·1662	0·5008	0·4998	0·1666	0·0004 +
(8)	0·1661	0·4986	0·4977	0·1659	0·0002 —
(9)	0·0830	0·2492	0·2488	0·0829	0·0001 —
(10)	0·0834	0·2494	0·2490	0·0830	0·0004 —

	Weight of NaCl taken. grm.	Weight of NaCl found. grm.	Corr. weight of NaCl found. grm.	Error in corr. weight of NaCl found. grm.	Weight of MgO found in NaCl. grm.
(11)	0·1113	0·1114	0·1116	0·0003 +	not det.
(12)	0·1066	0·1061	0·1065	0·0001 —	0·0002
(13)	0·1066	0·1058	0·1063	0·0003 —	trace
(14)	0·1064	0·1056	0·1062	0·0002 —	0·0001

	Weight of MgO taken. grm.	Weight of $MgSO_4$ found. grm.	Corr. weight of $MgSO_4$ found. grm.	Corr. weight of MgO found. grm.	Error in corr. weight of MgO found. grm.
(11)	0·0836	0·2496	0·2493	0·0831	0·0005 —
(12)	0·0835	0·2504	0·2499	0·0833	0·0002 —
(13)	0·1663	0·4979	0·4973	0·1658	0·0005 -
(14)	0·1665	0·4977	0·4970	0·1657	0·0008 —

	Weight of KCl taken. grm.	Weight of NaCl taken. grm.	Weight of chlorides found. grm.	Corr. weight of chlorides found. grm.	Error in corr. weight of chlorides found. grm.	Weight of MgO found in chlorides. grm.
(15)	0·0544	0·0529	0·1066	0·1076	0·0003 +	trace
(16)	0·0545	0·0531	0·1068	0·1077	0·0001 +	0·0004
(17)	0·1087	0·1063	0·2131	0·2142	0·0008 —	0·0002
(18)	0·1085	0·1063	0·2122	0·2134	0·0014 —	trace
(19)	0·1083	0·1064	0·2118	0·2137	0·0010	not det.

	Weight of MgO taken. grm.	Weight of $MgSO_4$ found. grm.	Corr. weight of $MgSO_4$ found. grm.	Corr. weight of MgO found. grm.	Error in corr. weight of MgO found. grm.
(15)	0·0827	0·2487	0·2475	0·0825	0·0002 —
(16)	0·0830	0·2495	0·2484	0·0828	0·0002 —
(17)	0·1664	0·5000	0·4987	0·1662	0·0002 —
(18)	0·1663	0·5007	0·4995	0·1665	0·0002 +
(19)	0·1660	0·5010	0·4987	0·1662	0·0002 +

These results speak for themselves. It is evident that we have here a fairly good quantitative method. The errors are generally negative. This is to be expected. The large negative errors in the weights of the insoluble chlorides, in experiments (26)–(28), are probably due to loss from manipulation. 0·2 grams of either the insoluble chlorides or magnesia are perhaps too large quantities to deal with.

10^{cc} of amyl alcohol hold 1·14 grm. of magnesium chloride in solution at 14° C. and 1·23 grm. at 50° C. In the majority of the experiments the residual volumes of alcohol were less than 10^{cc}. They might with safety have been further reduced, thus reducing the solubility corrections.

In experiments (7), (8), (13), (14), (18) and (19) two precipitations of the insoluble chlorides were made, decanting the liquid, washing the residue, redissolving it and repeating the precipitation. The advisability of this is questionable. A more complete separation may be thus effected but the possibilities of loss from manipulation seem to counterbalance this advantage. Almost the same degree of completeness of separation may be attained by redissolving the precipitate with as little water and acid as possible and repeating the precipitation in the original solution.

In dehydrating the mixed chlorides it was noticed that the nature of the precipitate depended much on the relative amounts of the magnesium and the insoluble chlorides. Roughly speaking, when the weight of magnesia is equal to or exceeds that of the insoluble chlorides, the precipitate is thrown out as a fine powder. When however the insoluble

chlorides are greatly in excess, the tendency to obey the laws in accordance with which they crystallize asserts itself and we have a more or less coarsely granular deposit. This is especially true in the case of sodium chloride. These facts have a bearing on the question of completeness of separation.

Consider the amounts of magnesia found in the alkalies. They bear no relation to the amount of magnesium chlorides involved. It seems probable that the magnesia there found has been carried mechanically, and that it is not there as the result of decomposition. How can we better explain the finding of magnesia in the insoluble chlorides of experiment (1) where but 9 mgrm. of magnesia were involved. Here it is essentially the result of inclusion.

The desirability of adding water to the amyl alcohol solution of magnesium chloride before completing the evaporation is to be emphasized. By so doing it is possible to expel the alcohol so completely that even those experiments where there was the maximum amount of magnesia gave no trouble from carbonization.

In adding sulphuric acid a great excess is to be avoided. In the above experiments about twice the amount demanded by theory was used. The result, in the end, is economy of time and less danger of loss. It is better to add sulphuric acid a second time and repeat the evaporation, ignition and weighing. In the experiments involving an amount of magnesium equivalent to 0·16 grm. of the oxide, the ignited sulphate was found in a few instances to increase its weight after a second treatment with sulphuric acid. The lesser amounts were almost without exception wholly converted into the sulphate by a single treatment.

In the course of the work it was found that amyl alcohol and concentrated hydrochloric acid mix in all proportions. Furthermore if amyl alcohol containing but a small quantity of the acid be boiled down to but a small fraction of its original volume the residue contains chlorine in some form. 30^{cc} of the alcohol, to which $0{\cdot}2^{cc}$ of concentrated hydrochloric had been added, having been reduced to 2^{cc} gave a decided test for chlorine. This suggested the possibility that the use of benzyl chloride was unnecessary. For, if amyl alcohol mixes with the concentrated acid and on being evaporated retains more or less of it to the last, the conditions which would prevent the decomposition of magnesium chloride are maintained. The easy solubility of the anhydrous magnesium chloride is beyond question. Possibly then, in the above experiments, the addition of benzyl chloride was uncalled for as in every case hydrochloric acid had been previously added to the salt solutions. To decide the question a few separations were made

without the benzyl chloride. Otherwise the conditions and methods were the same.

	Weight of KCl taken. grm.	Weight of KCl found. grm.	Corr. weight of KCl found. grm.	Error in corr. weight of KCl found. grm.	Weight of MgO found in KCl. grm.
(20)	0·1079	0·1078	0·1082	0·0003 +	trace
(21)	0·1081	0·1074	0·1079	0·0002 —	trace
(22)	0·1081	0·1076	0·1080	0·0001 —	0·0004
(23)	0·1080	0·1074	0·1079	0·0001 —	0·0003
(24)	0·1080	0·1071	0·1079	0·0001 —	0·0004
(25)	0·1076	0·1061	0·1070	0·0006 —	0·0002

	Weight of NaCl taken. grm.	Weight of NaCl found. grm.	Corr. weight of NaCl found. grm.	Error in corr. weight of NaCl found. grm.	Weight of MgO found in NaCl. grm.
(26)	0·1582	0·1576	0·1583	0·0001 +	trace
(27)	0·1591	0·1576	0·1582	0·0009 —	trace

	Weight of MgO taken. grm.	Weight of $MgSO_4$ found. grm.	Corr. weight of $MgSO_4$ found. grm.	Corr. weight of MgO found. grm.	Error in corr. weight of MgO found. grm.
(20)	0·0419	0·1250	0·1245	0·0415	0·0004 —
(21)	0·0418	0·1262	0·1257	0·0419	0·0001 +
(22)	0·0835	0·2508	0·2504	0·0835	0·0000
(23)	0·0827	0·2498	0·2493	0·0831	0·0004 +
(24)	0·1665	0·4996	0·4987	0·1662	0·0003 —
(25)	0·1667	0·5005	0·4995	0·1665	0·0002 —
(26)	0·1669	0·5009	0·5001	0·1667	0·0002 —
(27)	0·1662	0·4980	0·4973	0·1658	0·0004 —

It is evident that the benzyl chloride is not needed, further that its presence in the solution is harmless.

Summary.—In separating magnesium chloride from the chlorides of sodium and potassium, the treatment is as follows: evaporate the solution nearly or quite to dryness. Dissolve the residue in as little water as possible and add a few drops of hydrochloric acid. Then add 30–40^{cc} of amyl alcohol and expel the water by bringing the alcohol to the boiling. Continue the boiling until the volume of the solution is reduced to 10^{cc} or even considerably less. In filtering it is of great advantage to use a perforated crucible and an asbestus felt and to filter under pressure. In case the total chlorides exceed 0·2 grm. it may be advisable to decant the liquid, wash the residue, redissolve and repeat the precipitation. If this be not done the precipitate should be redissolved with the least possible quantity of water, a few drops of hydrochloric acid added

and the precipitation repeated in the original solution. The filtrate is transferred to a weighed platinum dish and evaporated. Water is added before the alcohol has been expelled and the evaporation continued. The residue is dissolved in water. Sulphuric acid is added in slight excess. This solution is evaporated to dryness, the residue ignited and weighed and the treatment with sulphuric acid is repeated. The residue of insoluble chlorides may be transferred to the weighed perforated crucible and dried at a temperature below their melting points or it may be dissolved and the solution transferred to a weighed platinum dish, evaporated and the residue dried, as above, and weighed.

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