ART. XXVIII.—*On the Arsenate Process for the Separation of Magnesium and the Alkalies*; by PHILIP E. BROWNING and W. A. DRUSHEL.

[Contributions from the Kent Chemical Laboratory of Yale University—clv.]

AMONG the methods which have been employed for the separation of magnesium from the alkalies the following are perhaps in most general use:

The barium hydroxide method, whereby the magnesium is precipitated as the hydroxide by barium hydroxide.

The mercuric oxide method, whereby the magnesia is precipitated by freshly prepared mercuric oxide acting upon the chlorides.

The ammonium carbonate method,* whereby the magnesium is precipitated as the double carbonate of magnesium and ammonium by a large excess of ammonium carbonate.

The amyl alcohol method,† whereby the magnesium chloride is dissolved in boiling amyl alcohol and the chlorides of sodium and potassium, not lithium, remain undissolved.

None of these methods, when employed with a view to the subsequent estimation of the alkalies, is free from objectionable features, such as difficulties of filtration, numerous transfers of filtrates, introduction of large amounts of reagents difficult of removal, and incomplete separation of the entire alkali group.

The work to be described is an effort to avoid some of the objections mentioned, by the precipitation of magnesium as the magnesium ammonium arsenate and the removal of the arsenate from the filtrate by reduction and volatilization of the arsenic salt. C. v. Hauer‡ suggested this general procedure and it has found other mention in the literature.§ The removal of the excess of arsenic was accomplished by ignition of the residue, obtained after evaporating the filtrate from the ammonium magnesium arsenate, with ammonium chloride. The method, however, has been criticized as inaccurate for the estimation of magnesium, and tedious. Recent work upon the precipitation of magnesium ammonium arsenate and upon the volatilization of arsenic compounds, suggested the possibility of obviating the difficulties which have kept this method from general use.

It is possible, with careful manipulation, to remove the arsenic by precipitating with hydrogen sulphide, but this procedure required an additional filtration and several transfers of

---

* Wulfing, Ber. xxxii, 2214.

† Riggs, this Journal [3], xliv, 103.

‡ Jahrb. der k. k. geolog. Reichanstalt, iv, 863.

§ Fresenius-Cohn, Quant. Anal., 6th edition, vol. i, 613.

liquid and was therefore abandoned in favor of the separation by volatilization.

The reagents used in this work were prepared as follows: The potassium chloride by igniting pure potassium chlorate and crystallizing; the sodium chloride by recrystallizing the so-called pure sodium chloride. Solutions of these salts were made approximately tenth normal and standardized by evaporating measured portions with sulphuric acid in a weighed platinum crucible, and weighing the residues after ignition at the full heat of a Bunsen burner, as the normal sulphates.

A solution of magnesium chloride was obtained by dissolving a weighed amount of pure magnesium in hydrochloric acid and diluting sufficiently to make the solution approximately tenth normal. The solution was standardized by estimating the magnesium in measured portions as the pyroarsenate.

To obtain ammonium arsenate, arsenious oxide was sublimed and oxidized by an excess of nitric acid. After the completion of the oxidation, the excess of nitric acid was removed by evaporation, the residue treated with a slight excess of ammonium hydroxide, and the solution thus obtained diluted sufficiently to make it approximately fifth normal.

From a mixture of known amounts of standardized solutions of the chlorides of magnesium and potassium or sodium, the magnesium was precipitated in a distinctly but not strongly ammoniacal solution by 40 per cent to 80 per cent excess of ammonium arsenate, with brisk stirring. When only a small amount of magnesium is present in a relatively large amount of solution, the precipitate forms slowly and becomes complete only on long standing. In a previous paper* from this laboratory, it has been shown that the precipitation of amounts of arsenic so small as not to be precipitated immediately by magnesium mixture may be brought about by freezing the solution after adding that reagent, and remains complete when melting takes place. This procedure was found equally applicable in the precipitation of magnesium. A similar result was obtained by adding alcohol amounting to 15 per cent to 20 per cent of the mixture and filtering as soon as the precipitate settled completely. The precipitate was collected under moderate pressure in an ignited and weighed perforated crucible containing a close felt of fine asbestos. It was washed with 40 to 50$^{cm^3}$ of ammoniacal water, after which it was dried at 125° C. to 140° C. and carefully ignited and weighed as magnesium pyroarsenate.

In a previous paper from this laboratory,† it has been shown that arsenic may be removed by distillation with potassium

---

* Gooch and M. A. Phelps, this Journal, xxii, 488, 1906.

† Gooch and I. K. Phelps, this Journal, xlviii, 216, 1894.

bromide and hydrochloric acid in a distilling apparatus. This suggested a method for the removal of the arsenic from the filtrate obtained after separating the magnesium ammonium arsenate. In some preliminary qualitative experiments, solutions containing from 0·1 to 0·2 grms. of ammonium arsenate were treated with 10^{cm^3} of hydrochloric acid (sp. gr. 1·20) and 10^{cm^3} of hydrobromic acid (sp. gr. 1·36) or 1 to 3 grms. of ammonium bromide, and evaporated in an open dish and the residues were ignited until fuming ceased. One such treatment was usually found to be sufficient; in fact, simple evaporation on a steam bath with the mixed acids, or with hydrobromic acid (not with hydrochloric acid alone), proved to be sufficient to remove the arsenic. Similar treatments made in the presence of definite amounts of the sodium or potassium chloride gave the results shown in Table I.

Table I.

	Ammonium arsenate calculated as As_2O_3 grm.	NaCl or KCl converted to Na_2SO_4 or K_2SO_4 and calculated as Na_2O and K_2O. Taken grm.	Found grm.	Error grm.
1	0·2	0·1171	0·1172	0·0001+
2	0·2	0·1171	0·1170	0·0001−
3	0·4	0·1873	0·1870	0·0003−
4	0·2	0·0468	0·0473	0·0005+

Some evaporations made with hydrochloric acid and sulphurous acid resulted in the removal of the arsenic, but three to five repetitions of the process were generally necessary.

The complete method as recommended for the estimation of magnesium and its removal from the alkalies, and the subsequent estimation of the alkalies, is as follows:

The magnesium is precipitated in a distinctly but not strongly ammoniacal solution by a 40 per cent to 80 per cent excess of ammonium arsenate. The completeness of the precipitation may be hastened by freezing the solution in an ice and salt mixture or by adding alcohol to about 15 per cent to 20 per cent of the total volume of the solution, which may vary from 100^{cm^3} to 250^{cm^3} according to the amounts of salt present. The magnesium arsenate obtained is filtered on an asbestos felt contained in a perforated platinum crucible, the crucible and felt having been previously ignited and weighed, and is dried, ignited and weighed as the pyroarsenate.

The filtrate is transferred from the filter flask to a platinum dish, and after the addition of 10^{cm^3} of hydrochloric acid (sp. gr. 1·20) and about the same amount of hydrobromic acid (sp. gr. 1·3), or 1 to 3 grms. of ammonium bromide evaporated to dryness under a draught-hood, the residue is gently ignited to remove the ammonium salts. The residue is then transferred to a weighed platinum crucible with a small amount of water, a little sulphuric acid (1–1) added, and the solution evaporated to remove the water and excess of sulphuric acid, by placing the crucible on a triangle in a porcelain crucible used as a radiator. After the sulphuric acid has ceased to fume, the crucible is removed from the radiator, and after ignition at the full heat of the Bunsen burner the alkali is weighed as the normal sulphate.

The results follow in Table II.

TABLE II.

	$(NH_4)_3AsO_4$ used calculated as As_2O_3 grm.	Dilution. cm³.	NaCl or KCl_1 converted to Na_2SO_4 or K_2SO_4 and calculated as Na_2O or K_2O			$MgCl_2$ converted into $Mg_2As_2O_7$ and calculated as MgO		
			Taken grm.	Found grm.	Error grm.	Taken grm.	Found grm.	Error grm.
1	0·1	100	0·1194	0·1191	0·0003 —	0·0199	0·0197	0·0002 —
2	0·2	150	0·1194	0·1196	0·0002 +	0·0399	0·0397	0·0002 —
3	0·45	250	0·1194	0·1195	0·0001 +	0·0998	0·0998	0·0000
4	0·45	250	0·1194	0·1194	0·0000	0·0998	0·0997	0·0001 —
5	0·45	250	0·2389	0·2385	0·0004 —	0·0998	0·0999	0·0001 +
6	0·4	250	0·0478	0·0481	0·0003 +	0·1198	0·1193	0·0005 —
7	0·35	250	0·0956	0·0957	0·0001 +	0·0998	0·0996	0·0002 —
8	0·35	250	0·0956	0·0957	0·0001 +	0·0998	0·0994	0·0004 —
9	0·45	250	0·0909	0·0915	0·0006 +	0·0998	0·0993	0·0005 —
10	0·1	100	0·0545	0·0549	0·0004 +	0·0006	0·0004	0·0002 —
11	0·1	100	0·1181	0·1184	0·0003 +	0·0040	0·0038	0·0002 —
12	0·1	100	0·1181	0·1184	0·0003 +	0·0040	0·0038	0·0002 —
13	0·1	100	-----	-----	-----	0·0040	0·0038	0·0002 —
14	0·1	100	0·1181	0·1184	0·0003 +	0·0040	0·0040	0·0000
15	0·2	100	0·1181	0·1183	0·0002 +	0·0040	0·0039	0·0001 —
16	0·45	250	0·1181	0·1179	0·0002 —	0·1002	0·1004	0·0002 +

In experiments 1 to 10, the precipitate of magnesium was allowed twelve to twenty-four hours to settle. In experiments 11, 12 and 13, 15 per cent alcohol was used to hasten the complete precipitation of the magnesium, and in experiments 14, 15 and 16 the salt and ice mixture was used for the same purpose.