ART. XLVI.—*The Precipitation of Barium Bromide by Hydrobromic Acid*; by NORMAN C. THORNE.

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

IN former articles from this laboratory,* processes for the separation and determination of certain chlorides, hydrous or anhydrous, by the action of hydrochloric acid have been studied. The present article deals with the similar separation and determination of barium bromide by the agency of hydrobromic acid.

The hydrobromic acid used in the experiments to be described was prepared by dropping from a stoppered funnel liquid bromine into naphthalene dissolved in kerosene, passing the hydrogen bromide evolved through a purifying tower charged in layers with glass-wool and red phosphorus and a water trap, and saturating distilled water with the gas thus purified.

Pure barium bromide was made by dissolving barium chloride in water, precipitating barium carbonate by ammonium carbonate and ammonium hydroxide, washing the precipitate by decantation and dissolving it in hydrobromic acid. This solution of barium bromide was evaporated to dryness and the barium bromide thus obtained was used in the following experiments.

In the first series of experiments a weighed amount of the barium bromide was dissolved in the least volume of water, and treated with hydrobromic acid or with a mixture of hydrobromic acid and ether in equal volumes. The liquid was saturated with hydrobromic acid gas and filtered upon asbestos, and the precipitate washed by a mixture of hydrobromic acid and ether, dried in air bath or over Bunsen flame and weighed as BaBr_2 . The details of these experiments are given in Table I.

TABLE I.

BaBr_2 taken. gram.	HBr. cm^3 .	HBr and ether. cm^3 .	BaBr_2 found. gram.	Error. gram.
0.2932	30		0.2934	+0.0002
0.1264	30		0.1260	—0.0004
0.1134	30		0.1132	—0.0002
0.1347		30	0.1367	+0.0020
0.1040		30	0.1035	—0.0005
0.0744		20	0.0748	+0.0004
0.1197		30	0.1211	+0.0014
0.4327	30		0.4345	+0.0018

* This Journal (3), xliii, 521 (Mar); (4), ii, 416 (Gooch and Havens); (4), iv, III (Havens); (4), vi, 45 (Havens); (4), vi, 396 (Havens).

Considerable difficulty was had in drying the barium bromide so as to obtain a constant weight, and the barium bromide prepared in the manner described did not dissolve completely. The results of these experiments are thereby lacking in uniformity. Presuming that the source of inaccuracy is to be looked for in the formation of an oxybromide, the precipitate in the next experiments, after filtering upon asbestos, was treated with ammonium bromide and then dried over a radiator,—at first at a low temperature and finally at a temperature high enough to drive off the ammonium bromide. When the thermometer inside of the radiator showed a temperature of 250° C. all the ammonium bromide disappeared and left a barium bromide which gave constant results, as shown in the following table.

TABLE II.

BaBr ₂ taken. gram.	HBr and ether. cm ³ .	BaBr ₂ found. gram.	Error. gram.
0.1330	30	0.1534	+ 0.0004
0.1013	30	0.1016	+ 0.0003
0.2769	30	0.2760	— 0.0009
0.2359	30	0.2353	— 0.0006
0.1580	30	0.1579	— 0.0001
0.2955	30	0.2947	— 0.0008
0.2822	30	0.2813	— 0.0009
0.1962	30	0.1962	0.0000
0.4127	30	0.4125	— 0.0002
0.2751	30	0.2750	— 0.0001
0.3181	30	0.3183	+ 0.0002
0.3049	30	0.3039	— 0.0010
0.3754	30	0.3752	— 0.0002

These results indicate plainly that barium bromide, prepared in a state of purity and free from oxybromide, may be completely precipitated from solution in water by treatment with a mixture of hydrobromic acid and ether in equal parts and saturation of the liquid with hydrogen bromide.

Some experiments in which precipitation was effected by a mixture of concentrated hydrobromic acid and ether in equal parts, without saturating with the gas, led to similar results. In these experiments the material weighed out was the crystallized hydrous barium bromide, BaBr₂ · 2H₂O.

TABLE III.

BaBr ₂ · 2H ₂ taken. gram.	HBr + ether 1:1. cm ³ .	BaBr ₂ found. gram.	BaBr ₂ calculated. gram.	Error. gram.
0.2008	30 cc.	0.1793	0.1790	+ 0.0003
0.2041	30	0.1822	0.1820	+ 0.0002
0.2047	30	0.1821	0.1825	— 0.0004
0.2171	30	0.1937	0.1936	+ 0.0001
0.3101	30	0.2768	0.2765	+ 0.0003
0.5035	30	0.4496	0.4490	+ 0.0006
0.5015	30	0.4476	0.4473	+ 0.0003

The action of hydrobromic acid upon barium chloride was next studied, with or without the presence of salts of calcium and magnesium.

A weighed amount of barium chloride, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, was dissolved in the least volume of water and treated with a mixture of hydrobromic acid and ether in equal volume. The whole solution was saturated with hydrobromic acid gas, filtered upon asbestos, and then, to make sure that no barium oxybromides might be formed, treated with ammonium bromide, dried and weighed as BaBr_2 .

TABLE IV.

$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ taken. gram.	CaCO_3 gram.	MgCO_3 gram.	HBr + ether 1:1. cm^3 .	BaBr_2 found. cm^3 .	Theory as BaBr_2 gram.	Error in BaBr_2 gram.
0.2253	----	----	30	0.2744	0.2741	+0.0003
0.2088	----	----	30	0.2538	0.2540	—0.0002
0.3273	----	----	30	0.3975	0.3982	—0.0007
0.3177	----	----	30	0.3864	0.3865	—0.0001
0.5041	0.5000	----	30	0.6134	0.6143	—0.0009
0.5083	0.5000	----	30	0.6185	0.6191	—0.0006
0.5046	0.5000	----	30	0.6139	0.6136	+0.0003
0.5022	0.5000	----	30	0.6110	0.6104	+0.0006
0.5018	0.5000	----	30	0.6106	0.6108	—0.0002
0.5007	----	0.3000	30	0.6087	0.6092	—0.0005
0.5048	----	0.3000	30	0.6144	0.6142	+0.0002

From these results it is obvious that barium may be separated and determined as the bromide in presence of salts of calcium and magnesium; and it appears also that when the proportion of hydrobromic acid to the barium chloride is that of the experiment and the precipitate ignited with ammonium bromide, the results are in practical accord with those which should be obtained if the precipitate consists entirely of barium bromide.

On the other hand, it appears from the following series of experiments that when a sufficiency of hydrochloric acid is added to the water solution of barium bromide the precipitate falls practically as the chloride.

TABLE V.

$\text{BaBr}_2 \cdot 2\text{H}_2\text{O}$ taken. gram.	HCl used. cm^3 .	Ether. cm^3 .	BaCl_2 found. gram.	BaCl_2 theory. gram.	Error in BaCl_2 gram.
0.2044	25	5	0.1279	0.1277	+0.0002
0.2011	25	5	0.1258	0.1257	+0.0001
0.5021	25	5	0.3138	0.3138	0.0000
0.5037	50	10	0.3148	0.3147	+0.0001
0.5020	25	5	0.3135	0.3137	—0.0002
0.3868	25	5	0.2418	0.2417	+0.0001

So it appears that precipitation is complete in presence of a sufficiency of either acid and that the precipitate will fall chiefly as the bromide or as the chloride according to the proportions of hydrobromic acid and hydrochloric acid present.

It was thought a matter of interest in this connection to test the constitution of the precipitates when incomplete precipitation is brought about by addition of one of these acids, the other being present in considerable proportion, though in amount wholly insufficient to produce by itself precipitation in the volume of water used for solution of the barium salts.

Following is the record of experiments in which 1 gram. of barium chloride, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, was dissolved in water, hydrochloric acid added to incipient precipitation, and then an amount of hydrobromic acid which by itself would produce no precipitation in the water solution. The precipitate was dried and weighed, and the content in bromine determined by the method of Baubigny and Rivals.*

$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ taken. gram.	Water for solution. cm^3 .	HBr added. cm^3 .	HCl added. cm^3 .	Precipitate. gram.	Bromine in precipitate. gram.	BaBr_2 in precipitate. gram.
1.	30	3	22	0.5037†	0.0129	0.0240
1.	42	5	31	0.6241†	0.0141	0.0263
1.	40	5	30	0.6338‡	0.0202	0.0375

The meaning of these results seems to be that the precipitation of the bromide is induced by the action of the hydrogen chloride upon the solvent, water. The production of free bromine ions and barium ions to the amount of the solubility product of barium bromide in water is, under the conditions, an impossibility. If this be admitted, it seems highly probable that precipitation of barium chloride is likewise conditioned by the action of the hydrogen chloride upon the solvent.

It has been customary on the part of some to explain the similar precipitation of other chlorides soluble in water, like sodium chloride, by large amounts of hydrochloric acid upon the assumption that insolubility is due to increased concentration of the chlorine ions, and such processes have been held to be typical of processes in which precipitation is affected by concentration of the free ions. It seems more probable, however, that it is the action of the hydrogen chloride upon the solvent which is the effective thing in such precipitations, as in the precipitation of barium bromide, after addition of hydrochloric acid, by an amount of hydrobromic acid wholly insufficient to cause precipitation in the water solution.

I wish to express my thanks to Prof. Gooch for suggestions and advice given during the progress of this work.

* Compt. rend., cxxv, 527, 607.

† Dried three months in desiccator over sulphuric acid.

‡ Dried 6 hours at 80° and 12 hours in desiccator over sulphuric acid.