

ART. XLVIII.—*The Influence of Free Nitric Acid and Aqua Regia on the Precipitation of Barium as Sulphate*; by PHILIP E. BROWNING.

[Contributions from the Kent Chemical Laboratory of Yale College—XXII.]

THE fact demonstrated by Dr. F. W. Mar<sup>†</sup> in an interesting series of experiments, that free hydrochloric acid even in large quantities does not interfere with the complete precipitation of barium as sulphate when sulphuric acid is present in

\* Pogg. Ann., 1864, B. 123, p. 187.

† Jarb. Minn., 1879, p. 536.

‡ This Journal, xl, 283.

sufficient excess, but rather renders the precipitate more crystalline, and therefore more easily and quickly filtered, suggested a similar series of experiments having as their object an investigation of the influence of free nitric acid on the same precipitation. Certain qualitative preliminary experiments showed a similar effect to that brought about by hydrochloric acid as regards the crystalline form and rapid settling of the precipitate. It therefore remained to determine whether the nitric acid present had any solvent effect upon the precipitate. Accordingly a standard solution of barium nitrate was prepared, free from alkali, by precipitating a soluble barium salt with ammonium carbonate, washing thoroughly with hot water and dissolving in nitric acid, care being taken to avoid an excess of the acid, and making up to measure. Definite portions of this solution were drawn from a burette into counterpoised beakers, and weighed as a check on the burette reading. Several precipitations of the barium in the form of sulphate were made, both in the presence of free hydrochloric acid and in neutral solution, and the mean of closely agreeing determinations was taken as the value of the standard solution. The mode of procedure in the testing was simple and may be outlined as follows:—Into a counterpoised beaker a definite amount of the standardized solution of barium nitrate was drawn and the weight taken as before described, the amount of nitric acid to be used was then added, and the whole volume brought up to 90 cm<sup>3</sup> by the addition of water. This acid solution was then brought to the boiling point and 10 cm<sup>3</sup> of the dilute sulphuric acid added, and the whole was allowed to stand for the length of time shown by the table before filtering on asbestos, igniting and weighing. It will be seen that the total volume of liquid taken in each determination was uniformly 100 cm<sup>3</sup>, the percentage of acid by volume being thus easily regulated. In no case did the amount of barium salt present exceed 0.4 gm. considered as the sulphate, and consequently the uniform amount of 10 cm<sup>3</sup> of dilute (1:4 by volume) sulphuric acid employed was always enough to assure the excess which Fresenius\* has shown to be necessary in the precipitation of barium as the sulphate in the presence of hydrochloric acid. By reference to Series I it is evident that in the presence of five per cent of nitric acid very little solvent action is shown, and it appears also that the sulphate may be safely filtered after an hour's time. In the presence of ten to fifteen per cent of the acid the solvent effect is very small when the solution is allowed to stand six hours or more. With twenty to twenty-five per cent of acid present we find the solubility to be slightly increased, but even then the average loss is less than 0.001 gram.

\* Zeitschr. f. anal. Chem., xxx, 455.

SERIES I.

	BaSO <sub>4</sub> equivalent to Ba(NO <sub>3</sub> ) <sub>2</sub> taken. gram.	BaSO <sub>4</sub> found. gram.	Error in terms of BaSO <sub>4</sub> . gram.	Averages. gram.	Time be- tween pre- cipitation and filtra- tion. hours.	Per cent by volume of strong HNO <sub>3</sub> .	Total volume. cm <sup>3</sup>
( 1 )	0·2540	0·2336	0·0004 —	0·0006 —	12	5	100
( 2 )	0·2489	0·2483	0·0006 —		"	"	"
( 3 )	0·2495	0·2489	0·0006 —		"	"	"
( 4 )	0·2492	0·2482	0·0010 —		"	"	"
( 5 )	0·2486	0·2483	0·0003 —	0·0002 —	6	"	"
( 6 )	0·2490	0·2490	0·0000		"	"	"
( 7 )	0·2555	0·2546	0·0009 —	0·0006 —	1	"	"
( 8 )	0·2538	0·2534	0·0004 —		"	"	"
( 9 )	0·4067	0·4057	0·0010 —	0·0006 —	12	10	"
(10)	0·2540	0·2533	0·0007 —		"	"	"
(11)	0·2492	0·2489	0·0003 —		"	"	"
(12)	0·2493	0·2488	0·0005 —		"	"	"
(13)	0·2494	0·2488	0·0006 —	0·0002 —	6	"	"
(14)	0·2492	0·2492	0·0000		"	"	"
(15)	0·2490	0·2489	0·0001 —	0·0016 —	"	"	"
(16)	0·2489	0·2484	0·0005 —		"	"	"
(17)	0·2540	0·2524	0·0016 —		1	"	"
(18)	0·2529	0·2515	0·0014 —	0·0007 —	12	15	100
(19)	0·2534	0·2522	0·0012 —		"	"	"
(20)	0·2533	0·2531	0·0002 —		"	"	"
(21)	0·2538	0·2532	0·0006 —		"	"	"
(22)	0·2497	0·2490	0·0007 —	0·0006 —	"	"	"
(23)	0·2489	0·2487	0·0002 —		"	"	"
(24)	0·2542	0·2528	0·0014 —		6	"	"
(25)	0·2486	0·2486	0·0000		"	"	"
(26)	0·2492	0·2487	0·0005 —	0·0015 —	"	"	"
(27)	0·2547	0·2532	0·0015 —		"	"	"
(28)	0·2489	0·2478	0·0011 —	0·0008 —	12	20	"
(29)	0·2486	0·2475	0·0011 —		"	"	"
(30)	0·2548	0·2546	0·0002 —		"	"	"
(31)	0·2548	0·2542	0·0006 —		"	"	"
(32)	0·2496	0·2486	0·0010 —	0·0008 —	"	"	"
(33)	0·2539	0·2527	0·0012 —		6	"	"
(34)	0·2488	0·2475	0·0013 —		"	"	"
(35)	0·2497	0·2497	0·0000		"	"	"
(36)	0·2486	0·2477	0·0009 —	0·0008 —	12	25	"
(37)	0·2491	0·2490	0·0001 —		"	"	"
(38)	0·2494	0·2484	0·0010 —		"	"	"
(39)	0·2538	0·2535	0·0003 —		"	"	"
(40)	0·2492	0·2484	0·0008 —	0·0007 —	"	"	"
(41)	0·2487	0·2471	0·0016 —		"	"	"
(42)	0·3414	0·3407	0·0007 —		"	"	"
(43)	0·2489	0·2481	0·0008 —		6	"	"
(44)	0·2485	0·2478	0·0007 —		"	"	"

Having shown that free nitric acid even though present in considerable amount has only a slight solvent influence upon barium sulphate it seemed interesting to try the effect of the combination of nitric and hydrochloric acids mixed in the proportion to form aqua regia (3HCl:1HNO<sub>3</sub>). The experiments

recorded in Series II show that aqua regia has even less effect as a solvent than nitric acid alone. In fact it seems to act like hydrochloric acid alone, which practically has no solvent effect, as shown by Dr. Mar's work previously cited.

## SERIES II.

	BaSO <sub>4</sub> equivalent to Ba(NO <sub>3</sub> ) <sub>2</sub> taken.	BaSO <sub>4</sub> found.	Error in terms of BaSO <sub>4</sub> .	Averages.	Time be- tween pre- cipitation and filtra- tion.	Per cent by volume of strong aqua regia. (3HCl: 1HNO <sub>3</sub> ).	Total volume. cm <sup>3</sup> .
	grm.	grm.	grm.	grm.	hours.		
(1)	0.2539	0.2534	0.0005—	0.0002—	12	5	100
(2)	0.2540	0.2538	0.0002—		"	"	"
(3)	0.2490	0.2490	0.0000		"	"	"
(4)	0.2491	0.2492	0.0001+		"	"	"
(5)	0.2488	0.2484	0.0004—	0.0001—	6	"	"
(6)	0.3419	0.3421	0.0002+		"	"	"
(7)	0.2491	0.2487	0.0004—	0.0006—	12	10	"
(8)	0.2486	0.2482	0.0004—		"	"	"
(9)	0.2549	0.2539	0.0010—		"	"	"
(10)	0.2543	0.2538	0.0005—		"	"	"
(11)	0.2487	0.2485	0.0002—	0.0002—	6	"	"
(12)	0.3416	0.3415	0.0001—		"	"	"
(13)	0.3417	0.3420	0.0003+	0.0003+	1	"	"
(14)	0.2547	0.2544	0.0003—		12	15	"
(15)	0.2492	0.2492	0.0000	0.0003—	"	"	"
(16)	0.2489	0.2479	0.0010—		"	"	"
(17)	0.3412	0.3412	0.0000		"	"	"
(18)	0.3418	0.3417	0.0001—		6	"	"
(19)	0.3413	0.3412	0.0001—	0.0001—	"	"	"
(20)	0.3411	0.3402	0.0009—		1	"	"
(21)	0.2492	0.2484	0.0008—	0.0005—	12	20	"
(22)	0.2486	0.2480	0.0006—		"	"	"
(23)	0.2491	0.2485	0.0006—		"	"	"
(24)	0.3412	0.3411	0.0001—		"	"	"
(25)	0.3417	0.3418	0.0001+	0.0000	6	"	"
(26)	0.3417	0.3417	0.0000		"	"	"
(27)	0.3414	0.3404	0.0010—	0.0010—	1	"	"
(28)	0.2491	0.2485	0.0006—	0.0003—	12	25	"
(29)	0.1701	0.1697	0.0004—		"	"	"
(30)	0.1708	0.1705	0.0003—		"	"	"
(31)	0.1710	0.1710	0.0000		"	"	"
(32)	0.3415	0.3410	0.0005—	0.0003—	6	"	"
(33)	0.3418	0.3418	0.0000		"	"	"
(34)	0.3412	0.3405	0.0007—	0.0007—	1	"	"

In this connection I append the results of a few experiments made to determine the effect of the presence of a considerable amount of free nitric acid, on the precipitations of barium as sulphate in cases where certain substances are present which under ordinary conditions tend to hold up the precipitate. Fresenius\* has demonstrated this property in the case of ammonium nitrate, Scheerer and Rube,† have shown that

\* Zeitschr. f. anal. Chem., ix, 62. † Erdm., Jour. prakt. Chem., lxxv, 113-116.

metaphosphoric acid acts similarly, and Spiller\* notes the same general effect where alkaline citrates are present. Series III shows the results obtained by precipitating definite portions of the standard solution of barium nitrate in the presence of stated amounts of the substances just mentioned. The total volume in every case was 100 cm<sup>3</sup>, the amount of dilute sulphuric acid used 10 cm<sup>3</sup>, and the time between precipitation and filtration twelve hours. Upon filtering, igniting and weighing the barium sulphate an excess of weight, due undoubtedly to contamination of the precipitate, was found. It became necessary, therefore, to purify the precipitate as first weighed in order to determine whether all the barium was actually precipitated or whether a partial loss was covered by the amount of included impurity. The method of purification employed was that successfully applied by Dr. Mar in the work previously mentioned. The contaminated sulphate, collected on paper and treated according to the familiar method (on account of the difficulty attending the complete removal of the precipitate from asbestos for purposes of purification), was dissolved in warm concentrated sulphuric acid, and evaporated quickly and without spattering by means of the Hempel burner, the barium sulphate being left after this treatment in coarse granular crystals. The crystallized sulphate was warmed with a little water containing a drop of sulphuric acid, filtered upon an asbestos felt contained in a perforated platinum crucible, the crucible and felt having been previously ignited and weighed.

SERIES III.

Impurity present to the amount of 5 gram.	BaSO <sub>4</sub> equivalent to Ba(NO <sub>3</sub> ) <sub>2</sub> gram.	Apparent amount of BaSO <sub>4</sub> found. gram	BaSO <sub>4</sub> after purifica- tion. gram.	Error after purifica- tion. gram.	Percentage of strong HNO <sub>3</sub> by volume.
(1) Ammonium nitrate	0.1710	0.1800	0.1702	0.0008—	10
(2) " "	0.3415	0.3440	0.3410	0.0005—	"
(3) " citrate	0.3412	0.3442	0.3407	0.0005—	"
(4) Sodium "	0.1360	0.1730	0.1366	0.0006+	"
(5) Metaphosphoric acid	0.3461	0.3511	0.3470	0.0009+	"

The results show that in the presence of nitric acid amounting to one-tenth by volume of the entire liquid these salts exert no apparent interference with the precipitation of the barium.

The entire work would seem to show that the presence of an excess of nitric acid or aqua regia amounting to ten per cent by volume of the liquid treated is not only not to be avoided in estimating barium as the sulphate, but is actually beneficial. Ordinarily the advantage is found in the tendency

\* Chem. News, viii, 280-281.

of the precipitate to fall coarsely crystalline under the conditions. In certain special cases in which certain substances mentioned, which would otherwise exert solvent action, are present the precipitation is made complete. The contaminating effect of such substances when complete precipitation is induced may be corrected by dissolving the precipitate in sulphuric acid and recrystallizing by evaporation.