ART. XXXII.—*On certain points in the Estimation of Barium as the Sulphate;* by F. W. MAR.

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

IN the received mode of precipitating barium as barium sulphate, three conditions are carefully observed—absence of excess of acid, slow mixing of the reagents and rest, before filtration, of twelve hours or until the precipitate has completely subsided. Usually, in this process, the precipitate is thrown out in a finely divided, milky condition and settles very slowly. My observation that the precipitate, under certain circumstances, is formed in a more crystalline condition

and settles rapidly led me to investigate the conditions of so rapid a precipitation. These quickly settling precipitates were noticed, in the first instance, in the action of sulphuric acid upon solutions containing a very large amount of potassium chloride with hydrochloric acid in excess. In the course of five or ten minutes the precipitate had completely settled and was found to be in a distinctly crystalline condition and much coarser than the usual form of precipitated barium sulphate.

At the time, it was thought that the cause of this rapid subsidence was the alkaline salt present, and, accordingly, a series of experiments was made in which potassium, sodium and ammonium hydroxides were added in varying amounts to about 400 cm^3 of water, hydrochloric acid added to more than acidity (but not in measured amount), 0·5 grm. of barium chloride introduced, and precipitation brought about by adding dilute sulphuric acid. Sometimes these precipitates settled rapidly, but as often came down in the familiar milky condition. Later, another series of experiments, in which the different conditions were more carefully regulated, was made thus: in 400 cm^3 of water were dissolved 0·5 grm. of barium chloride, 10 cm^3 of strong hydrochloric acid, and amounts of the alkaline chlorides varying from 5 grms. to 0·05 grm., the whole being precipitated with 10 cm^3 of a solution of sulphuric acid made by diluting the concentrated acid with three parts of water. These precipitates all settled rapidly, and the variation in the amounts of alkali seemed to exert no very marked influence. Finally, these experiments seeming to point to hydrochloric acid as the influential factor, a series of experiments was made to test the effect of varying the amount of this acid. From a solution containing in 400 cm^3 0·5 grm. of barium chloride and amounts of hydrochloric acid varying from 1 cm^3 to 50 cm^3, the barium was thrown out by means of 10 cm^3 of dilute sulphuric acid. This series showed that the hydrochloric acid had a very marked effect upon the precipitation of the barium sulphate. When only one or two cubic centimeters of hydrochloric acid were present, the precipitate appeared immediately, in a milky condition, and settled slowly; as the amount of acid was increased, a point was soon reached where the precipitate was not so quickly apparent, but settled out much more quickly and in a coarser condition. With 10 cm^3 to 15 cm^3 of strong hydrochloric acid in the solution, the precipitate settled clear in ten or twelve minutes and was in excellent condition for filtration. When the solution contained 50 cm^3 of the acid, the precipitate settled clear in five minutes. Upon adding the sulphuric acid to such very acid solutions, no precipitate shows for a moment, but then it separates in beautiful crystalline condition and falls almost immedi-

ately. It can be safely filtered with or without pressure in ten minutes. In one instance, in the course of the experiments just detailed, 2 grms. of barium chloride were precipitated in the presence of 30 cm³ of hydrochloric acid, the precipitate was allowed to settle clear, and was then filtered and washed, the whole operation being completed in seven minutes. This rapid subsidence of the precipitate is seen in hot solutions only —75° C. being the lowest temperature compatible with the attainment of good results, and 85° to 90° better.

To ascertain whether small amounts of barium would be precipitated in like manner from these acid solutions, a series of experiments was made with solutions containing in 400 cm³, 10 cm³ of hydrochloric acid and 5, 10, 15, 20, 25, 30 and 50 milligrams of barium chloride, precipitation being brought about as in the experiments above. These solutions remained clear a few minutes and then a very transparent precipitate appeared, but in no case was it as pronounced as the more finely divided precipitate produced in a neutral solution containing 5 milligrams of barium chloride by the same amount of sulphuric acid. However, by giving a circular motion to the solution in the beaker, after about 20 minutes a small conical heap of barium sulphate was collected in each case in the center of the beaker.

Experiments were next undertaken to ascertain whether barium is completely thrown out of solution when precipitated under the conditions related above. The barium salt used in all the experiments described below, was obtained by finely powdering selected crystals of barium chloride and drying by pressure between blotting papers. Portions of the same sample were used throughout. The hydrochloric acid used was the chemically pure article of commerce and had a specific gravity of 1·20. The sulphuric acid used was obtained by diluting the pure concentrated acid with three parts of water and had a specific gravity of 1·28.

In the first series the barium salt was dissolved in about 400 cm³ of water, 15 cm³ of hydrochloric were added, and precipitation was brought about by adding 10 cm³ of the dilute sulphuric acid. The precipitates were filtered, after standing about ten minutes, upon asbestos felts in perforated platinum crucibles.

	$BaCl_2 . 2H_2O$ taken.	$BaSO_4$ found.	Error.
(1)	0·5002 grm.	0·4760 grm.	0·0016 grm.—
(2)	0·5042 "	0·4812 "	0·0006 " —
(3)	0·5038 "	0·4786 "	0·0025 " —
(4)	0·5002 "	0·4760 "	0·0016 " —
(5)	0·5046 "	0·4812 "	0·0006 " —
(6)	0·5038 "	0·4804 "	0·0006 " —

The results of these determinations indicate plainly a loss of barium sulphate, but inasmuch as the felts used had been made very thin and it had been subsequently observed that a small quantity of the sulphate could be collected in one of the filtrates of the series by giving a circular motion to the water, it was thought that the thinness of the felts might offer an explanation of the loss and of the varying results of the series. The following series was, therefore, made in exactly the same manner except that care was taken to have the felts carefully made and reasonably thick.

	$BaCl_2 . 2H_2O$ taken.	$BaSO_4$ found.	Error.
(7)	0·5014 grm.	0·4785 grm.	0·0004 grm.—
(8)	0·2227 "	0·2122 "	0·0005 " —
(9)	0·5003 "	0·4773 "	0·0004 " —
(10)	0·5046 "	0·4814 "	0·0004 " —

These results are uniform and indicate a trifling loss only; though in the filtrates of these experiments, also, a very slight, but, as it proved upon refiltering, unweighable amount of the sulphate could be collected. The precipitate in the last of these experiments was filtered off almost immediately after precipitation, and before it had completely subsided. In another case the whole operation, including the three weighings necessary was conducted to a finish in forty-five minutes.

In spite of the appearance of the trifling deposit in the filtrate, the deficiency in barium sulphate in these determinations was not greater than should be expected from the accepted solubility of that salt in water. To ascertain the effect of strongly acid solutions upon the solubility of barium sulphate the following determinations were made.

In experiment (11) the same amounts of the sulphuric and hydrochloric acids, 10 cm^3 and 15 cm^3 respectively, were used as before, but the total volume was reduced to 100 cm^3. In (12) and (13) the same total volume as before, 400 cm^3, was used, but this volume contained 150 cm^3 of the strong hydrochloric acid instead of 15 cm^3 as in the preceding experiments.

	$BaCl_2 . 2H_2O$ taken.	$BaSO_4$ found.	Error.
(11)	0·5016 grm.	0·4888 grm.	0·0002 grm.—
(12)	0·5004 "	0·4779 "	0·0000 "
(13)	0·5001 "	0·4776 "	0·0000 "

It appears from these experiments that, as in the preceding series, the solubility of barium sulphate in solutions constituted as described is not increased by the free hydrochloric acid, and that the effect upon the solubility when this acid is present in

great strength is to make the precipitate rather more insoluble, if anything, than it is in water. In this connection, it should be remarked that experiments of Fresenius,* together with somewhat similar experience gained by the writer in another line of work not included in this account, point to the fact that the presence of an excess of sulphuric acid is an important condition of this high degree of insolubility. The exact amount of such excess has not been determined, but the amount used in the foregoing experiments seems to be sufficient.

In the preceding experiments, barium chloride was used in considerable quantity. The following determinations were made to ascertain whether very much smaller quantities of barium would come down as completely and as soon, or whether it is necessary to let the precipitations stand longer before filtration. In these experiments the barium salt was measured from a standard solution, containing 200 milligrams of the chloride to the liter. The amounts of hydrochloric and sulphuric acids, 15 cm^3 and 10 cm^3 respectively, and the whole volume of the solution was the same as in the former experiments.

	$BaCl_2.2H_2O$ taken.	$BaSO_4$ found.	Time in minutes between precipitation and filtration.	Error.
(14)	0·0030 grm.	0·0024 grm.	120	0·0004 grm. —
(15)	0·0050 "	0·0046 "	150	0·0002 " —
(16)	0·0050 "	0·0023 "	5	0·0025 " —
		0·0043 "	60	0·0005 " —
(17)	0·0050 "	0·0031 "	5	0·0016 " —
(18)	0·0050 "	0·0040 "	10	0·0007 " —
(19)	0·0100 "	0·0078 "	10	0·0017 " —
(20)	0·0100 "	0·0085 "	15	0·0010 " —
(21)	0·0100 "	0·0083 "	30	0·0012 " —
(22)	0·0100 "	0·0087 "	60	0·0007 " —

From these results it would appear that the precipitation, in the presence of hydrochloric acid to the amount indicated, does not take place so rapidly when the amount of the barium salt is small, but that two or three hours are sufficient for reasonably complete separation of the precipitate in any case.

In all the experiments described above there was no attempt at a gradual admixture of the reagents but they were measured out and at once added to the solutions, the whole being well stirred. From the results obtained, it appears to be established, as regards the usual precautions in precipitating barium by means of sulphuric acid, that, contrary to former usage, it is

* Zeitschrift für Anal. Chem., vol. ix, p. 62.

highly advantageous to have the solution strongly acid with hydrochloric acid; that it is not necessary to add the reagents drop by drop, but that the whole quantity required to complete the reaction may be added at once; that ordinary quantities of barium salts, in presence of a considerable excess of sulphuric and hydrochloric acids, are precipitated completely and at once, but that when only a few milligrams are present, the precipitate requires more time to separate under the same conditions. Two or three hours are, however, sufficient, and in no case is the excessive time of twelve hours required.

In the light of the fact demonstrated in the preceding account, that hydrochloric acid may be introduced freely, and without detriment to the quantitative exactness of the precipitation of barium in the form of sulphate from pure solutions, it seemed desirable to look somewhat into the question as to what the influence of a large excess of hydrochloric acid might be upon the well known contaminating effect of alkaline salts present during precipitation, especially as it is customary to attempt the purification of barium sulphate thrown down in the reverse of this process—the determination of sulphuric acid by means of a soluble barium salt—by digestion of the washed precipitate in hydrochloric acid. The following series of experiments was undertaken with this end in view. The details are shown in the tabular statement, precipitation being effected in the presence of free acid and the alkaline salt.

	$BaCl_2.2H_2O$ taken.	$BaSO_4$ found.	Error.	HCl in solution.	Alkaline Salts present.	
(23)	0·5092 grm.	0·5032 grm.	0·0169 grm.	+ 110 cm^3	$KClO_3$	3 grm.
(24)	0·5027 "	0·4907 "	0·0107 "	+ 10 "	"	"
(25)	0·5026 "	0·4944 "	0·0154 "	+ 100 "	KCl	5 grm.
(26)	0·5045 "	0·4939 "	0·0122 "	+ 10 "	"	"
(27)	0·5020 "	0·4931 "	0·0137 "	+ 10 "	"	"
(28)	0·5013 "	0·4849 "	0·0061 "	+ 10 "	NaCl	"

From the results it is plain that, whatever may be the effect of digesting the washed precipitate in hydrochloric acid, the presence of this acid in large excess during precipitation in the presence of alkaline salts, does not prevent contamination of the precipitate. On the contrary, the greatest contamination seems to have occurred in those cases in which the acid was present to the largest degree, but, in view of the slight variation in contamination as compared with the great differences in the amount of acid employed, it does not appear probable that the increase of acid has very much to do with the amount of contamination.

It likewise seemed to be a matter of some interest in this connection, to investigate the process by which it is currently

supposed* that barium sulphate carrying alkaline salts may be effectually purified, viz: by the solution of the washed precipitate in strong sulphuric acid and reprecipitation by water. Accordingly the determinations of the following series were undertaken. The barium sulphate, precipitated from solutions containing 5 grms of potassium chloride and 10 cm^3 of hydrochloric acid, was collected upon a filter, either paper or asbestos, and, after burning the paper or removing the precipitate from the asbestos (by tapping the crucible which held it and brushing out with a camel's hair brush), was dissolved by warming with concentrated sulphuric acid in a large porcelain crucible and, after cooling, poured into water containing 15 cm^3 to 20 cm^3 of hydrochloric acid. The water into which the solutions in strong acid was poured was warmed with a view to diminish the milkiness of the precipitate, but care must be taken to keep the temperature below 60° C. to avoid danger of spattering on the addition of the sulphuric acid. In the last two of the experiments recorded a large amount of ammonium chloride was added to the water into which the solutions in acid were poured, but this appears to have been without influence upon the purification or the character of the precipitation. The precipitates, after settling clear, were filtered upon asbestos, ignited and weighed, the original felts being employed in those cases in which asbestos was used in the first instance. Those marked with an asterisk were gathered in the first filtration upon paper, the paper being burned in the crucible in which solution of the precipitate was subsequently effected. The remainder were filtered originally upon asbestos.

	$BaCl_2.2H_2O$ taken.	$BaSO_4$ found.	Error.
(29)	0·5026 grm.	0·4746 grm.	0·0044 grm. —
(30)	0·5035 " *	0·4830 "	0·0022 " +
(31)	0·5016 "	0·4767 "	0·0024 " —
(32)	0·5025 "	0·4804 "	0·0050 " +
(33)	0·5046 " *	0·4829 "	0·0010 " +
(34)	0·5004 "	0·4825 "	0·0047 " +

These results show, evidently, that this process of purification is not satisfactory. It is possible that the losses observed may have been mechanical, and due to the violent action of the strong acid upon the water, but the excess in weight which is noticed in the majority of the determinations can only be attributed to residual contamination.

Certain experiments, on the other hand, in which the solvent action of sulphuric acid upon barium sulphate is utilized in a different manner resulted more favorably. When a solution of barium sulphate in sulphuric acid is evaporated to dryness, the

* Fres. Quant. Anal., vol. i, p. 547.

salt, as is well known, is deposited in large crystals, which can be filtered off as readily as sand. The following series of experiments show the result of an attempt to utilize this property of comparatively slow and large crystallization in purifying the precipitate. Solution of the precipitate was effected as in the experiments described above, and the evaporation of the acid was effected over a matting of asbestos, or by means of a ring burner, in porcelain, which is preferable to platinum when the evaporation is carried on as slowly as is necessary. After the acid was completely evaporated, the crystals were washed upon a felt of asbestos, ignited and weighed. Five grams of potassium chloride and 10 cm^3 of hydrochloric acid were added to the solution of barium chloride in each case.

	$BaCl_2 . 2H_2O$ taken.	$BaSO_4$ found.	Error.
(35)	0·5029 grm.	0·4796 grm.	0·0006 grm. —
(36)	0·5008 "	0·4783 "	0·0001 " +
(37)	0·5038 "	0·4810 "	0·0001 " —
(38)	0·5087 "	0·4861 "	0·0003 " +
(39)	0·5025 "	0·4795 "	0·0006 " +

These results are plainly good and satisfactory so far as concerns the purification of the salt, but, when the evaporation is conducted in the manner described, several hours are needed for the evaporation, and great care must be exercised to obviate the danger of snapping which becomes manifest in the later stage of the evaporation.

By the aid, however, of a Hempel evaporating burner* the operation can be finished safely, and with but little care, in the course of half an hour. The following determinations were made exactly like those of the last series, with the exception that the evaporation was effected by means of the Hempel apparatus.

	$BaCl_2 . 2H_2O$ taken.	$BaSO_4$ found.	Error.
(40)	0·5050 grm.	0·4824 grm.	0·0002 grm. +
(41)	0·5069 "	0·4838 "	0·0000 "
(42)	0·5041 "	0·4825 "	0·0021 " +
(43)	0·5021 "	0·4812 "	0·0018 " +
(44)	0·4033 "	0·4801 "	0·0005 " —

Though not an absolutely perfect process, the purification of barium sulphate by this method of solution and evaporation is evidently better, by far, than the old method of solution and reprecipitation by dilution.

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* Ber. d. deutsch. chem. Ges., xxi. p. 909.