judgment is based on the similarity of their behavior toward certain reagents and when heated in melting-point tubes; neither exhibits a definite melting point, but the one duplicates closely the behavior of the other at like temperatures.

Titration of Hydrazine Dioxalate with Standard Alkali.—Salts of hydrazine, such as the dichloride[1] and the disulphate, show an acid reaction in aqueous solution.

One-half of the acid in the salts behaves as so much free acid[2] and may be titrated with alkalies. In agreement with the other diacid salts, hydrazine dioxalate is likewise acid in its reactions. Consequently attempts were made to titrate its free acid.

In previous titrations methyl orange has been employed, but on account of its lack of sensitiveness to oxalic[3] acid it could not be used in these experiments.

Curtius[4] has shown that the indicators—methyl orange, cochineal, corallin, tropeolin, fluorescein and litmus—give definite end points when used in the titration of hydrazine hydrate with $0.1\,N\,H_2SO_4$. He did not show, however, what the condition of the hydrazine at this end point was with respect to its combination with the acid. Cohn states that litmus and corallin are sensitive to oxalic acid. The titration of hydrazine dioxalate with azolitmin and with rosolic acid as indicators fail to give with any degree of sharpness the point of neutralization of that salt. Titrations with standard sulphuric acid with the extremely sensitive indicator, erythrosin, however, of a solution made alkaline by the addition of a definite volume of standard sodium hydroxide, gave results which indicated that the neutral point corresponds to the presence in the solution of only the monoxalate. The reaction may be represented by the following equation:

$$2N_2H_4.H_2C_2O_4 + 2NaOH = (N_2H_4)_2.H_2C_2O_4 + Na_2C_2O_4 + 2H_2O.$$
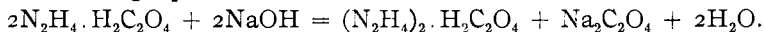
With phenolphthalein as indicator, the whole of the oxalic acid may be titrated with sodium hydroxide solution. In the case of none of the indicators tried was a sharp end point obtained.

CORNELL UNIVERSITY, September, 1909.

THE EXACT DETERMINATION OF SULPHUR IN SOLUBLE SULPHATES.

BY E. T. ALLEN AND JOHN JOHNSTON.

It was in the course of an investigation of the sulphides of iron that our attention was first directed to the inaccuracy of the ordinary sulphur

[1] Curtius and Schulz, *J. prakt. Chem.*, **42**, 521 (1890).

[2] Stollé, *Ibid.*, [2] **66**, 332–8 (1902).

[3] Cf. Cohn, "Indicators and Test-papers," 2nd Ed., p. 114.

[4] Curtius and Schulz, *loc. cit.*

determination. Without going into the details of the analytical methods, it is finally necessary in all of them to precipitate the sulphur from a mixture of sulphate and chloride. The results we obtained were invariably low, and here surprisingly so, as the errors are magnified by the large percentage of sulphur in these compounds (53.4 per cent. in FeS_2). The ordinary methods, which, even in very careful work, easily involve a loss of 2 per cent. or more of the total sulphur, were inadequate for the purposes of our problem, and we were therefore forced to investigate them. The complications we encountered led us somewhat farther afield than we at first intended, though the importance of the analytical problem and some considerations of a more general nature seemed to justify this. Several sources of error were discovered, satisfactorily accounting, in the end, for all the losses. Some of these, it is true, have been noted by other observers, for the field is an old one, but nowhere in the literature has the subject been treated on a systematic, quantitative basis.

The most important of the errors are involved in the precipitation of the sulphur after it has been transformed into soluble sulphate, and to these we will confine our attention in this paper.

Richards and Parker[1] and Hulett and Duschak[2] have studied the precipitation of *sulphuric acid* by barium chloride and of barium chloride by sulphuric acid. Their work shows that the barium sulphate thrown down under these conditions always weighs too much, because it is contaminated with barium chloride which cannot be washed out; and that exact results may be obtained by determining the chlorine in the precipitate and deducting the barium chloride equivalent to it from the weight of the crude barium sulphate. This part of the subject appears to be satisfactorily settled. The little we have done on it only confirms the statements of the authors quoted.

We have devoted nearly all of our attention to the precipitation of sulphur from *soluble sulphates*—a case which occurs much more frequently in actual practice. Here the results are always low, at least this is true of the sulphates of sodium, potassium and ammonium. We will consider first the precipitation of solutions of pure sodium sulphate.

A. The Precipitation of Sodium Sulphate by Barium Chloride.

The purity of the salt we used in our work was carefully tested in the following manner:

To free it from moisture, a thin layer of the powdered salt was heated in platinum to 200–225° for an hour or more. After the heating, we found it could be melted without losing more than 0.02 per cent. of its weight. Then it was transformed into sodium chloride by the addition

[1] *Proc. Am. Acad.*, **31**, 67 (1896); *Z. anorg. Chem.*, **8**, 413 (1895).
[2] *Z. anorg. Chem.*, **40**, 196 (1904).

of a slight excess of barium chloride; the barium sulphate was filtered out and the soluble chloride in the filtrate evaporated to dryness, heated to incipient redness, and weighed. To this quantity was added a correction for a certain amount of sodium, calculated to chloride, which was carried down by the precipitate.[1]

(a) 1.2160 g. Na_2SO_4 gave 1.0026 g. NaCl.   Calculated, 1.0008 g.
(b) 1.2156 g. Na_2SO_4 gave 1.0009 g. NaCl.   Calculated, 1.0003 g.

Potassium was sought for by treating the total chlorides (from another portion of salt) with an equivalent quantity of chloroplatinic acid and evaporating to dryness on the steam bath. The residue was treated with successive portions of 93 per cent. alcohol till the greater part was dissolved, when the remainder was dried, a little more platinum solution added, and the procedure repeated. A little characteristic golden yellow residue was obtained.

(a) 0.995 g. chlorides gave 2.9 mg. K_2PtCl_6, equivalent to 0.08 per cent. K_2SO_4 in the original salt.
(b) 0.997 g. chlorides gave 3.3 mg. K_2PtCl_6, equivalent to 0.09 per cent. K_2SO_4.

The precipitated barium sulphate was also examined for potassium, but none was found in it. This quantity of another sulphate is, of course, too small to make any appreciable difference in the weight of our barium sulphate precipitates. The only other impurity noted in the sodium sulphate was a trace of iron.

Method of Precipitation.—The sulphate, dried as previously described, was, in some cases, weighed directly, but in general, to avoid exposing the anhydrous substance frequently to the air, a given quantity of salt was made up to a given weight of solution and weighed portions of this were taken for individual determinations.

About 24.35 grams dried sodium sulphate, weighed carefully to the milligram, was put into a tared flask and diluted till the solution weighed about 1000 grams. The weight was determined to the nearest centigram. Portions of this solution of about 50 grams were then weighed to the milligram in a weight burette, making all necessary corrections for the buoyancy of the air. This was then diluted in a Jena glass beaker to 350 cc. with hot water, acidified with a measured quantity of hydrochloric acid, heated to boiling, and precipitated by a slight excess of 10 per cent. solution of barium chloride (*i. e.*, a solution containing 100 grams $BaCl_2.2H_2O$ in 1 l.). Two grams $BaSO_4$ requires 20.9 cc. 10 per cent. $BaCl_2$ solution; while we used 22–22.5 cc.[2] The reagent was let into the sulphate solution from a burette, either drop by drop, or, better, in a thin stream which flowed down the side of the beaker.

[1] The method of this correction will be described later (page 594).
[2] A greater excess was shown to exert no appreciable influence on the results (see p. 597).

The precipitates were commonly allowed to stand for about 18 hours, filtered on paper, and thoroughly washed till the filtrate showed only the merest opalescence with silver nitrate;[1] this required 1 to $1\frac{1}{2}$ hours' washing with precipitates of 2 grams. The moist precipitate and filter are then burned *very slowly and carefully* in a platinum crucible. The filter must not be allowed to take fire, for in spite of some statements to the contrary, we find the sulphate is readily reduced and not easy to oxidize completely, once reduction has taken place—at least this is true of large precipitates. As soon as the filter is entirely burned, the crucible cover is moved to one side to admit the air, the temperature raised and the heating continued till the weight is constant. Once the paper is burned, a further heating of 20 minutes will very nearly suffice.

Gooch crucibles were also tried. They obviate all danger of reduction, of course, and are well adapted to small precipitates; but large precipitates are inclined to clog the filter and demand much time in washing. For this reason the results are likely to be somewhat high when Gooch crucibles are used.

The precipitates prepared as described weighed about 2 grams each. We chose this quantity for two reasons: first, it is about the quantity of barium sulphate yielded by 0.5 gram of iron pyrites; and second, and more important, it is a quantity sufficiently large to trace the small percentage errors with some degree of certainty.

Determinations of the sulphur in pure sodium sulphate carried out in this manner are always too low, the deficit varying with the conditions from 0.3 per cent. to 0.5 per cent., and sometimes even more. We will now take up these errors in order.

1. Loss Due to "Solubility."[2]—This is the most obvious source of error, and though the least important, unless the precipitate is quite small, it is much increased by free acid. We have determined it in the usual way by evaporating the filtrate and washings to dryness in a platinum basin, adding a little water to the residue, and filtering on a very small ashless paper. Great pains were taken to remove any adhering film from the dish, to avoid loss of any material by running through the filter, and to wash the precipitate completely. Table I shows the losses from solubility. It will be noted that these increase with the concentration of acid in the original solution, and therefore that the less acid one chooses, the better, so far as this loss is concerned. Later, it will ap-

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[1] A test with a very dilute standard solution showed the chlorine at this stage to be equal to about 0.005 mg. in 25 cc. of the washings.

[2] These losses are not in every case to be referred entirely to the solubility of barium sulphate in the supernatant liquid; but may be in some cases partly due to the well-known tendency of barium sulphate to creep. Hence the figures given in the table are to be taken, not as quantitative measurements of this solubility, but as analytical corrections.

TABLE I.—LOSSES (IN MG.) DUE TO THE SOLUBILITY OF BaSO₄.

Total volume = 350 cc. + 350 cc. washings.

cc. 20 per cent. HCl.						Mean.
0.2	—1.3	1.0	0.9	0.6	0.7	0.9
1.0	—1.6	1.4	. . .	. . .	. . .	1.5
5.0	3.5	3.1	. . .	. . .	. . .	3.3
10.0	4.1	3.7	. . .	. . .	. . .	3.9
20.0	14.3	10.0	. . .	. . .	. . .	12.0
100.0	36.5	. . . .	. . .	. . .	. . .	36.0

pear that another and more important error is influenced by the same cause. In most of our work we have used one of two acid concentrations, *viz.*, 2 cc. of 2 per cent.[1] or 1 cc. 20 per cent. hydrochloric acid, the volume of the solution being 350 cc. The stronger acid has the advantage that the precipitates formed in its presence are somewhat denser and more convenient to handle, but the weaker acid is to be recommended, since the sum of the corrections in that case is smaller. The quantity of free acid *ordinarily* used in the sulphate determination is doubtless too great, and may cause large percentage errors on precipitates which weigh only a few hundred milligrams.[2]

The statement has been made by several chemists that alkaline chlorides greatly increase the solubility of barium sulphate.[3] Determinations of the solubility by the above method in solutions containing 10 grams sodium chloride in 350 cc. showed that the chloride was practically without influence. As these results were perfectly consistent with the rest of our work on sodium sulphate, nothing more was done on the question, but as regards the solvent effect of potassium and ammonium chlorides which is commonly held to be greater, we have definitely disproved that in another way (see Tables XX and XXV).

2. *The Occlusion*[4] *of Sodium Sulphate by Barium Sulphate.*—Table II gives a number of determinations of barium sulphate from a weighed quantity of sodium sulphate, and the corresponding deficits. It will

TABLE II.—TOTAL LOSSES (IN MG.) IN THE PRECIPITATION OF PURE SODIUM SULPHATE.

cc. 20 per cent. HCl in the solution.	0.2.					1.0.			
BaSO₄ calc....	2002.2	1995.4	2044.5	2039.9	2036.6	2002.6	2037.4	1998.0	1994.5
BaSO₄ found..	1994.7	1985.5	2032.6	2035.7	2029.4	1995.5	2030.3	1985.7	1987.4
Deficit in mg.	7.5	9.9	11.9	4.2	7.2	7.1	7.1	12.3	7.1

[1] For convenience, both will be stated in terms of 20 per cent. acid.

[2] Thus Folin (*J. Biochem.*, 1, 147 (1906)) prescribes as safe limits of acidity 1–4 cc. conc. hydrochloric acid in 150 cc. solution, *i. e.*, 4.5 cc. -18.5 cc. 20 per cent. acid in 350 cc.

[3] R. Fresenius and E. Hintz, *Z. anal. Chem.*, 35, 75 (1896); Lunge and Stierlin, *Z. angew. Chem.*, 18, 1929 (1905); Folin, *J. Biochem.*, 1, 142 and 144 (1906).

[4] By occlusion we mean, simply, retention by the precipitate without implying its nature.

be seen at once that the solubility correction (Table I) accounts for only a small part of the total loss.

In the sixth German edition of his "Quantitative Analysis" (Vol. I, p. 230, (1875)), Fresenius says that, when barium is precipitated by sulphuric acid in the presence of alkalies, small portions of alkali sulphates are carried down with the precipitate, but he gives no data. Hintz and Weber[1] found that, when barium sulphate, which had been precipitated from an ammonium sulphate solution, was heated in a glass tube, a sublimate containing sulphate was obtained. Lunge and Stierlin[2] give results of four determinations of sodium and potassium sulphates in crude barium sulphate, by digesting the latter with dilute hydrochloric acid. No evidence as to the completeness of the separation is offered.[3] We examined the weighed precipitate for impurities as follows:

The precipitate was dissolved in about 15 cc. pure conc. sulphuric acid in a platinum dish. The solution was cooled and poured in a thin stream into about 350 cc. water with vigorous stirring. The solution and precipitate were heated to facilitate filtering, after which the solution was evaporated over a free flame till fumes of sulphuric acid appeared, and then carried to dryness in a hood with good draft. The residue in the platinum basin was now dissolved in a little water and filtered through a 5.5 cm. filter into a small tared platinum dish. The contents were evaporated to dryness on the steam bath, then heated carefully to redness, cooled and weighed. The white soluble salt obtained could hardly be anything but sodium sulphate, nevertheless one of the residues was converted into barium sulphate and the point proved. 0.0234 gram residue gave 0.0386 gram $BaSO_4$; calc. for Na_2SO_4, 0.0385 gram. In order to find whether all the sodium sulphate is recovered from the precipitate by the above method, the precipitate obtained by pouring the sulphuric acid solution into water was dried, ignited, and again dissolved in sulphuric acid and reprecipitated by water. The results of four such experiments follow:

Na_2SO_4 (in mg.) from first extraction............	10.1	11.8	24.8	26.2
Na_2SO_4 (in mg.) from second extraction.........	0.8	1.3	2.1	2.0

The second extraction recovers so nearly 10 per cent. of the amount obtained by the first extraction that in all subsequent data the amount *actually obtained* by one extraction will be given, but the correction will be made on a quantity 10 per cent. greater. This probably is as accurate as a direct determination would be.

Table III shows the amount of sodium sulphate found in precipitates

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[1] *Z. anal. Chem.*, **45**, 39 (1906).

[2] *Z. angew. Chem.*, **18**, 1921 (1905).

[3] We later discovered that water alone will extract from an *ignited* precipitate about 80 per cent. of the alkali salt.

formed under the conditions stated above, and also the corresponding corrections. Since all the sodium sulphate in the precipitate should, of course, have been converted into barium sulphate, the precipitate weighs too little. The numbers designated "correction" in the table are obtained by multiplying the weight of the occluded sodium sulphate, plus 10 per cent., by the factor $91.37/142.07 = (BaSO_4 - Na_2SO_4)/Na_2SO_4$.

TABLE III.—OCCLUSION OF SODIUM SULPHATE BY BARIUM SULPHATE.
Na_2SO_4 (in mg.) occluded by 2 grams precipitate[1] with the corrections.

0.2 cc. 20 per cent. HCl..	8.7	7.1	9.1	5.3	8.3	4.7	11.9	11.6
Corrections............	6.1	5.0	6.4	3.7	5.8	3.3	8.3	8.1
1.0 cc. 20 per cent. HCl..	11.6	8.4	11.4	12.0	10.3	7.1	7.7	9.4
Corrections............	8.1	5.9	8.0	8.4	7.2	5.0	5.4	6.5

This sodium sulphate is originally present as such in the barium sulphate. It is not present in the form of sodium chloride, as one might suspect. At least, this is true of the *ignited* precipitates. We have repeatedly tested our precipitates for chlorine by the quick and accurate method of Hulett and Duschak.[2] This consists in dissolving the precipitate in sulphuric acid, in a simple apparatus of glass swept by a current of air which carries the free hydrochloric acid into a solution of silver nitrate. We heated directly with a small flame, instead of a hot water bath, as Hulett and Duschak did, thereby dissolving the precipitate in a much shorter time, though now and then a determination is lost by the cracking of the tube. The silver chloride was determined gravimetrically instead of volumetrically, which was more convenient and sufficiently accurate for our purpose.

Precipitates prepared and washed as we have directed in the foregoing never gave more than 0.5 mg. of chlorine *after ignition*, and we have repeatedly reduced the quantity to 0.1 mg., even when the original solution contained 15 to 30 grams sodium, potassium, or ammonium chloride per liter. This is shown in Table IV. We will later show that

TABLE IV.—CHLORINE (IN MG.) IN 2 GRAMS IGNITED PRECIPITATE.
From Na_2SO_4 solutions containing HCl as below; V = 350 cc.

Grams NaCl.	cc. 20 per cent. HCl in soln.						
	1 drop	0.1	0.2	1.0	5.0	20.0	100.0
0	1.0	0.2	0.4	0.2 and 0.4	0.1	0.6	4.0
4	...	...	...	0.1	...	...	...

the washed, but unignited, precipitates contain usually 1–2 mg. of chlorine, which is probably present as barium chloride; this is considerably increased when the precipitate is rapidly formed. The chlorine is practically all lost on ignition, if the precipitate has been slowly formed.

[1] Volume of original solution = 350 cc.
[2] *Loc. cit.*, p. 197.

The next step in the investigation was naturally to study the causes which condition the occlusion of sodium sulphate by the precipitate.

Influence of Various Factors on the Composition of the Precipitate.

(*1*) *The Effect of Concentration of the Sodium Sulphate.*—Table V gives a comparison of the quantities of sodium sulphate found in 2 grams barium sulphate precipitated from sodium sulphate solutions of several

TABLE V.—EFFECT OF CONCENTRATION OF SODIUM SULPHATE.
Quantities of sodium sulphate occluded by 2 grams precipitate.

Volume in cc.	cc. 20 per cent. HCl.	Mg.						
350	1	11.6	8.4	11.4	12.0	10.3	...	...
1000	5	6.0	8.9	....	....	....	...	...
2000	10	8.0	6.9	6.9	8.2	8.9	6.4	5.3
8000	5	10.9	[precipitated cold]					
8000	25	9.6	[precipitated cold]					

concentrations, the other conditions remaining the same. It will be seen that increasing the volume from 350 to 2000 cc. reduces the quantity slightly. The last two experiments are instructive. Equivalent solutions of barium chloride and sodium sulphate, each 100 cc. in volume and of such a concentration as to give about 2 grams of barium sulphate, were allowed to drop slowly and at the same rate (100 cc. in about 4 hours) into 8 liters of cold water, which was vigorously stirred during the whole process. The conditions in the two experiments differed only in the amount of acid in the solution. The quantity of sodium sulphate occluded, instead of being reduced by this high dilution, was a trifle increased thereby, though possibly this increase may be due to the fact that these precipitates were thrown down in the cold. It is evident from this that dilution alone is of little influence in reducing occlusion of sodium sulphate.

(*2*) *Effect of the Rate of Addition of the Reagent.*—The rate at which the solution is precipitated has some influence on occlusion, though it is not very great. Thus, if the reagent is allowed to flow as rapidly as possible from the burette (time = 9 seconds in the burette we used), the quantity of sodium sulphate taken up by the precipitate is reduced somewhat, though the results here are not so uniform as they are when the rate is slower (see p. 603).

(*3*) *The Effect of Pouring the Sulphate into the Barium Chloride.*—The few results obtained in this way indicate that no effect is to be attributed to this cause. In the three following experiments the barium chloride solution was diluted to 350 cc., acidified, and heated to boiling. Then the sulphate solution in 50 cc. volume was poured as slowly as possible into it with constant stirring. In three different experiments, the quantities of sodium sulphate occluded in 2 grams precipitate were 11.6 mg., 8.4 mg., and 12 mg.

(4) *The Effect of Acid Concentration.*—The concentration of the hydrochloric acid in the sulphate solution was found to reduce the occluded alkali sulphate very slowly, as may be seen from Table VI, but free acid increases the other errors more than it diminishes this one.

TABLE VI.—EFFECT OF ACID CONCENTRATION ON OCCLUSION.

Na_2SO_4 (in mg.) in 2 grams precipitate. V = 350 cc.

cc. 20 per cent. HCl.	0.2.	1.	5.	10.	20.	100.
. . . .	8.7	7.1	7.7	4.1	3.6	2.5
. . . .	9.1	7.7	. . .	5.1	. . .	. . .
. . . .	7.1	9.4	. . .	. . .	. . .	. . .

(5) *Influence of Time.*—There is a noticeable change in the composition of the precipitate if it is left to stand in the supernatant liquid. A precipitate which is filtered and washed immediately after precipitation always contains more sulphate than one which has been left to stand,

TABLE VII.—EFFECT OF THE TIME OF STANDING ON OCCLUSION.

Mg. sodium sulphate in 2 grams precipitate.

Time. Hours.	Vol. cc.	NaCl. Gms.	cc. 20 per cent. HCl.					
1/4	350	0	0.2	11.9	11.6	. . . .	. . . .	. . . .	. . . .
1/4	350	5	0.2	22.6	22.7	. . . .	. . . .	. . . .	. . . .
3	350	5	0.2	18.3	19.0	18.5	19.7	18.4	19.7
3	2000	0	1.0	6.9	6.9	8.2	8.9	. . . .	. . . .
18	350	0	0.2	8.7	9.1	. . . .	. . . .	. . . .	. . . .
18	350	5	0.2	17.3	17.1	17.5	17.2	17.9	. . . .
18	2000	0	1.0	8.0	5.3	6.4	. . . .	. . . .	. . . .
45	350	0	0.2	5.3	. . .	. . . .	. . . .	. . . .	. . . .
45	350	5	0.2	14.0	14.2	. . . .	. . . .	. . . .	. . . .
70	350	5	0.2	12.6	11.9	. . . .	. . . .	. . . .	. . . .

and the difference is considerable when the initial quantity of occluded sodium sulphate is large.

(6) *Effect of Digesting the Precipitate.*—In order to test this point, a number of precipitations were made in the usual way from solutions of sodium sulphate containing 5 grams sodium chloride and 0.2 cc. 20 per cent. hydrochloric acid. Of these precipitates two were allowed to stand in contact with the original supernatant liquid for three hours on the steam bath; the precipitate was then filtered off, and the occluded sodium sulphate, determined in the usual way, was (1) 18.3 mg., and (2) 19.0 mg. In the other four cases, the supernatant liquid was poured off immediately after the precipitation and the precipitate was treated as follows, the time of contact with the liquid being in each case three hours on the steam bath.

Amount of
Na_2SO_4 in mg.

(3) Filtered and washed ppt. until free from Cl.; added 350 cc. hot water. 18.4

(4) Added 350 cc. hot water. 19.7

(5) Added 350 cc. hot water containing 1.2 grams Na_2SO_4. . . . . 18.5

(6) Added 350 cc. hot water containing 1.0 gram $BaCl_2$. 19.7

From these results it is evident that the amount of sodium sulphate still occluded by the precipitate at the end of three hours on the steam bath, is independent of the composition and concentration of the supernatant liquid. The explanation of these results appears to be that the impurities in the precipitate react chemically with one another, forming barium sulphate and sodium chloride, and that it is the latter—not sodium sulphate—which diffuses out into the supernatant liquid (see paragraph 5). At any rate, it is evident that in an analysis nothing is gained by digesting the precipitate with a large excess of reagent.

(7) *Influence of Concentration of Sodium Chloride.*—It has been shown that a considerable variation in the concentration of a sodium sulphate solution exerts only a small influence on the content of the same in the barium sulphate precipitated from it. When the concentration of the sodium is increased by adding *sodium chloride* to the original solution, the occlusion of sodium sulphate is markedly increased. In Table VIII

TABLE VIII.—EFFECT OF SODIUM CHLORIDE ON THE OCCLUSION OF SODIUM SULPHATE.
Mg. sodium sulphate in 2 grams precipitate.

NaCl. Grams.	cc. 20 per cent. HCl.	Time. Hours.		
0	0.2	18	8.3	(Average from Table III)
0	1.0	18	8.0	(Average from Table III)
0	5.0	18	7.7	
2	0.2	$\frac{1}{2}$	14.0	
2	5.0	$\frac{1}{2}$	10.0	
5	0.2	18	17.4	(Average from Table III)
5	5.0	$\frac{1}{2}$	16.4	
5	5.0	18	11.5	
10	0.2	$\frac{1}{4}$	24.8	26.2
10	0.2	18	17.8	
10	1.0	18	23.6	

this influence is brought out. It appears that a concentration of sodium chloride of about 30 grams per liter causes an error of about 0.75 per cent. of the total sulphur from this source alone. The importance of this error is evident when it is remembered that alkali chlorides are commonly present in considerable quantity in solutions which have to be analyzed for sulphur. The effect of concentrations of chlorides greater than the above were not studied. Again, it should be stated that the presence of sodium chloride does not occasion the occlusion of the chloride as such. The ignited precipitates contain only a minute trace of chloride. Later we found that precipitates before ignition contained a small quantity, but the evidence goes to show that it is present as barium chloride, and that it is partly eliminated as hydrochloric acid during ignition.

The Volatilization of Sulphuric Acid when Precipitates Are Heated.

In many instances the losses due to solubility and the occlusion of sodium sulphate, together, make up nearly the whole deficit in sulphate

determinations, but in others, *e. g.*, where the quantity of acid or of sodium chloride is considerable, the loss still unaccounted for may be equal to the sum of the above-named errors. As we could conceive of no other possibility, we tried experiments to find if the precipitates lost anything when they were heated.

To this end precipitates prepared and washed as usual were dried (in a toluene bath) at 105°. They were then carefully detached from the paper by tapping, and put into a tubulated platinum crucible (Gooch's) adapted to the determination of any volatile product.[1] The joint between cover and crucible was sealed with sodium tungstate, and the outlet tube was connected with a Liebig potash bulb which contained 10 cc. water and 1 cc. Merck's perhydrol free from sulphur. A current of pure dry air was drawn through the apparatus while the crucible was heated strongly by means of a Bunsen burner, the outlet tube from time to time being also heated with the free flame to drive out the volatile products. The contents of the bulb proved to contain sulphuric acid when tested in the usual way. A large number of subsequent experiments showed that barium sulphate precipitates thrown down from acidified sodium sulphate solutions, *always* lose sulphuric acid when they are ignited in this way. The tubulated crucible was used for all the earlier determinations given in this paper. For the greater losses caused by the chlorides of potassium and ammonium, it gave, for some reason, results entirely too low. A platinum combustion tube[2] and boat were therefore substituted. The tube must be heated with a blast, otherwise the barium sulphate in the boat does not reach a temperature comparable with that in an ordinary sulphur determination. In cases where the loss is large, two bulbs are required for complete absorption. Perhydrol must be used in the bulbs, otherwise there is a partial loss of sulphur dioxide which is formed by the dissociation of the sulphuric acid. Blanks were tried at various times but no trace of sulphuric acid was ever obtained from any of them. At first it was suspected that the volatilized sulphur came from a decomposition of the barium sulphate. This was disproved by the fact that the precipitates soon reach a constant weight, a point which is further supported by the work of Mostowitsch,[3] who found that barium sulphate does not appreciably dissociate under 1400°. The possibility of a reduction of the sulphate to sulphide, either by fibers of filter paper or by the hydrogen of the flame passing through the hot platinum, and a decomposition of the sulphide by moisture at the same time, was also considered. The flame surely had nothing to do with the

[1] See W. F. Hillebrand, *Bulls. U. S. Geol. Surv.*, Nos. 305 and 422, where the apparatus is described and applied to the determination of water in minerals.

[2] The authors wish to acknowledge their indebtedness to Mr. P. H. Walker, of the Bureau of Chemistry, for the loan of the combustion tube.

[3] *Metallurgie*, **6**, 450 (1909).

case, because the results were the same when the crucible was heated by a resistance furnace to a temperature of about 1000°. Numerous tests on precipitates which had been heated in either way proved that they were not alkaline after ignition. These tests were very carefully conducted with hot boiled water and a drop of phenolphthalein. The solution never changed color; isolated grains sometimes turned pink, but a drop of 0.01 N acid was sufficient to dispel the color. This sets at rest any question of the decomposition of barium sulphate. Finally, it was shown that the quantity of sulphuric acid lost by volatilization varies greatly according to the conditions under which the precipitate was formed, but keeps pace with the deficits found on precipitates prepared under parallel conditions. Experiments showed that nearly all the loss occurs above 500°, but to heat the precipitates to this temperature would not remedy the difficulty; firstly, because water is retained by the precipitate at that temperature, and secondly, because the real difficulty is the failure to convert the sulphuric acid into barium sulphate during precipitation.

Influence of Various Factors on the Loss by Volatilization.

In general, these factors are the same as those which condition occlusion; but the degree of their influence is different.

(*1*) *Effect of Acid Concentration.*—Table IX shows how this loss varies with the concentration of hydrochloric acid in the solution from which the barium sulphate is thrown down. The loss is given in terms of bar-

TABLE IX.—SULPHURIC ACID (IN TERMS OF BARIUM SULPHATE) LOST BY 2 GRAMS PRECIPITATE.

Precipitation from Pure Sodium Sulphate; $V = 350$ cc.

cc. 20 per cent. HCl.	Mg. BaSO$_4$.									Mean. Mg.
0.1	0.5	0.3	...	...	...	...	...	...	...	0.4
0.2	0.4	0.6	...	...	...	...	...	...	...	0.5
1.0	2.4	1.8	2.0	2.6[1]	2.7	1.6	2.4[1]	2.1	2.7	2.2
5.0	5.4	6.4[1]	3.8[1]	4.3	3.8	4.8[1]	5.1	4.5[1]	...	4.7
10.0	3.1	2.9	3.4[1]	2.6[1]	2.8[1]	3.1	...	...	...	2.9
20.0	1.8	2.4	1.7	1.3	1.7	...	...	...	...	1.8

ium sulphate, since the sulphuric acid volatilized should have been converted into barium sulphate during precipitation. It will be noted that the loss increases with the strength of acid up to 5 cc. of 20 per cent. hydrochloric acid in 350 cc., and then falls again. As said before, nearly all our work has been done with 0.2 cc. and 1.0 cc. of 20 per cent. hydrochloric acid in a total volume of 350 cc. (lines 2 and 3). Here the loss seems nearly proportional to the acid concentration, which again is a reason for using the smaller quantity of acid. If the sulphate is poured into the barium chloride instead of *vice versa*, the volatilization losses are reduced. Two different precipitates, of about 2 grams each, formed in

[1] The figures marked [1] were derived by doubling the results obtained on 1 gram.

this way, in solutions containing 1 cc. 20 per cent. hydrochloric acid, lost sulphuric acid which yielded 0.3 mg. and 0.8 mg. barium sulphate, respectively. The quantities marked 1 in the table were derived by doubling the results obtained from 1 gram of precipitate, thus showing that the losses are proportional to the weight.

(2) *Effect of Sodium Chloride.*—Table X shows that when barium sulphate is precipitated from solutions containing sodium chloride, the acid remaining constant, the loss by volatilization is greatly increased. As chlorides are usually present where sulphates are to be determined, the importance of this fact will be instantly recognized.

(3) *Influence of Time.*—The data on this point show higher losses when precipitates are filtered and washed immediately after precipitation, and a gradual reduction of the losses when the precipitates are allowed to stand in contact with the supernatant liquid. A few data on this point are given in Table X. Where accuracy in the determination

TABLE X.—EFFECT OF NaCl ON VOLATILIZATION LOSS.

H_2SO_4 (in mg. $BaSO_4$) lost by 2 grams precipitate.

Grams NaCl.	0.2 cc. 20 per cent. HCl.		1.0 cc. 20 per cent. HCl.			5.0 cc. 20 per cent. HCl.	
0	0.5[1]	...	2.2[1]	...	...	4.7[1]	...
2	1.7	3.4[2]	4.6	...	...	...	6.6[2]
5	5.4	5.3[3]	10.0	...	...	11.9	...
..	5.1	5.1	8.8	...	...	10.1	...
10	8.8	...	13.7	11.9	14.1[2]	...	...
..	7.1	...	11.6	12.0	6.8[4]	...	...
..	...	...	...	...	12.9	...	...

of sulphur is required, it is therefore evident that there is a real gain in allowing the precipitate to stand. We have shown that the errors, both from occlusion of sodium sulphate and from volatilization, are in this direction and the same must be true of "solubility," if there is any difference at all.

(4) *Effect of Rate of Addition of the Reagent.*—We have stated previously that the rate at which the reagent is added to the solution makes little difference in the quantity of alkali sulphate retained by the precipitate. The loss by volatility, however, is markedly lowered by increasing the rate (Table XI).

The Composition of Rapidly Formed Precipitates.

The direct and natural inference from the results in this table is that rapid precipitation reduces the amount of "free" acid in the precipitate. A closer study proved this to be true. Rapid precipitation has also another effect, *viz.*, to increase the quantity of chlorine in the precipitate.

[1] Averages from Table IX.

[2] Filtered immediately after precipitation.

[3] Stood 3 hours on the steam bath.

[4] Stood 70 hours in the cold. All others stood 18 hours.

TABLE XI.—EFFECT OF RATE OF PRECIPITATION ON VOLATILIZATION LOSS.
H$_2$SO$_4$ (in mg. BaSO$_4$) lost by 2 grams precipitate.

Grams NaCl.	0.2 cc. 20 per cent. HCl. Time of precipitation.		1 cc. 20 per cent. HCl. Time of precipitation.		5 cc. 20 per cent. HCl. Time of precipitation.	
	3-6 min.[1]	9 sec.	3-6 min.[1]	9 sec.	3-6 min.[1]	9 sec.
0	0.5	0.4	2.2	...	4.7	0.4
5	5.2	0.6	...	...	...	...
..	...	0.7	...	...	...	...
10	...	...	12.4	3.7	...	...
..	...	...	...	4.6	...	...

Indeed, all *unignited* barium sulphate precipitates contain chlorine, however carefully they are washed. Four solutions of identical composition, *viz.*, 1.21 grams Na$_2$SO$_4$ + 5 grams NaCl + 0.2 cc. 20 per cent. hydrochloric acid in 350 cc., were precipitated in pairs, two slowly and two rapidly. The time for each of the first pair was 3–6 minutes, for the second pair 9 seconds. After the usual washing, these precipitates were dried at 105°. The chlorine was determined by Hulett and Duschak's method. 6.3 mg. and 7.2 mg., respectively, of silver chloride were obtained from the first pair, the 17.8 mg. and 20.9 mg. from the second pair. We have previously seen that the total sodium is slightly diminished by a rapid precipitation, which could not be the case were the chlorine taken up in the form of sodium chloride. Now, since barium sulphate, which is precipitated from *sulphuric acid*, also contains chlorine which Hulett and Duschak have shown to be likewise increased by rapid precipitation, and which in their case must be in the form of barium chloride, we conclude that the chlorine in all the precipitates is in the same form.

Since both "free" sulphuric acid and barium chloride exist together in the same precipitate, it is not surprising to find that during ignition some hydrochloric acid is always volatilized, formed, of course, by the chemical reaction of the two substances. We at first supposed that by this means the rapidly formed precipitates, containing as they do more chloride, reduced the volatilization of sulphuric acid. But experiment showed that the amount of hydrochloric acid thus formed is about the same, whether the precipitate had been formed slowly or rapidly; consequently the washed precipitate must contain *less* "free" sulphuric acid in the latter case. A slowly formed precipitate loses, in this way, practically all its chlorine, but a rapidly formed precipitate still contains a considerable amount. Two such precipitates formed in solutions containing 5 grams NaCl + 0.2 cc. 20 per cent. hydrochloric acid in 350 cc. retained 10.3 mg. and 10.8 mg. chlorine (in terms of silver chloride).[2] In

[1] The values given for slow precipitation are average values from Tables IX and X.

[2] Our precipitates are thus, at least partially, analogous in composition to Hulett and Duschak's, though apparently the amount of sulphuric acid their precipitates absorb, if any, is always less.

spite of this fact, we may still lose several milligrams of sulphuric acid (in terms of barium sulphate) on heating. After ignition one may extract from such a precipitate both sodium chloride and sodium sulphate, though not the total quantity of the sodium (Table XII).

TABLE XII.—WATER EXTRACT (IN MG.) FROM IGNITED PRECIPITATES.

Precipitation from Na_2SO_4 + 5 grams NaCl ÷ 0.2 cc. 20 per cent. HCl; V = 350 cc.

	Water extract.			Na_2SO_4 left in precipitate after extraction by water.[1]	Total sodium, calc. as Na_2SO_4.[2]
	Total.	NaCl.	Na_2SO_4.		
Precipitated in 9 sec..........	8.6	7.1	1.5	2.0	12.1
Precipitated in 9 sec.........	8.8	6.0	2.8	2.0	12.1
Precipitated by pouring }	8.6	4.5	4.1	4.0	13.6
Na_2SO_4 into $BaCl_2$ in 10 sec {	11.8	2.5	9.3	3.3	15.1
Precipitated in about 3 min...	14.5	trace	14.5	...	14.5
Precipitated in about 3 min...	16.2	trace	16.2	...	16.2

We have treated the subject of rapid precipitation so much in detail because it has been advocated as the essential condition of an analytical method for the determination of sulphur by Hintz and Weber.[3] From the preceding it will now be understood that the losses by volatilization of sulphuric acid and occlusion of sodium sulphate are in the first place reduced by reason of a more complete conversion of the original sulphate into barium sulphate, and in the second place, partially compensated by an absorption of barium chloride by the precipitate. Our own results, obtained by rapid precipitation, which are given in Table XIII, prove it

TABLE XIII.—RESULTS FROM RAPID PRECIPITATION (IN 9 SEC.).

From solution as below: V = 350 cc.

Salts. cc. 20 per cent. HCl.	Na_2SO_4 0.2		Na_2SO_4 + 5NaCl 0.2	Na_2SO_4 + 10NaCl 1	K_2SO_4 + 10KCl. 0.2	
$BaSO_4$ (calc.)	2.0199	2.0224	2.1352	2.0069	2.0105	2.0223
$BaSO_4$ (found)...........	2.0142	2.0163	2.1354	2.0090	2.0089	2.0160
Chlorine[4]................	...	0.4	2.6	1.0	0.8	...
Chlorine (corr.)...........	...	—1.2	—7.5	—3.1	—2.5	—2.5
Alkali sulphate..........	5.3	4.7	8.9	4.4	9.1	10.1
Do. (corr.)..............	3.7	3.3	6.2	3.0	3.7	4.1
Sy. (corr.)..............	2.1	1.9	1.0	1.0	2.4	2.4
Vy. (corr.)..............	0.6	0.6	0.6	2.1	5.0	4.4
Sum of corrs............	6.4	4.6	0.3	3.0	8.6	8.4
Deficit.................	5.7	6.1	—0.2	—2.1	1.6	6.3
	—0.7	1.5	—0.5	—5.1	—7.0	—2.1

[1] Presumably only Na_2SO_4 remained in the precipitate; chlorine was not tested for.

[2] Had an extraction with sulphuric acid, instead of water, been made, all would have been changed to sulphate.

[3] Z. anal. Chem., 45, 31 (1906).

[4] After ignition the chlorine is doubtless present in the precipitate as sodium chloride; still it makes no difference whether it is regarded as combined with sodium or barium. The sodium is always more than equivalent to the chlorine and we may regard (1) all the chlorine as $BaCl_2$ and all the sodium as sulphate, or (2) all the chlo-

far superior to the ordinary slow precipitation. It should be stated that the conditions we followed were not exactly those recommended by Hintz and Weber. They used 1 cc. conc. hydrochloric acid in 450 cc., and, having previously diluted the reagent to 100 cc. and heated to boiling, poured it in all at once. We adopted the variations in the hope of greater uniformity. The results obtained are, in fact, similar to theirs, both in uniformity and accuracy. They are not so reliable as the corrected results when the precipitation is done slowly, but they are often surprisingly good.

Total Sulphuric Acid Occluded by Barium Sulphate Precipitates.

It is now evident that the total quantity of free sulphuric acid originally present in all barium sulphate precipitates is greater than that lost by volatilization; a part of it is held back by the barium chloride which the precipitates also retain, and an equivalent of hydrochloric acid is volatilized in its place. Although no part of the analytical problem, we regarded it as a matter of some interest to determine the total quantity of sulphuric acid occluded under various conditions. Accordingly, the volatile products were collected as usual and both the hydrochloric and sulphuric acids were determined in each. Table XIV shows the quantities

TABLE XIV.—EFFECT OF RATE OF PRECIPITATION ON CHLORINE[1] VOLATILIZED IN THE IGNITION OF PRECIPITATES.

Chlorine (in mgs. AgCl) in 2 grams precipitate.

Time of precipitation.

	0.2 cc. 20 per cent. HCl.		1 cc. 20 per cent. HCl.		5 cc. 20 per cent. HCl.		10 cc. 20 per cent. HCl.	20 cc. 20 per cent. HCl.
NaCl.	3–6 min.	9 sec.	3–6 min.	9 sec.	3–6 min.	9 sec.	3–6 min.	3–6 min.
0	0.6	2.8	4.8	...	2.3	5.3	2.6	0.6
..	...	...	5.9	...	1.8	...	1.3	2.0
5	6.3	3.4	5.6	...	...	...	...	...
..	3.1	4.0	5.0	...	...	...	...	...
10	6.0	...	3.5	8.7	...	...	...	...
..	4.8	...	3.4	5.1	...	...	...	...

of hydrochloric acid (in terms of silver chloride) which are lost by precipitates formed under stated conditions. Table XV gives, in parallel columns, the quantities of hydrochloric acid volatilized, in terms of sulphuric acid, and the quantities of sulphuric acid which are lost as such.

rine as NaCl and the rest of the sodium as sulphate. If $a = $ Cl found and $b = $ Na$_2$SO$_4$ extracted with sulphuric acid, the corrections would be:

$$(1)\ b\ \frac{BaSO_4 - Na_2SO_4}{Na_2SO_4} - a\ \frac{BaCl_2}{2Cl}. \quad (2)\ \left[b - a\frac{Na_2SO_4}{2Cl}\right]\frac{BaSO_4 - Na_2SO_4}{Na_2SO_4} -$$

$$\frac{2NaCl}{2Cl}\ a = \frac{BaSO_4 - Na_2SO_4}{Na_2SO_4}\ b - \frac{BaSO_4 - Na_2SO_4 + 2NaCl}{2Cl}\ a,$$

which is identical with (1).

[1] This quantity equals the total quantity occluded in slow precipitations; it is less than the total in rapid precipitations.

TABLE XV.—SULPHURIC ACID (IN MG.) OCCLUDED BY 2 GRAMS PRECIPITATE

cc. 20 per cent. HCl	0.2			1.0			5.0			10.0			20.0		
Volatilized as	HCl.	H₂SO₄.	Total.	HCl.	H₂SO₄.	Total.	HCl.	H₂SO₄.	Total.	HCl.	H₂SO₄.	Total.	HCl.	H₂SO₄.	Total.
Grams NaCl.					A. Slow Precipitation.										
0	1.6	0.2	1.8	1.8	0.9	2.7	0.7	1.9	2.6	0.7	1.2	1.9	0.4	0.7	1.1
5	1.6	2.2	3.8	1.8	3.9	5.7	...	4.6	...	...	...	...	...	...	...
10	1.8	3.4	5.2	1.2	5.2	6.4	...	...	...	...	...	...	...	...	...
					B. Rapid Precipitation.										
0	1.2	0.3	1.5	...	...	...	1.8	0.2	2.0	...	...	...	...	...	...
..	1.3	0.3	1.6	...	...	...	...	...	...	...	...	...	...	...	...
..	1.0	0.2	1.2	...	...	...	...	...	...	...	...	...	...	...	...
10	...	...	...	3.0	1.5	4.5	...	...	...	...	...	...	...	...	...
..	...	...	...	1.7	1.9	3.6	...	...	...	...	...	...	...	...	...

A comparison of the figures for slow and rapid precipitation shows that the hydrochloric acid volatilized is not much influenced by the rate of precipitation, though it is usually a little greater when the precipitation is rapid. The results on page 600 show, however, that the *total* chloride present in the precipitate is much increased by the rate at which it is thrown down. It follows that rapidly formed precipitates must occlude less free sulphuric acid, and thus a rapid rate of formation reduces the volatility loss.

The Correction of Sulphate Determinations.—The following tables (XVI–XVIII) contain a series of determinations of sulphur in sodium sulphate under stated conditions, giving the proper corrections for "solubility," occlusion, and volatility. From the horizontal lines designated "deficit" the original percentage loss may be seen to vary

TABLE XVI.—CORRECTION OF SULPHATE DETERMINATIONS.
Pptn. from Na₂SO₄; V = 350 cc. : 0.1 cc. 20 per cent. HCl.

	1.	2.	3.	4.	Mean.
BaSO₄ (calc.)	2037.3	2051.0	2041.6	2016.3	....
BaSO₄ (found)	2030.9	2046.1	2033.2	2010.0	....
Na₂SO₄ (found)	8.7	7.1	9.1	8.3	8.2
Na₂SO₄ (corr.)	6.1	5.0	6.4	5.8	5.7
Sy. (corr.)	1.0	0.9	1.0	1.0	1.0
Vy. (corr.)	0.3	0.3	0.3	0.3	0.3
Sum of corrs.	7.4	6.2	7.7	7.1	7.0
Deficit	6.4	4.9	8.4	6.3	6.5
Loss	—1.0	—1.3	0.7	—0.8	0.8
Percentage loss	0.05	0.07	0.03	0.04	0.04
Percentage error with average corr.	0.03	0.10	0.07	0.0	....

Figures in italics in this and all subsequent tables include calculated corrections; also corrections not experimentally determined in the case under consideration.

In 4 the precipitate was boiled for 3 hours with 10 grams BaCl₂ in 300 cc. water.

from 0.25–0.79 per cent., while after correction the error falls to 0–0.15 per cent.   In the great majority of cases it is 0.10 per cent. or less.   The greater errors in all instances occur in determinations where the conditions were later found to be faulty.

TABLE XVII.—CORRECTION OF SULPHATE DETERMINATIONS.
Precipitation from Na$_2$SO$_4$;   V = 350 cc.: 0.2 cc. 20 per cent. HCl.

	1.	2.	3.	4.	5.	6.
BaSO$_4$ (calc.)	2002.2	2000.0	2040.7	2037.4	1995.4	2044.5
BaSO$_4$ (found)	1996.7	1992.5	2035.7	2029.4	1985.5	2032.6
Na$_2$SO$_4$ (found)	9.2	9.8	11.9	11.6	11.3	10.5
Na$_2$SO$_4$ (corr.)	6.4	6.9	8.3	8.1	7.9	7.3
Sy. (corr.)	1.0	1.0	0.6	0.7	1.0	1.0
Vy. (corr.)	0.6	0.6	0.6	0.6	0.6	0.6
Sum of corrs.	8.0	8.5	9.5	9.4	9.5	8.9
Deficit	5.5	7.5	5.0	8.0	9.9	11.9
Loss	—2.5	—1.0	—4.5	—1.4	0.4	3.0
Percentage loss	0.12	0.05	0.22	0.07	0.02	0.15

3 and 4 filtered in $^1/_2$ hour; volatility loss a little doubtful.
5 and 6 filtered through Gooch crucible.

TABLE XVIII.—CORRECTION OF SULPHATE DETERMINATIONS.
Precipitation from Na$_2$SO$_4$.   V = 350 cc.

cc. 20 per cent. HCl.	1. 0.5	2. 1.0	3. 1.0	4. 1.0	5. 1.0	6. 1.0
BaSO$_4$ (calc.)	2020.6	2052.8	2020.1	2031.9	1997.5	2026.3
BaSO$_4$ (found)	2013.2	2044.2	2008.1	2016.1	1986.9	2011.2
Na$_2$SO$_4$ (found)	8.0	...	6.9	6.9	8.2	8.9
Na$_2$SO$_4$ (corr.)	5.6	5.5	4.9	4.9	5.8	6.3
Sy. (corr.)	1.0	1.6	3.0	6.4	4.4	4.3
Vy. (corr.)	2.2	2.2	2.2	2.2	2.2	2.2
Sum of corrs.	8.8	9.3	10.1	13.5	12.4	12.8
Deficit	7.4	8.6	12.0	15.8	10.6	15.1
Loss	—1.2	0.7	1.9	2.3	—1.8	2.3
Percentage loss	0.06	0.03	0.10	0.12	0.09	0.11

Table XIX gives corrected determinations of sulphur in the presence of various quantities of sodium chloride—a very common case in practice.   The errors range from 0.8–1.8 per cent. before correction and are reduced by correction to from 0.03–0.14 per cent. with a mean error of only 0.08 per cent.

The determinations given in Tables XVI, XVII and XVIII are uniform enough to make satisfactory corrections by the use of the constants which are the means of the different determinations.   Thus, in Table XVIII, the constants are, for 2 grams precipitate, volatility, Vy. = 2.2 mg.; occlusion, Oc. = 5.1.   For solubility in this case individual cor-

TABLE XIX.—CORRECTION OF SULPHATE DETERMINATIONS WHEN CHLORIDES ARE PRESENT.

Precipitation from Na_2SO_4.

	0.2 cc. 20 per cent. HCl.			1.0 cc. 20 per cent. HCl.				
Grams NaCl.	5.0	5.0	10.0	3.0	5.0	8.0	10.0	10.0
$BaSO_4$ (calc.).	2011.5	2002.8	2021.7	2007.4	1977.0	2013.7	2015.3	1990.9
$BaSO_4$ (found)	1991.4	1986.7	1997.4	1990.2	1954.3	1990.3	1991.5	1955.0
Na_2SO_4 (found)	17.1	17.5	17.8	11.4	13.5	11.2	10.6	23.6
Na_2SO_4 (corr.)	12.0	12.3	12.5	8.0	9.5	7.9	7.4	16.7
Sy. (corr.)...	1.1	0.7	2.3	1.6	1.6	1.6	1.6	2.7
Vy. (corr.)....	5.3	5.3	8.8	6.0	10.0	11.8	13.7	13.7
Sum of (corr.)	18.4	18.3	23.6	15.6	21.1	21.3	22.7	33.1
Deficit.......	20.1	16.1	24.3	17.2	22.7	23.4	23.8	35.9
Loss.........	1.7	—2.2	0.7	1.6	1.6	2.1	1.1	2.8
Percentage loss.....	0.08	0.11	0.03	0.08	0.08	0.10	0.05	0.14

rections are required because Experiments 1 and 2 were filtered after 18 hours, the rest in a short time. In one or two instances, also, a little fine precipitate was washed over the top of the paper and was recovered in the filtrate, thus increasing the usual correction. In Table XVI, the average corrections are: Vy. = 0.3 mg., Oc. = 5.7 mg., Sy. = 1.0 mg., total = 7.0 mg. In Table XVII, the corrections are: Vy. = 0.6 mg., Sy. = 1.0, Oc. = 7.5; total = 9.1. Here the average cannot be applied quite so well as the individual corrections. In Table XIX, which includes cases where sodium chloride is originally present, Vy. and Oc. are much larger and both are quite sensitive to conditions. It is wise in such cases to apply individual corrections, making a duplicate precipitation under identical conditions, on which the volatility is determined.

B. The Precipitation of Potassium Sulphate by Barium Chloride.

The same sources of error occur in precipitating barium sulphate from potassium as from sodium sulphate.

Losses Due to "Solubility."—The loss from solubility is of the same order of magnitude and is increased only very slightly by the addition of potassium chloride to the sulphate solution, in spite of the statements to the contrary, already quoted (see p. 592). It is not surprising that many who have noted large errors in the determination of sulphur where alkali chlorides are present should have suspected that these were due to solubility. Of course, if this view is correct, the loss will depend, not on the quantity of the precipitate, but on other conditions, chiefly the volume and composition of the solution. Our results show, on the contrary, that the errors depend on the quantity of the precipitate, *i. e.*, they are percentage errors.

A weighed quantity of one of our precipitates, which had been heated

to redness, was put into a beaker, to which was added 10 g. potassium chloride, 350 cc. water, and 0.2 cc. 20 per cent. hydrochloric acid.   This was heated to boiling and kept on the steam bath, with occasional stirring, for several hours.   Then it was left to stand over night.   Next morning it was filtered on a small filter, washed free of chlorine and weighed.

	Gram.		Gram.
$BaSO_4$ taken...........	0.0683	Found in precipitate........	0.0668
$BaSO_4$ found...........	0.0694	" " filtrate............	0.0026
$BaSO_4$ loss.............	0.0011		0.0694

Objection might be taken to the use of a *heated precipitate* here, on the ground that there might be an irreversible change in barium sulphate on heating, leaving finally another phase of different solubility.   A microscopic examination made by Dr. F. E. Wright, of this laboratory, showed that the index of refraction of the substance was little affected by heating.   It remained about 1.63, the value for natural barite, and in no other respect did the substance appear to be changed, except that the crystallization became somewhat coarser.   Still, to leave no doubt in the matter, further experiments were tried on the unheated substance.

A weighed quantity of pure dry potassium sulphate was dissolved in 350 cc. water, with given quantities of potassium chloride and hydrochloric acid.   The solutions were precipitated boiling hot by 0.5 cc. more than the calculated quantity of barium chloride, kept hot a few hours and allowed to stand over night, after which the procedure was similar to that in the experiment just described.

TABLE XX.—DIRECT DETERMINATION OF THE SOLVENT INFLUENCE OF POTASSIUM CHLORIDE ON BARIUM SULPHATE.

Precipitation of K_2SO_4 + KCl + 0.2 cc. 20 per cent. HCl; V = 350 cc.

KCl. Grams.	K_2SO_4. Gram.	$BaSO_4$ calc. Gram.	$BaSO_4$ found in ppt. Gram.	$BaSO_4$ found in filtrate. Gram.	Loss. Gram.
5	0.0689	0.0923	0.0896	0.0013	0.0014
10	0.0873	0.1169	0.1128	0.0014	0.0027

TABLE XXI.—LOSSES (IN MG.) DUE TO SOLUBILITY OF $BaSO_4$.

Precipitated from solutions containing sulphates and chlorides (as below); and 0.2 cc. 20 per cent. HCl.   Original volume 350 cc., total volume 650–700 cc.

From solutions containing	Na_2SO_4 + NaCl (as below).			K_2SO_4 + KCl (as below).			$(NH_4)_2SO_4$ + NH_4Cl (as below).		
	0.	5 gms.	10 gms.	0.	5 gms.	10 gms.	0.	5 gms.	10 gms.
$BaSO_4$ (in mg.)....0.9[1]	1.1	2.7	1.0	2.3	2.6	1.4	...	1.4	
In filtrate........ ...	0.7	2.3	0.8	2.6	2.8	1.2	...	...	
...	...	...	...	...	2.8	1.2	...	...	
...	...	...	...	1.3[2]	1.4[2]	...	1.2[2]	1.4[2]	
Mean......... 0.9	0.9	2.5	0.9	2.1	2.4	1.2	1.2	1.4	

[1] This value is the mean of those given in Table I, line 1.

[2] In these determinations the total quantity of $BaSO_4$ was less than 0.1 gram; in all the others, it amounted to 2.0 grams.

Thus the barium sulphate recovered from the filtrate is not only of the same order of magnitude as it is where no alkaline chloride is present, but the total loss is greatly reduced when the mass of the precipitate is reduced. The evidence is very clear that potassium chloride has no influence on the solubility of barium sulphate within the limits of error of this method. Table XXI compares the solubility losses occasioned by the chlorides of sodium, potassium, and ammonium (which will be treated in detail in the next section), with the losses found when no chlorides are originally present.

Occlusion of Potassium Sulphate.—Barium sulphate occludes sodium and potassium sulphates in about equal quantity when the conditions are similar. The correction for potassium sulphate, $59/174 = (BaSO_4-K_2SO_4)/K_2SO_4$, is, however, evidently less. The quantity of potassium sulphate obtained from a precipitate by a single extraction with sulphuric acid (see p. 593) is about 80 per cent. of the total quantity.

		Mg.	Mg.	Mg.
1st extraction K_2SO_4	=	16.1	19.1	3.4
2d extraction K_2SO_4	=	3.3	4.8	0.7

It will be within the limits of experimental error, since the total quantities are so small, if we make a single extraction and add to the quantity obtained 25 per cent. more. The corrections in Tables XXIII and XXIV are made in this way.

Loss by Volatilization.—Precipitates from potassium sulphate lose notably more on ignition than precipitates from sodium sulphate. Even with very weak acid (0.2 cc. 20 per cent. in 350 cc.) and no potassium chloride in the original solution, the losses are 0.3 per cent. from this source alone if the precipitation is slow; with 10 grams potassium chloride and the same concentration of acid, the losses reach 0.7 per cent., and with 10 grams potassium chloride and 1 cc. 20 per cent. hydrochloric acid, 1.5 per cent. Others have noticed greater losses when potassium chloride was present, but have ascribed them to increased solubility. The data are tabulated in Table XXII.

Chlorine.—The chlorine is negligible in ignited precipitates from potassium sulphate, if the precipitation is slow.

Correction of Sulphur Determinations.—The corrected results in Table XXIII, on the sulphur in potassium sulphate, leaves little to be desired. The losses vary from —0.07 per cent. to +0.07 per cent. If potassium chloride is present in quantity, the important conditions to be followed are a small quantity of free acid and close attention to rate of precipitation. In Tables XXIV, Nos. 3, 5, 6, and 7, the rate was carefully regulated by attaching to the burette a capillary tip, both in the determination itself and in the duplicate precipitations for the determination of the volatility loss. Although the errors are large, the final losses vary

from —0.07 to +0.06 per cent. Nos. 1, 2, and 4 were done at an earlier stage of the work; they were precipitated more rapidly and without measuring the rate. The corrections which were made on precipitates slowly formed are therefore not applicable to them; the sum of the corrections is greater than the deficits, as our study of the composition of barium sulphate precipitates shows should be the case.

TABLE XXII.—EFFECT OF KCl ON THE LOSS OF SULPHURIC ACID BY VOLATILIZATION.
Losses in mg. $BaSO_4$ per 2 grams precipitate.

Grams KCl.	cc. 20 per cent. HCl.	Mg.	
0	0.2	6.4	....
5	0.2	13.7	14.3
5	1.0	23.9	21.8
10	0.2	18.1	17.6
10	1.0	30.7	....

TABLE XXIII.—CORRECTION OF SULPHATE DETERMINATIONS.
Precipitation from K_2SO_4; V = 350 cc.; 0.2 cc. 20 per cent. HCl.

$BaSO_4$ (calc.)	2002.8	20022.7	2013.0	2006.7
$BaSO_4$ (found)	1992.8	2009.3	2002.6	1995.2
K_2SO_4 (found)	10.1	11.4	...	...
K_2SO_4 (corr.)	4.1	4.7	4.4	4.4
Sy. (corr.)	1.0	0.8	1.0	1.0
Vy. (corr.)	6.4	6.4	6.4	6.4
Sum of corrs.	11.5	11.9	11.8	11.8
Deficit	10.0	13.4	10.4	11.2
Loss	—1.5	1.5	—1.4	—0.6
Percentage loss	0.08	0.07	0.07	0.03

TABLE XXIV.—CORRECTION OF SULPHATE DETERMINATIONS.
Precipitation from K_2SO_4 + KCl; V = 350 cc.; 0.2 cc. 20 per cent. HCl.

No.	5 grams KCl.			10 grams KCl.			
	1.	2.	3.	4.	5.	6.	7.
$BaSO_4$ (calc.)	2016.4	2017.2	2000.3	2019.2	1963.3	1998.5	2000.2
$BaSO_4$ (found)	2000.0	1997.7	1978.9	2000.3	1937.5	1969.4	1972.7
K_2SO_4 (found)	14.6	16.1	11.1	10.2	15.7	19.1	14.2
K_2SO_4 (corr.)	6.0	6.6	4.5	4.2	6.4	7.8	5.8
Sy. (corr.)	2.3	2.6	2.1	2.8	2.6	2.8	2.4
Vy. (corr.)	14.3	14.3	14.3	18.1	18.1	18.1	18.1
Sum of corrs.	22.6	23.5	20.9	25.1	27.1	28.7	26.3
Deficit	16.4	19.5	21.4	18.9	25.8	29.1	27.5
Loss	—6.2	—4.0	0.5	—6.2	—1.3	0.4	1.2
Percentage loss	—0.31	—0.20	—0.02	—0.31	—0.07	0.02	0.06

C. Precipitation of Ammonium Sulphate by Barium Chloride.

So far as the composition of a precipitate from ammonium sulphate is concerned, it does not differ essentially from precipitates previously

considered, *i. e.*, it contains ammonium sulphate, "free" sulphuric acid, and chlorine in quantities which increase with the rate of precipitation. This case differs from all others, however, in one respect—that the ammonium sulphate in it is almost entirely volatile at a red heat; therefore the loss from occlusion is much greater than it is in other cases.

The ammonium sulphate used in all the experiments described was entirely volatile at a red heat. It was dried to a constant weight at 130°.[1]

Losses Due to Solubility.—The influence of ammonium chloride on the solubility of barium sulphate has been treated exactly like the influence of potassium chloride, and it is shown in Table XXV that when small quantities of sulphur are determined in solutions containing ammonium chloride the total losses are almost negligible; hence the great losses when the quantities of sulphur are large could not be due to solubility.

TABLE XXV.—DIRECT DETERMINATION OF THE SOLVENT INFLUENCE OF AMMONIUM CHLORIDE ON BARIUM SULPHATE.

Precipitation of $(NH_4)_2SO_4 + NH_4Cl + 0.2$ cc. 20 per cent. HCl; V = 350 cc.

NH₄Cl. Grams.	(NH₄)₂SO₄. Gram.	BaSO₄ calc Gram.	BaSO₄ found in ppt. Gram.	BaSO₄ found in filtrate. Gram.	Loss.
5	0.0147	0.0259	0.0253	0.0012	—0.0006
10	0.0281	0.0495	0.0471	0.0024	0

Ammonium Sulphate Occluded by Barium Sulphate.—This was determined on 2 gram precipitates as follows:

The precipitate dried at 105° was dissolved in about 15 cc. concentrated sulphuric acid with gentle warming, cooled and poured into about 250 cc. cold water and filtered. The filtrate was then distilled with a slight excess of pure soda, and the distillate collected in excess (10 cc. 20 per cent.) of dilute hydrochloric acid. The latter was evaporated almost to dryness on the steam bath, then further with addition of platinum chloride. The ammonium chloroplatinate was separated with alcohol and dried at 130° in the usual way. The ammonium was calculated by the use of the empirical factor 0.081.[2] Not improbably one extraction with sulphuric acid may fail to remove the total quantity of ammonium sulphate, but, judging from experience with sodium and potassium sulphates, the amount left in the precipitate cannot be large, and since the exact quantity is not needed for correction purposes, this point was not settled.

An inspection of the data in Table XXVI shows that the losses from occlusion ($BaSO_4$ equiv.) are equal to about 1.2 per cent. of the total sulphur under the above conditions. The quantity of ammonium sulphate occluded by the precipitate varies little with the rate of precipita-

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[1] See Lunge and Stierlin, *Loc. cit.*

[2] See Treadwell, "Quantitative Analysis" (translated by Hall), p. 54.

TABLE XXVI.—OCCLUSION OF AMMONIUM SULPHATE (IN MG.) BY BARIUM SULPHATE.
Precipitation from 1.14 grams $(NH_4)_2SO_4 + NH_4Cl + 0.2$ cc. 20 per cent. HCl;
V = 350 cc.

	Time of precipitation.					
	5 g. NH$_4$Cl.		10 g. NH$_4$Cl.		10 g. NH$_4$Cl. 4 min.	
	6 min.	9 sec.	6 min.	9 sec.	6 min.	9 sec.
$(NH_4)_2PtCl_6$ obtained..........	48.8	45.9	51.6	50.4	5.0	4.5
Blank for reagents............	2.2	2.2	2.2	2.2	2.2	2.2
	46.6	43.7	49.4	48.2	2.8	2.3
$(NH_4)_2SO_4$ equiv.............	13.8	13.1	14.7	14.3	0.8	0.7
$BaSO_4$ equiv.................	24.4	23.1	25.9	25.2	...	...

tion; it is slightly less when the rate is rapid, just as it is with sodium and potassium salts. After the precipitates have been ignited, as the table shows, they contain only a trace of ammonium sulphate. It may be noted in passing that we have here a simple method for preparing pure barium sulphate.[1]

Loss by Volatilization.—We have seen in the preceding paragraph that all but a trace of the occluded ammonium sulphate is lost by heating, and, since this should have been converted into barium sulphate, the loss is comparatively large. The *total* loss by volatilization is still greater, because these precipitates, in complete analogy with others which we have considered, contain also "free" sulphuric acid. Table XXVII gives the losses due to volatilization. The column headed "free

TABLE XXVII.—LOSSES BY VOLATILIZATION (IN MG.) FROM 2 GRAMS PRECIPITATE.
Precipitation from $(NH_4)_2SO_4 + NH_4Cl$ and 0.2 cc. 20 per cent. HCl; V = 350 cc.

0 gram NH$_4$Cl.			5 grams NH$_4$Cl.			10 grams NH$_4$Cl.		
Due to $(NH_4)_2SO_4$.	Due to "free" H_2SO_4.	Total.	Due to $(NH_4)_2SO_4$.	Due to "free" H_2SO_4.	Total.	Due to $(NH_4)_2SO_4$.	"Due to free" H_2SO_4.	Total.
....	....	11.2	24.4	3.9	28.3	25.9	11.3	37.2
....	....	11.1	24.4	5.5	29.9	25.9	9.6	35.5

sulphuric acid" is obtained by difference. The determination of the total volatility gave a good deal of trouble. Very low results were obtained with the tubulated crucible. This may have been due to the retention of some of the sulphate by the sodium tungstate used to seal the joint. The platinum combustion tube and boat gave, when sufficient heat was applied, nearly correct results. As previously stated, two bulbs should be used for complete absorption.

Correction of Sulphate Determinations.—The following determinations in Table XXVIII will serve to show the magnitude of the losses, when sulphur is determined in ammonium sulphate, with or without ammonium chloride. It hardly need be said that these errors, reaching 2 per cent. at the maximum, would be very considerably increased in the presence

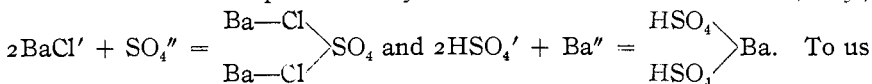[1] These two precipitates were ignited before testing for ammonium.

TABLE XXVIII.—CORRECTION OF SULPHATE DETERMINATIONS.

Precipitation from $(NH_4)_2SO_4 + NH_4Cl$. V = 350 cc.; 0.2 cc. 20 per cent. HCl.

	0 gram NH₄Cl.		5 grams NH₄Cl.	10 grams NH₄Cl.	
$BaSO_4$ (calc.).........	2014.2	2015.4	2015.2	2018.4	2013.8
$BaSO_4$ (found)......	2000.6	2000.6	1984.2	1979.2	1972.1
Corr. for Vy.........	11.2	11.2	28.3	37.2	37.2
Corr. for Sy.........	1.4	1.4	1.4	1.4	1.4
Sum of errors........	12.6	12.6	29.7	38.6	38.6
Deficit.............	13.6	14.8	31.0	39.2	41.7
Loss...............	1.0	2.2	1.3	0.6	3.1
Percentage loss.....	0.05	0.11	0.07	0.03	0.15

of more free acid. These data also make it evident why ammonium salts should be avoided, if possible, in solutions where sulphur is to be determined. Nevertheless, although the errors are large, it will be noticed in the table that the sum of the corrections very nearly make up the deficits found in actual determinations. It is therefore possible to get very good results in the presence of ammonium salts by applying the proper corrections.

D. Precipitation of Magnesium Sulphate by Barium Chloride.

Hulett and Duschak[1] found that magnesium sulphate gave, with barium platinocyanide, precipitates which agreed in weight with the calculated quantity. Their explanation was that the impurities in precipitates formed from sulphuric acid and barium chloride were due to the formation of complex salts by the union of intermediate ions; e. g.,

$$2BaCl' + SO_4'' = \begin{array}{c} Ba-Cl \\ \\ Ba-Cl \end{array}\Big\rangle SO_4 \text{ and } 2HSO_4' + Ba'' = \begin{array}{c} HSO_4 \\ \\ HSO_4 \end{array}\Big\rangle Ba. \text{ To us}$$

it seemed not improbable that the purity of the precipitates from magnesium sulphate might be due to the fact that barium sulphate has not the power to occlude magnesium sulphate while it can occlude the sulphates of the alkalies. If this view is correct, any salt of barium would do as well as the platinocyanide. The sequel shows that barium chloride, at least, gives similar results.

A standard solution of magnesium sulphate was prepared in the following manner: A solution of sulphuric acid of about the right strength was titrated against pure anhydrous sodium carbonate (heated to 300°). This was then neutralized by pure magnesium oxide and diluted to a definite weight. Details follow:

58.470 grams H_2SO_4 soln. required 1.0495 grams Na_2CO_3.
55.946 grams H_2SO_4 soln. required 1.0042 grams Na_2CO_3.

The titration was made at boiling temperature using phenolphthalein as indicator. Making corrections for buoyancy of the air,

[1] Loc. cit.

1 gram sol. = 0.016589 gram H_2SO_4 or 0.039488 $BaSO_4$.

1 gram sol. = 0.016591 gram H_2SO_4 or 0.039500 $BaSO_4$.

500.05 grams of this solution were now transferred to a platinum basin and evaporated with magnesium oxide (which had been especially freed from lime, sulphuric acid and water) until litmus paper showed that the solution was neutral. The undissolved excess of magnesium oxide was filtered off and thoroughly washed. It retained after washing 0.0173 gram SO_3. $BaSO_4$ found = 0.0503. The solution with washings was cooled and again diluted in a tared flask to a given weight, *viz.* 500.17 grams. After making corrections for buoyancy and subtracting the sulphur found with the undissolved magnesia, 1 gram solution = 0.039384 gram $BaSO_4$.

The results in Table XXIX are all obtained by the slow precipitation of weighed quantities of this standard solution under the same conditions as are found described on page 590. These data reveal the fact that very little magnesium sulphate is found in the precipitate, and show that the errors are much smaller than they are with the alkali sulphates. The volatility loss was a mere trace, immeasurable in three instances; in one case 0.3 mg. barium sulphate was found. In accord with this the chlorine is a little higher, though always less than 1 mg. As seen from the table, the original errors range from 0.01 to 0.21 per cent. in seven instances, while one result is 0.27 per cent. low.

TABLE XXIX.—CORRECTED RESULTS FOR $MgSO_4$.

	0.2 cc. 20 per cent. HCl.		1 cc. 20 per cent. HCl.				2 cc. 20 per cent. HCl.		Average.
Grams $MgSO_4$ soln.	51.265	50.697	50.991	51.199	50.283	50.301	51.384	49.882	...
$BaSO_4$ calc.	2019.8	1996.6	2001.2	2015.1	1980.3	1980.1	2022.3	1964.9	...
$BaSO_4$ found	2019.6	1998.0	1995.7	2013.6	1978.8	1980.8	2018.0	1962.4	...
Deficit	0.2	—1.4	5.5	1.5	1.5	—0.7	4.3	2.2	2.1
$MgSO_4$ in ppt	2.9	3.1	2.0	1.7	3.4	...	1.3	...	...
Cl in ppt	0.9	0.8	...	0.9	0.8	...	0.6	...	...
Vy. (corr.)	0	0	0	0	0	0	0	0	...
$MgSO_4$ corr.	2.7	2.9	1.9	1.6	3.2	2.3	1.2	2.3	...
$BaCl_2$ calc.	3.6	2.3	2.3	2.6	2.3	2.3	1.8	2.3	...
Sy. (corr.)	1.2	1.2	1.2	1.2	1.2	1.2	2.0	2.0	...
Loss	—1.1	—3.2	4.7	1.3	—0.6	—1.9	2.9	0.2	2.0

The results have been corrected for solubility, which was determined with two concentrations of acid, for magnesium sulphate and for chlorine. As shown on pages 602-3, it makes no difference whether we assume that magnesium chloride + magnesium sulphate are present, or that all the magnesium is in the form of sulphate and the chlorine in the form of barium chloride. The corrected results are only a trifle better than the uncorrected.

The Effect of Nitrates on the Precipitation of Barium Sulphate.

According to statements found in the literature,[1] nitrates must

[1] Treadwell, "Quantitative Analysis" (translated by Hall), p. 281; Folin, *J. Biochem.*, 1, 145 (1906).

removed from solutions in which sulphur is to be determined, otherwise the results are too high. Our work confirms these assertions. We have tried only the nitrate of sodium, but the same is probably true of potassium nitrate. Table XXX shows that when as little as 1 g. of nitrate

TABLE XXX.—EFFECT OF NITRATES ON SULPHATE DETERMINATIONS.

Results for $Na_2SO_4 + NaNO_3$.   Amount of 20 per cent. HCl = 0.2 cc.

	Grams $NaNO_3$.			
	1	2	5	10
$BaSO_4$ calc...........	2027.5	1968.8	2030.3	2057.5
$BaSO_4$ found.........	2036.7	1982.1	2046.3	2072.2
Na_2SO_4 found........	14.6	16.5	......	30.1
Sy. (corr.)	......	......	......	1.6
Surplus (uncorr.)......	9.2	13.3	16.0	14.7

is contained in 350 cc. solution, the results are nearly 0.5 per cent. too high. Five grams nitrate caused an error of 0.8 per cent. and 10 grams nitrate had practically the same effect. The cause of the error is not far to seek. The table shows that the precipitates contain an unusual amount of sodium. One of them, when boiled with water, gave up free alkali very slowly. Evidently, the precipitate occludes the nitrate, which forms caustic soda on ignition. On account of the hygroscopic nature of the impurity, the readiness with which it attacks platinum, and, moreover, the readiness with which it is avoided, it was not thought worth while to study this subject any further. It has been suggested that the low results obtained in the determination of sulphur might be compensated by the addition of the correct amount of nitrate to the solution before it is precipitated. A fair degree of approximation might perhaps be reached in this way.

Nature of the Precipitate.

We have seen that barium sulphate precipitates even when thrown down from solutions of rather simple composition are, nevertheless, themselves pretty complex. The form in which the impurities are held in the precipitate is a question worthy of interest. The facts indicate that not all of them sustain the same relation to it. The barium chloride, for example, is present in very small quantity (about 0.15 per cent.) in slowly formed precipitates, reaching several times that quantity in those which are rapidly formed. Now, as rate of formation is a condition which especially governs the fineness of the precipitate, and the finest precipitates contain the greatest amount of this impurity, it is natural to conclude that we have here a case of adsorption. Hulett and Duschak made similar observations in the precipitation of barium chloride by sulphuric acid. Rapidly formed, fine-grained precipitates contained the most barium chloride; one in particular, which was formed very slowly indeed, contained only 0.03 per cent.

of chlorine (about 0.08 per cent. barium chloride). If the substance were held in a purely mechanical way, one would expect all the impurities to be increased, diminished or removed by the same conditions. This, as we have seen, is not the case. It is equally difficult to see how the alkali sulphate in the precipitate can be retained mechanically. Not only are the different impurities differently affected by the same conditions, but the absorption is a markedly selective phenomenon. No alkali chloride seems to be taken up, nor are all the sulphates. The sulphates of sodium, potassium, ammonium, ferric iron, and probably aluminium,[1] are absorbed, while magnesium sulphate (see p. 613) is scarcely absorbed at all. The selective nature of the absorption indicates a solid solution. The fact that barium sulphate has an affinity for other sulphates is in accord with this. What we may call the secondary conditions seem to change comparatively little the quantity of the sulphate which is taken up. After a precipitate has been ignited the greater part of the soluble sulphate may be extracted by water (Table XII).

It is not unusual to find that the solubility of one salt in another decreases markedly with rise in temperature, but one would expect the system to return to its former state on cooling. The rapidity of the cooling, however, might prevent this. On the other hand, the mechanical conception would explain this fact as well. The ignition might be supposed to disrupt compact grains of the precipitate, thus exposing the soluble impurities to the action of the solvent.

The "free" sulphuric acid in the precipitate may be supposed to have been dissolved in the form of acid sulphate of the alkali metal. The quantity decreases much with rapid precipitation, which may mean that the fine-grained material is changed more readily by the barium chloride, on standing in the supernatant liquid. We know that the sodium sulphate changes somewhat also, but to a less extent.

At present there seems to be little prospect of adding to our knowledge of such fine-grained substances by microscopic investigation, so that we are not even certain of the homogeneity of the precipitates, and we are free to confess, in conclusion, that the facts we have accumulated are insufficient to decide the question of their true nature.

Summary.

1. The errors in the determination of sulphur in soluble sulphates have been investigated for those cases which most frequently occur in experimental work. Solutions of sodium, potassium, ammonium and magnesium sulphates have been studied, both in a state of purity and in the presence of varying quantities of hydrochloric acid and alkali chlorides. In a few systems the influence of sodium nitrate has also been studied.

[1] Schneider, *Z. physik. Chem.*, 10, 425 (1895); Creighton, *Z. anorg. Chem.*, 63, 53 (1909).

2. The most important sources of error are three in number, one arising from the solubility of the precipitate and the others from its composition. Two minor sources may also be mentioned.

a. The error from solubility depends chiefly on the quantity of free acid present. Contrary to the common belief, we find that the chlorides of sodium, potassium, and ammonium exercise a hardly appreciable influence on it. Under easily regulated conditions (0.2 cc. 20 per cent. HCl in 350 cc. original solution) it amounts to 1–2 mg. only. It is self-evident that this error (almost negligible for precipitates of 1 g. or more) becomes increasingly important, the smaller the precipitate.

b. All barium sulphate precipitates carry down with them quantities of the alkaline sulphates, varying with many conditions. In the case of pure acidulated sulphates, this quantity is not far from 0.5 per cent. It is especially affected by alkali chlorides, and may be more than doubled in this way. The correction depends of course on the atomic weight of the alkali metal. About 0.75 per cent. is the maximum quantity of ammonium sulphate absorbed by precipitates under conditions which have been investigated by us; the correction for it is, however, comparatively large (1.25 per cent.), because ammonium sulphate is entirely volatilized when the precipitate is ignited. Magnesium sulphate is scarcely absorbed at all by barium sulphate. The peculiar selective adsorption which barium sulphate exhibits, suggests the formation of solid solutions. The evidence on the subject is, however, too meager for a proof.

c. Barium sulphate, when precipitated from alkali sulphates, always occludes a certain amount of "free" sulphuric acid, which is probably taken up as acid sulphate of the alkali metal. It arises, of course, from the free acid added to the original solution and increases with it up to a certain point. Alkali chlorides decidedly increase the amount of it, and in the presence of much of the latter, it becomes the chief source of error. Aside from one or two qualitative observations, this loss seems to have been thus far entirely overlooked. It is greater for potassium than for sodium sulphate solutions. In one case a solution of the former containing 10 grams KCl and 5 cc. 20 per cent. HCl in 350 cc. lost 1.7 per cent. in this way.

d. All barium sulphate precipitates contain barium chloride. If the precipitation is made slowly (3–6 min. for 2 grams BaSO$_4$), the amount of this is only about 0.15 per cent. in the unignited precipitate, and since all but a trace of it is eliminated as hydrochloric acid during ignition, it is not a source of error. When a precipitate is very rapidly formed the amount of the barium chloride is multiplied several times and the chlorine is no longer entirely eliminated on ignition. The more rapid the precipitation, the finer the precipitate, and since the barium chloride

retained increases with the fineness, we regard it as probably held by adsorption.   The other impurities are diminished by rapid precipitation.

e. Sodium nitrate, and probably other nitrates also, are occluded by barium sulphate, giving results which are therefore too high.

3. An exact determination of sulphur, so far as we know, can only be done by correcting for the above-named errors.   Nitrates are to be avoided, also chlorides and ammonium salts as far as possible.   Corrections for occlusion and solubility can be made directly, but for volatility, unless one has a specially constructed platinum apparatus, a duplicate precipitation must be made under identical conditions.

We recommend the following conditions: Acidulate the solution (V = 350 cc.) with 2 cc. 2 per cent. hydrochloric acid and heat to boiling.   Precipitate slowly (about 4 min. for 2 grams precipitate) with constant stirring.   The rate may be regulated by a burette with a capillary tip attached.   Let the precipitate stand 18 hours before filtering; the losses from occlusion and volatility are both considerably higher when the filtration is done immediately.   Filter on paper and wash till 25 cc. of the washings show a barely perceptible opalescence with silver nitrate. Burn very slowly and carefully and heat over the burner to a constant weight.   To this result should be applied the corrections for the errors just discussed.   If the solution contains only alkali sulphate and known quantities of alkali chloride and hydrochloric acid, and if the directions above are carefully followed, the correction constants determined by us may be applied.   A more accurate result might perhaps be reached by the application of corrections experimentally determined for the case in hand.   Detailed methods for these are given in the body of the paper. In unknown mixtures of alkali chlorides the corrections must, of course, be actually determined.   To correct for the occlusion in such cases it would only be necessary to take the weight of the mixed alkali sulphates extracted from the precipitate, to convert them into barium sulphate and weigh; the difference between the weights of the barium sulphate and the mixture is the correction.   A carefully corrected determination of sulphur for the cases given should be accurate to 0.1 or 0.2 per cent. of the total sulphur.   A very good uncorrected determination may be obtained by precipitating *rapidly*, but it is due to partial compensation of variable errors, and is not in any case so reliable as one which is made by slow precipitation and corrected as described.

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