THE PHENOMENON OF OCCLUSION IN PRECIPITATES OF BARIUM SULFATE, AND ITS RELATION TO THE EXACT DETERMINATION OF SULFATE.

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In a previous publication from this laboratory[1] it was shown that barium sulfate precipitated from acidified solutions of alkali sulfate and chloride is in general contaminated by a number of impurities, the amount of which may be so great as to cause errors in sulfate determinations of one per cent. or more. Thus, precipitates made from acidified solutions of sodium sulfate and chloride contain, *before ignition*: (*a*) chloride, almost certainly as barium chloride;[2] (*b*) sodium sulfate; (*c*) sodium hydrogen sulfate; the amounts of these depend upon (1) the composition of the original solution, (2) the method of precipitation, (3) the length of the interval between precipitation and filtration. On igniting the precipitate, the barium chloride reacts with the sodium hydrogen sulfate as follows: $BaCl_2 + 4NaHSO_4 = BaSO_4 + Na_2SO_4 + 2HCl$; the hydrochloric acid gas escapes, and along with it is lost some *free sulfuric acid* by decomposition of the sodium hydrogen sulfate, if, as is usually the case, the amount of the latter is more than equivalent to the barium chloride originally present in the precipitate. The precipitates, *after ignition*,[3] therefore contain sodium sulfate (part of which is derived from the sodium hydrogen sulfate), and further may contain in certain cases chloride, most probably as barium chloride. The presence of chloride in the precipitate tends, of course, to make the analytical results too high; the alkali sulfate, on the other hand, tends to make the results of sulfate determinations too low, since we are weighing some sodium sulfate, but calculating as if the precipitate were pure barium sulfate. The precipitates from potassium and ammonium salts are entirely similar, except that no ammonium sulfate is found in the ignited precipitate, because it is lost by volatilization during ignition. The impurities in precipitates made from magnesium salts are similar in character, but smaller in amount.

It appeared very desirable to extend our knowledge of the nature of such precipitates, first, because of its intrinsic importance, and second, because of its general interest; for it is highly probable that entirely analogous phenomena are to be met with in the precipitation of many other substances. Consequently the present investigation was undertaken;

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[1] E. T. Allen and John Johnston, THIS JOURNAL, 32, 588–617.

[2] It seems to be impossible to determin with certainty whether alkali chloride is present or not; the evidence indicates that, if it is present, the amount must be, in general, relatively small. cf. *Loc. cit.*, p. 602, footnote.

[3] It is presumed that no barium sulfate was reduced during ignition—a condition easily fulfilled in practice.

as a result of which, a fairly complete and satisfactory discussion of the various factors which condition this occlusion is now possible.

We have confined ourselves almost entirely to determinations under standard conditions of the "occlusion," *i. e.*, of the total quantity of sodium sulfate in the ignited precipitate. The "volatility," *i. e.*, the amount of sulfuric acid lost during ignition, which is[1] a measure of the quantity of sodium hydrogen sulfate present in the unignited precipitate, is, as was shown in the previous paper, affected in the same way as is the "occlusion" by all the conditions, with the exception of the acidity of the original solution. This was to be expected, since we are dealing with the occlusion of sodium sulfate on the one hand, and of sodium hydrogen sulfate on the other; the amount of each depends upon the concentration of undissociated Na_2SO_4 and $NaHSO_4$ (making the usual assumption that the amount of occlusion is proportional to the concentration of undissociated molecules[2]); the latter in turn depends upon the concentration of acid in the original solution. Moreover, determinations of "volatility" would have entailed more than double the work.

In order to obtain comparable results on the amount of "occlusion," it is necessary that the work be performed under standard conditions; in the experiments to be described it was our aim to vary only one factor at a time: *e. g.*, the salt content of the original solution was varied, while the acid concentration, the rate of precipitation and the time of standing before filtration, were kept constant. The procedure followed is identical with that previously described,[3] except that in the case of the heavy metals, the amount of metal in the final residue was determined by a suitable method. The results given are in terms of the sulfate of the metal, and represent the amount obtained from one extraction. It is not pretended that the figure after the decimal point is significant; it is given merely as it was actually obtained; some of the figures given represent the mean from duplicate experiments, which did not differ from one another by more than 1 milligram.

In the previous work, it was found that the amount of occlusion is influenced by: (*A*) the concentration of metallic chloride in the original solution; (*B*) the concentration of hydrochloric acid; (*C*) the rate of precipitation; and (*D*) the length of the interval between precipitation and filtration. It may here be said that all the available evidence now indicates that the amount of occlusion is dependent upon (1) the composition of the original solution; (2) the fineness of grain of the precipitate, which in turn is conditioned by the degree of solubility of barium sulfate

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[1] With low rates of precipitation at least.

[2] Cf. Richards, *Z. anorg. Chem.*, **23**, 383 (1900).

[3] Cf. Allen and Johnston, *Loc. cit.*, p. 590; *J. Ind. Eng. Chem.*, **2**, 198; *Z. anorg. Chem.*, **69**, 108.

in the particular medium, the rate of precipitation, and the time and manner of standing between precipitation and filtration. The above factors will now be considered separately.

A. Effect of Increasing the Chloride Concentration.

Series of experiments were made, as above described, with sodium, lithium and potassium salts, with the results presented in Table I.

TABLE I.—EXPERIMENTAL RESULTS ON THE EFFECT OF ADDED CHLORIDE ON THE AMOUNT OF OCCLUSION OF ALKALI SULFATE.

Milligrams of alkali sulfate occluded by 2 grams BaSO$_4$.

Total vol. of soln. 350 cc.; 2 cc. 2 per cent. HCl; time of pptn. 4 mins.; time of standing 18 hours.

Sodium.		Lithium.		Potassium.	
Added chloride. Grams.	Occluded sulfate. Mg.	Added chloride. Grams.	Occluded sulfate. Mg.	Added chloride. Grams.	Occluded. sulfate. Mg.
0	8.2	0	7.4	0	11.2
5	17.4	5	12.8	5	13.4
10	19.0	25	23.0	10	16.4
20	24.4	50	28.0	40	25.4
30	31.4	70	29.4	80	35.0
50	38.4	100	47.6		
70	47.6				
100	45.8				

It is evident that an increase in the concentration of chloride in the original solution in each case causes an increase in the amount occluded. With sodium the amount occluded appears to reach a steady value when about 70 grams of sodium chloride are present; with lithium and potassium, it appears to be still increasing at the greatest concentrations studied.

In view of the similar behavior of the alkali metals in this respect, and of the fact that these occlusions have no precise or generally applicable physical significance, it seemed sufficient to investigate the occlusion of the other available metals at a few chloride concentrations only. Consequently the occlusion was determined for each sulfate in solutions (350 cc.) containing initially (*a*) 0 gram, (*b*) 5 grams, and (*c*) 25 grams of the chloride; the results are given in Table II.

The figures to which references to footnotes are attached are not strictly comparable with the others; in these cases, the addition of a larger quantity of acid was necessary in order to prevent hydrolysis. It proved impossible to make really comparable experiments with solutions containing ferric iron, owing to the hydrolysis of its salts in solutions containing little free acid; there is little doubt however that the amount of occlusion of ferric sulfate by precipitates of barium sulfate is of the same order of magnitude as that observed with the other metals. This would cause a greater error in an analysis, however, because the occluded ferric sulfate on heating loses all its sulfur trioxide, and consequently is weighed as oxide; it is better therefore, before precipitating, to reduce the iron to the ferrous state; it is still better to remove the iron entirely, if this course is possible.

TABLE II.—EXPERIMENTAL RESULTS ON THE AMOUNT OF OCCLUSION OF THE OTHER SOLUBLE SULFATES.

Milligrams of each sulfate occluded by 2 grams $BaSO_4$.
Conditions as in Table I, except where noted otherwise.

		Occluded sulfate in ppts. from solutions containing:		
Metal.	Formula of chloride.	0 grams chloride. Mg.	5 grams chloride. Mg.	25 grams chloride. Mg.
Cu	$CuCl_2.2H_2O$	13.2	17.6	21.0
Cd	$CdCl_2.2H_2O$	32.4	41.6	63.8
Zn	$ZnCl_2$	12.8	12.2[1]	14.6[1]
Ni	$NiCl_2.6H_2O$	9.6	15.4	20.6
Mn	$MnCl_2.4H_2O$	19.2	29.6	37.0
Al	$AlCl_3.6H_2O$	11.6	17.0	..
Fe″	$FeCl_2.4H_2O$	11.4[2]	25.0[2]	..
Mg	......	3.0	..	..

In order to facilitate comparison, Table III was prepared by recalculation and interpolation of the results contained in Tables I and II; the figures given therein represent the number of millimols of each sulfate (or of each metal) occluded in 1 gram of a precipitate made from a solution, the equivalent chloride concentration of which was initially (*a*) 0, (*b*) 0.1 *N* and (*c*) 0.1 molar.

TABLE III.—EFFECT OF CONCENTRATION OF THE METALLIC CHLORIDE ON THE AMOUNT OF OCCLUSION OF METALLIC SULFATE.

Millimols of sulfate occluded by 1 gram $BaSO_4$, when pptd. from solns. about 0.003 *N* in HCl, containing the metallic chlorides at the initial[3] concs. (*a*) 0, (*b*) 0.1 *N*, (*c*) 0.1 molar. Time of pptn. 4 mins.; time of standing 18 hours.

	Millimols sulfate occluded by 1 g. $BaSO_4$.		
Metal.	(*a*)	(*b*)	(*c*)
Mg	0.024	...	...
Li	0.033	0.040	0.040
Na	0.029	0.043	0.043
K	0.033	0.035	0.035
Al	0.017	0.02	0.03
Fe″	0.037	0.06	0.09
Ni	0.031	0.05	0.06
Cu	0.041	0.05	0.06
Zn	0.040	0.05	0.06
Mn	0.064	0.08	0.10
Cd	0.080	0.09	0.10

[1] Amount of acid was 5 cc. 20 per cent. HCl. With no added chloride and 2 cc. 20 per cent. HCl, the occlusion was only 2.6 mg.

[2] Amount of acid was 6 cc. 2 per cent. HCl.

[3] The final chloride concentration is in each case greater by about 0.025 equivalent normal.

This table shows that occlusion occurs with all the metals investigated, *i. e.*, with all the common metals, the sulfates of which are soluble in water; that the amount of this occlusion, expressed in mols, is of the same order of magnitude for all the metals, and is nearly identical for similar metals. It is to be noted, however, that the above figures only represent values deduced from a series of experiments in which we attempted to fix all the known variables except the initial chloride concentration, and have no meaning except when the various conditions prescribed are fulfilled. This reservation applies, *mutatis mutandis*, to all the data on occlusion presented in this paper.

In the literature there are a few isolated experiments on the amount of occlusion by barium sulfate precipitated from solutions containing salts; the results, in so far asthey are comparable, agree with ours. It has long been known that barium sulfate precipitated from solutions of ferric salts occludes iron in some form.[1] In 1892 this phenomenon was investigated quantitatively by E. A. Schneider,[2] who obtained results of the same order of magnitude as ours, and found that the percentage amount of iron occluded under given conditions was independent of the total weight of the precipitate; but since his conditions, in so far as they are stated, differ from ours, it is futil to institute quantitative comparison between the results. Others[3] have since that time repeated and discussed Schneider's data, all of whom doubt his conclusion that this occlusion is a case of solid solution. H. J. M. Creighton[4] investigated the occlusion of aluminium sulfate by barium sulfate, and arrived at results similar to those obtained by Schneider, but again not strictly comparable with ours on account of dissimilarity of the conditions of precipitation. The only other quantitative work known to us along this line is that of Paul Frion,[5] who studied the occlusion when precipitation was made from solutions containing magnesium nitrate or lanthanum nitrate.

The data presented above suffice to show, we believe, that all of the metals investigated—namely, those with soluble sulfates—are occluded by barium sulfate precipitates; that in each case the amount of this occlusion is of the same magnitude under the same conditions of precipitation, and is similarly affected by similar variation of the conditions.

B. Effect of Increasing the Acid Concentration.

The data of the previous paper,[6] which bear upon this point, have been amplified and extended; the mean results are presented in Table IV

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[1] *E. g.*, Jannasch and Richards, *J. prakt. Chem.*, 39, 321 (1889).

[2] *Z. physik. Chem.*, 10, 425 (1892).

[3] Küster and Thiel, *Z. anorg. Chem.*, 19, 97; 22, 424 (1899); Ostwald, *Z. physik. Chem.*, 29, 340 (1889); Korte, *J. Chem. Soc.*, 87, 1503 (1905).

[4] *Z. anorg. Chem.*, 63, 53 (1909).

[5] *J. chim. phys.*, 7, 101 (1909).

[6] *Loc. cit.*, Table VI, p. 596.

and confirm the conclusion that an increase in the acidity causes a slow decrease in the amount of occlusion. A few isolated experiments bearing on this point made with other metals[1] also confirm this conclusion.

TABLE IV.—EXPERIMENTAL RESULTS ON THE EFFECT OF ACID CONCENTRATION ON THE AMOUNT OF SODIUM SULFATE OCCLUDED.

Milligrams of Na_2SO_4 occluded by 2 grams $BaSO_4$.

Total vol. of soln., 350 cc.; time of pptn., 4 mins.; time of standing, 18 hours; amounts of conc. HCl and of NaCl as undernoted.

Solution contains NaCl. Grams.	Solution contains 40 per cent. HCl in cc. 0.1 Mg.	0.5 Mg.	2.5 Mg.	5 Mg.	10 Mg.	50 Mg.
0	9.0	8.4	7.8	4.6	3.6	2.6
5	17.4	13.6	11.6	.	.	3.8
10	19.0	..	..	.	.	4.6

C. Effect of Rate of Formation of the Precipitate.

It had been observed that the occlusion of sulfate[2] is nearly independent of the rate of addition of the precipitant or at least of such variations in rate as would occur in analytical practice. It seemed desirable to test this more thoroughly; accordingly a series of experiments was performed, in which the two solutions diffused together at such a rate that 2 grams of barium sulfate were formed in the course of several days.

Various schemes to ensure sufficiently slow diffusion were tried; the method found most satisfactory was to put the requisit amounts of sodium sulfate and of barium chloride into separate small beakers or crucibles; to lower these very carefully—to prevent premature mixing—into a large bulk of solution, contained in a larger beaker; and then to keep this system continuously at 100° by enclosing it in a steam bath of suitable construction. The solution contained known amounts of hydrochloric acid and sodium chloride; evaporation of solution and condensation of steam were alike prevented by a thin floating layer of paraffin. Under these conditions there formed in the course of some days beautiful transparent crystals of barium sulfate, many of which were 1–2 mm. long. The crystals, after washing until the washings were free from choride, contained no chloride and less than 0.05 per cent. sodium sulfate. This amount does not exceed the probable error in such a determination; consequently we may conclude that barium sulfate when precipitated *very slowly* at 100° is free from contamination.

A few diffusion experiments were tried at room temperature, which, however, were not so successful. Convection currents set up by temperature fluctuations caused too great a rate of diffusion, and this,

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[1] See Table II, footnotes.

[2] This does not hold for chloride, the amount of which occluded is markedly increased if the whole quantity of the reagent is added quickly, *i. e.*, in a few seconds. This increase is due to the fact that $BaSO_4$ precipitated quickly is much finer-grained, and consequently absorbs more material.

combined with the diminished solubility of barium sulfate under these conditions, resulted in the formation of much smaller crystals, which were contaminated to some extent by both chloride and sulfate.

The main purpose in these diffusion experiments was to make large crystals, some physical property of which—as for instance, the refractive index—might be made to afford information regarding the state in which the impurities are present. This purpose was defeated by the discovery that all of the large crystals of barium sulfate prepared in this way contained no appreciable quantity of impurity.

This observation effectually disposes of the idea that the impurities are present in the form of a solid solution; for, if the concentration of such a solution depends upon the time at all, the variation should be in the direction of an increased concentration, whereas we have found a decrease of concentration with time.

D. Effect of Time of Standing.

The data of the preceding paper,[1] relating to this point, were confirmed and extended by a series of experiments in some of which much longer intervals elapsed between precipitation and filtration. In another series the precipitate and supernatant liquid were kept at 100° during the whole time.

TABLE V.—EFFECT OF TIME OF STANDING ON THE AMOUNT OF OCCLUSION.

Milligrams Na_2SO_4 occluded by 2 grams $BaSO_4$.

Time of standing and temperature during that period as undernoted; other conditions as before.

		Length of interval.							
Orig. soln. contained NaCl. Grams.	Temp.	¼ hr. Mg.	3 hrs. Mg.	18 hrs. Mg.	2 days. Mg.	4 days. Mg.	48 days. Mg.	150 days. Mg.	210 days. Mg.
0	About 20°	11.8	..	9.0	..	..	8.4	.	.
5	About 20°	22.6	19.0	17.4	14.0	12.2	10.4	8.2	7.6
5	About 100°	22.6	14.4	13.4	10.6	10.2	..	.	.
10	About 20°	27.6	..	17.8	..	..	..	.	.

The mean results, which are presented in Table V, show that the amount of occlusion diminishes notably during the first two days, and progressively, though very slowly, thereafter; that increased temperature causes a greater diminution in occlusion during the first few hours, but is without especial effect thereafter; and that the amount remaining even after long intervals depends on the original amount, and therefore on the composition of the original solution.

The graph obtained by plotting the amounts of occlusion (m) against log t (t being the length of the corresponding interval in days) appears to be a straight line, so that the relation is given by the equation $m = a + b \log t$, which is equivalent to the equation $t = ce^{km}$. The form of this relation is identical with that of the relations generally used to express

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[1] *Loc. cit.*, p. 596.

diffusion and absorption phenomena. In any case the results of Table V show conclusively that the amount of occlusion would be entirely negligible if sufficient time were given. This shows again that the figures given by Schneider, and by Creighton, and those contained in the tables of the present paper are not absolute physical constants (although they are definit enough under definit conditions); and constitute a further proof that we are here dealing with absorption phenomena and not with solid solution, *a fortiori* not with compounds of any description. It is certain that the diminution of the amount occluded could be materially hastened by shaking or stirring; this was not tried, mainly for the reason that such a procedure would generally be impracticable in careful analytical work.

In the previous paper a few experiments on the effect of digesting the precipitates were described, from which it was concluded that the amount of occlusion, at the end of three hours on the steam bath, is independent of the composition and concentration of the supernatant liquid.[1] This conclusion would ordinarily be correct in analytical work where the acid concentration of the solution is not great, but it does not hold if the solution exerts a marked solvent effect upon the precipitate, as *e. g.*, if hydrochloric or nitric acid is present in considerable amount. This is shown by the following experiments.

Effect of Digesting the Precipitate with Acid.

Precipitates were made in the usual way from solutions containing Na_2SO_4 + 5 g. NaCl + 0.2 cc. 20 per cent. HCl; after standing 18 hours, the supernatant liquid was decanted off, and 50 cc. 20 per cent. hydrochloric acid were poured over the precipitate. After standing thus for 24 hours, the occlusion was determined. The mean result found was 0.43 per cent., as compared with 0.70 per cent., the amount of occlusion after contact with the supernatant liquid for a similar interval. In other experiments, the barium sulfate was precipitated from neutral solution (containing 5 g. sodium chloride), and immediately after precipitation (*a*) 60 cc. 40 per cent. hydrochloric acid and (*b*) 50 cc. conc. nitric acid were added. The amount of occlusion after 18 hours' contact with these solutions was (*a*) 0.32 per cent., (*b*) 0.44 per cent.; whereas, without the acid, the amount is 0.90 per cent.

There is no doubt that the greatly increased rate of diminution of occlusion in presence of these acids is directly due to the increased rate of recrystallization of the precipitate, which is, in turn, a consequence of the notably greater solubility of barium sulfate in hydrochloric and nitric acids.[2] The amount of occlusion is thus greatly reduced by contact

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[1] *Loc. cit.*, p. 597.

[2] Banthisch, *J. prakt. Chem.*, 29, 54 (1884); through Seidell's "Solubilities of Inorganic and Organic Substances."

with a solution containing 60 cc. 40 per cent. hydrochloric acid added after precipitation; but not so much as if the same amount of acid is present in the solution before precipitation. Under these conditions we found only 0.16 per cent., and observed that the amount was practically independent of the time of standing, as might be expected from the fact that precipitates formed in this way are quite coarse-grained, and to that degree less easily purified.

General Discussion of Results.

In the preceding pages it has been shown that precipitates of barium sulfate carry down some, or all, of the other salts present in the solution; that the amount of the occlusion varies (1) with the concentrations of the salts; (2) with the rate of precipitation, solubility of the barium sulfate in the supernatant liquid and with the age of the precipitate at filtration; in a word, it varies with the fineness of the precipitate, which in turn is controlled by the above three factors. Proof of this statement is afforded in a series of papers[1] by von Veimarn which deal with the size and appearance of the particles of barium sulfate, formed by mixing solutions of barium thiocyanate and manganous sulfate, the concentration of which varied between wide limits. His conclusions have a direct bearing on the problem considered in the present paper, and may therefore be briefly recapitulated.

von Veimarn's general thesis is that amorphous bodies are not precipitated as such from solution; *i. e.*, that the particles of so-called amorphous precipitates are always crystallin; and consequently that the differences between the various modifications of the solid state are in degree and not in kind, in the state of aggregation of the particles and not in differences of structure between the particles themselves. Starting from this point of view, he enunciates the theorem that, if a substance A (*e.* g., $BaSO_4$) is formed by the interaction of two solutions B and C ($Ba(CNS)_2$ and $MnSO_4$), the form in which it appears depends upon the concentration of the ions Ba'' and $SO_4^=$ in the mixture of B and C, relative to their concentrations in the solution which is saturated with $BaSO_4$ under the conditions of experiment.

To demonstrate this, he mixed a solution of barium thiocyanate with manganous sulfate of the same concentration (which ranged from about 0.0001 N to about 7 N) and examined the precipitates at frequent intervals. His observations led him to divide the whole range of concentrations into five regions, each of which, of course, merges into the adjacent regions. The dilutions given are those of each solution before mixing; their reciprocals therefore represent approximately (except in the very strongest solutions) the equivalent concentration of Ba'' and of $SO_4^=$ at the moment of precipitation.

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[1] P. P. von Veimarn, *Z. Chem. Ind. Kolloide*, 2, 3, *passim.*

(1) At dilutions greater than 7000, the precipitate does not separate at all.

(2) At dilutions between 7000 and 600, one obtains in the course of time recognizable crystals by the slow transformation of the form originally precipitated, which is that usually known as amorphous. These "amorphous" grains however, equally with the finest grains obtainable by mechanical means, have the power of inhibiting supersaturation. The general behavior within this region is indicated by the following table.

Dilution approx.	Distinct opalescence appears in:	The bulk of the ppt. settles in:	Remarks
5000	..	1 month	
3000	6–8 hours	24 hours	Initially an ultramicroscopic suspension; transformed after 6 months into good crystals about 0.001 cm. long.
2000	2–3 hours	10–12 hours	Initially fine-grained spherical aggregates, transformed after 6 months into good crystals of smaller size than the preceding.
1000	3–5 mins.	2–3 hours	
600	a few secs.	½–1 hour	

Further experiments at the dilution 2000 showed that the process of recrystallization requires several months, while the direct crystallization requires but a few hours at room temperature, without shaking. On the other hand supersaturation is removed within a few minutes, the length of this interval depending largely on the slowness of diffusion in the neighborhood of the crystal grains.

(3) At dilutions between 600 and 1 the number of good crystals diminishes, and the formation of skeletons and needles increases with increase in concentration. At 200 the skeletons may be about 0.0005 cm. in length, while the size of the needles varies from perhaps 10 μ down to the smallest points visible in the microscope. At a dilution of 10 the precipitate consists entirely of needles; about 1 the formation of amorphous precipitate begins.

(4) At dilutions between 1 and 0.1 one obtains initially jelly-like amorphous precipitates, which may be differentiated into aggregates microscopically; these quickly become turbid, and change into voluminous fine-grained precipitates.

(5) At the greatest concentrations, jellies are obtained, the particles of which initially cannot be differentiated, even with the ultramicroscope: they remain transparent for several hours, but in about 24 hours are transformed into a plastic mass. This does not change its structure in many months when preserved under water at low temperature; but in boiling water a considerable part of it recrystallizes in three weeks, while in a hot concen-

trated solution of hydrochloric acid, complete recrystallization takes place in a few days.

From the above observations von Veimarn shows in two ways that the "amorphous" precipitates are composed of crystallin material: first, because with increasing concentration—which is equivalent to decreasing relative amounts of Ba″ and $SO_4^=$ in the solution—there is a progressive diminution in the size of the crystals, but no sudden change to amorphous; and secondly because all precipitates are capable of recrystallization. The process of recrystallization consists in the inhibition by the larger crystals of the supersaturation (with respect to them) of the solutions formed by the greater solubility of the smaller crystals.[1] The slowness of this process is plausible, when account is taken of the degree of supersaturation and of the very small absolute amount of material. Naturally too the finest grained material may require considerable time to grow to recognizable crystals.

von Veimarn's papers have been summarized above rather fully because they show that the fineness of the precipitate depends upon the concentration of Ba″ and $SO_4^=$ relative to that of a saturated solution of barium sulfate in the particular medium;[2] or in other words, the fineness of grain is conditioned by the degree of supersaturation of the barium sulfate in the solution. This is confirmed by other observations: thus, whereas von Veimarn obtained in concentrated solutions particles about 5 $\mu\mu$ in diameter, we were able to obtain crystals 1–2 mm. long in diffusion experiments, in which the degree of supersaturation was kept very small, and crystals up to 4 cm. in length have been found in the Teplitz springs in which barium could not be detected by ordinary analytical methods.[3]

Since the size of the crystal particles depends upon the degree of supersaturation, it follows that the degree of fineness of the particles is increased by a rapid addition of the precipitant; is diminished by precipitating in a medium in which barium sulfate is more soluble; and is further diminished, when the precipitate remains in contact with a medium in which it is soluble, by the process of recrystallization, the rate of which depends upon this solubility. Now these are precisely the conditions which affect the occlusion, when the precipitates are made from identical solutions. We are therefore justified in concluding that this occlusion is a phenomenon of absorption at the surface of the grains of the precipitate; and that its amount depends upon (*a*) the composition of the original solution and

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[1] See G. A. Hulett, *Z. physik. Chem.*, 37, 396 (1901).

[2] This is equivalent to the statement that diminution of solubility causes an increase in the number of centers of crystallization. It may be noted that the number of centers increases also with the viscosity of the medium; for increased viscosity decreases the motion of the centers, and therefore increases their number, since the total amount of substance precipitated remains the same.

[3] F. Becke, *Min. petrog. Mitt.*, 5, 82 (1883).

(*b*) the initial fineness of the precipitate and the amount of recrystallization which has taken place.

This explanation, besides accounting for our own results, also accords with those of Richards and Parker[1] and of Hulett and Duschak,[2] who studied the precipitates obtained by mixing solutions of barium chloride and sulfuric acid; moreover it does not conflict with any reliable experimental evidence with which we are acquainted.

These considerations might be applied to elucidate and correlate the enormous number of mineralogical papers dealing with the composition and crystal habit of natural and artificial barite. This would however lead too far at present. It may suffice to mention perhaps the latest of these, a paper by Hilda Gerhart:[3] crystals of barite were made by the action of various solutions on barium chloride through a layer of gelatinous silicic acid; and it was found that alum and nitric acid exert the greatest influence in modifying the crystal habit. Now, these substances are absorbed to a considerable extent by barium sulfate. This renders it plausible that one factor in the modification of crystal habit is the occlusion by the growing crystal of foreign substances from the supernatant liquid.

The Exact Determination of Sulfate.

By the method given in the previous paper,[4] accurate determinations of sulfate are possible only if three corrections are applied, one of which at least—the correction for "volatility"—is somewhat troublesome to determin. Series of experiments were therefore made in order to find out if it be possible by the application of the principles stated above to devise a general method for the accurate determination of sulfate, in which only slight and easily determined corrections should be necessary. This endeavor to find a generally applicable simple method has not been altogether successful; it was found possible to obtain correct results in some particular instances, but in general these were due to a compensation of errors, all of which were small.

In actual analytical work, the only readily variable effective conditions are the acidity of the original solution and of the supernatant liquid, and to some extent the rate of addition of the precipitant; accordingly we attempted by variation of these conditions, to obtain coarse-grained precipitates, and thereby correct results. The attempts, which were made on solutions of sodium sulfate containing in general sodium chloride, are briefly described below, and the reasons of their failure are indicated. The manipulation and methods used, *e. g.*, in treating the precipitate, are identical with those described in the previous paper; the total volume

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[1] *Proc. Am. Acad.*, 31, 67 (1898); *Z. anorg. Chem.*, 8, 413 (1895).

[2] *Z. anorg. Chem.*, 40, 196 (1904).

[3] *Min. petrog. Mitt.*, 29, 185–91 (1910).

[4] Allen and Johnston, *Loc. cit.*

of the solution was always 350 cc. and the time of precipitation about 4 mins., except where it is expressly stated otherwise.

(*a*) Precipitation in Strongly Acid Solution.

When the original solution is strongly acid, the solubility becomes important, as it amounts to over 30 mg. in the most acid solutions used (50 cc. conc. (40 per cent.) hydrochloric acid in 350 cc. solution). The solubility was taken into account: (*a*) by evaporating the filtrate[1] to dryness, taking up with a little water, filtering, weighing separately, and adding this to the weight of the main portion of the precipitate; (*b*) by evaporating the whole solution (with the precipitate) to dryness[1] immediately after precipitation, taking up with water, filtering, washing and igniting as usual. The results of both methods are identical; they are presented in Table VI, in the column headed "$BaSO_4$ found." In Table VI is also given the amount of occlusion wherever it was determined, together with the correction corresponding to the assumption that all of the sodium sulfate found was originally present as $NaHSO_4$, the reaction $2NaHSO_4 = Na_2SO_4 + H_2SO_4$ taking place on ignition of the precipitate, with a consequent loss of half of the total quantity of SO_3 occluded. For such acid solutions, this assumption must be more nearly correct than the simpler one made previously—namely, that the correction is given by $(BaSO_4 - Na_2SO_4)/Na_2SO_4$; on the newer assumption the correction is exactly twice as great as this.

Table VI.—Sulfate Determinations in Strongly Acid Solutions.

Orig. soln. contained					Occlusion.		
NaCl. Grams.	40 per cent HCl. Cc.	$BaSO_4$ calc. Grams.	$BaSO_4$ found. Grams.	Deficit (uncor.). Grams.	Found. Mg.	Correction.[1] Mg.	Error (cor. for occl.).[2] Per cent.
0	25	1.9955	1.9882	7.3	4.4	*6.0*	*—0.06*
5	25	1.9938	1.9810	12.8	.	.	..
5	50	1.9894	1.9902	—0.8	3.2	*4.4*	*0.26*
5	50	1.9965	1.9967	—0.2	.	*4.4*	*0.23*
5	50	2.0022	2.0014	0.8	.	*4.4*	*0.18*
10	50	1.9905	1.9812	9.3	4.6	*6.4*	*—0.14*
0	50[3]	1.9750	1.9811	—6.1	2.1	*3.0*	*0.45*
5	50[3]	2.0076	2.0152	—7.6	1.4	*2.0*	*0.48*

The numbers in the last column represent the percentage error of the determination, after the above correction has been applied. It is evident that this error is nearly constant for any given original solution and tends to be positive; this is easily accounted for by the fact that the precipitates all contained a trace of chloride, the amount of which was not

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[1] This is best done in platinum vessels.

[2] On the assumption that the sulfate occluded is wholly $NaHSO_4$.

[3] In these two experiments, precipitation was rapid—in about 10 secs.; they are therefore not strictly comparable with the others.

determined quantitatively and has not been allowed for. The influence of the chloride is especially marked in the last two experiments, in which the precipitation was made rapidly—in about 10 secs.; this condition is, conformably with what we had previously found by actual determinations of the chloride, favorable to increased occlusion of chloride. Moreover, the concentration of hydrochloric acid would decrease greatly the ionization of the barium chloride, and hence tend to increase the occlusion of the latter, other things being equal; in somewhat stronger acid solution, precipitation of barium chloride might even occur.[1] It is evident however from Table VI that, by making slow precipitations in presence of much free hydrochloric acid (50 cc. 40 per cent. in 350 cc. original solution) and taking the solubility into account, fair results are obtained, especially with solutions containing 5 grams sodium chloride—a quantity such as is very commonly present in actual work. Correcting for occlusion tends to make the results high, because the precipitates are also contaminated with barium chloride, which is not allowed for in that correction. Incidentally it may be mentioned that the manipulation of the precipitates obtained from acid solutions is much easier and more rapid, by reason of their coarseness of grain.

(*b*) **Precipitation by means of an Acid Solution of Barium Chloride.**

For these experiments we made up a solution containing 23 grams $BaCl_2 2H_2O$ in a liter of 10 per cent. HCl;[2] 90 cc. of this solution are required for the precipitation of 2 grams of barium sulfate. In the precipitation, 100 cc. were run slowly (in about 10 minutes) into the boiling and constantly stirred solution of the sulfate. The remaining manipulation was exactly as in (*a*); but the occlusion was not determined. The results follow.

Orig. solution contained.				
NaCl. Grams.	40 per cent. HCl. Cc.	$BaSO_4$ calc. Grams.	$BaSO_4$ found. Grams.	Deficit (uncor.). Mg.
0	0	1.9923	1.9878	4.5
5	0	2.0183	2.0017	16.6
0	25	1.9894	1.9884	1.0
5	25	2.0039	1.9980	5.9

In this method of precipitation, the concentration of the barium chloride is much smaller (2 per cent. as against 10 per cent.) and consequently the amount of chloride occluded is smaller; furthermore, the bulk of the precipitate is formed in a less strongly acid solution than in (*a*), and therefore the occlusion of sulfate is greater. These two influences together make the deficits larger than in (*a*). Consequently this method is not so

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[1] The solubility of barium chloride is enormously diminished by hydrochloric acid; for quantitative data see Engel, *Ann. chim. phys.*, [6] 13, 371 (1888).

[2] This corresponds nearly to saturation.

good as the former, in which all the acid was present in the original solution; it is besides less convenient.

(*c*) Precipitation in Neutral Solution and Subsequent Digestion of the Precipitate with Concentrated Hydrochloric Acid.

In these experiments the precipitation was made slowly in neutral solution; immediately thereafter, the whole was evaporated to dryness, and then digested, with occasional stirring, for 24 hours at 100° with 50 cc. 40 per cent. HCl. It was then evaporated to dryness, taken up with water, filtered and washed as usual. The ignited precipitates were very hard and flinty, thus indicating considerable contamination; this was confirmed on determining the amount of sulfate occluded. The results, after applying the correction for occlusion of sulfate (on the assumption in this case that it was entirely Na_2SO_4), are considerably too high, and indicate the occlusion of considerable chloride in addition to the sulfate, the presence of which was shown directly.

Orig. soln. contained.					Occlusion.		
NaCl. Grams.	HCl. Cc.	$BaSO_4$. calc. Grams.	$BaSO_4$. found. Grams.	Deficit (uncor.). Mg.	Found. Mg.	Correction.[1] Mg.	Error (cor. for occlusion.)[1] Per cent.
0	0	2.0020	2.0023	—0.3	6.4	4.5	0.24
5	0	2.0076	2.0040	3.6	12.5	8.7	0.26

Here, therefore, although the agreement between the amounts of barium sulfate found and calculated is fairly good, it depends upon a compensation of large errors, conditioned by the fineness of the precipitate. Barium sulfate precipitated from neutral solution is extremely fine-grained; the contamination is not removed with sufficient completeness even by digestion for 24 hours with hot concentrated hydrochloric acid. This method is also burdened with the added difficulty of manipulating the very fine-grained precipitates, which exhibit a marked tendency to adhere to all surfaces with which they come in contact.

General Conclusions on the Exact Determination of Sulfate.

The method given by Allen and Johnston gives correct results but has the disadvantage for general analytical work that one must apply three corrections, two of which are somewhat troublesome to determin. This inconvenience is in part obviated by the fact that the corrections are constant for any particular set of conditions, and so need only be determined once for all. A better plan would probably be to calibrate the method by sulfate determinations on *pure dry* sodium (or potassium) sulfate dissolved in a medium as similar as possible to that in which the sulfate to be analyzed is dissolved. Sodium (or potassium) sulfate is easily obtained in a pure dry state,[2] so that the errors inherent in such a method

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[1] On the assumption that the occluded sulfate is wholly Na_2SO_4.

[2] By recrystallizing (if necessary) and heating to 200° in an air bath for an hour; its purity may be easily controlled by an accurate determination of its sulfate content.

of calibration should be very slight, if the conditions of precipitation were reproduced at all closely.

The foregoing experiments show that none of the methods tried is suitable for accurate work because their apparent correctness depends upon a compensation of errors. In the precipitations in strongly acid solutions, however, these errors are all small and the results are consequently reproducible with considerable accuracy; this method might then well be calibrated in the way suggested above. It possesses the advantage, as compared with the method of the previous paper, that it is easier to manipulate and much more rapid; for one may evaporate to dryness *immediately* after precipitation, and the precipitate, being coarse-grained, does not adhere at all to the vessel, is quickly filtered and easily washed; and with less danger of loss in any of the operations. By making concurrent comparison determinations it should be possible in the course of a few hours to determin sulfate with an accuracy of ±0.05 per cent. in any solution, the composition of which is known approximately—a condition which very frequently obtains in practice.[1] It would of course be preferable always to have the original solution free from the heavy metals and nitrates, as is usually the case in making sulfate determinations.

In conclusion we may express our belief that there is little chance of discovering any exact method which shall at the same time be generally applicable and require no corrections, and yet not owe its accuracy to a compensation of errors; for the reason that some of the requisit conditions appear to be mutually incompatible.

Summary.

The occlusion by barium sulfate of other sulfates is a general phenomenon. The amount of this occlusion depends upon (*a*) the composition of the original solution, (*b*) the fineness of the precipitate, which in turn is conditioned by the degree of solubility of barium sulfate in the particular medium, the rate of precipitation, and the time and manner of standing between precipitation and filtration. The phenomenon is therefore in all probability an absorption at the surface of the grains of the precipitate, since it is affected by the factors just mentioned.

On the basis of the knowledge gained in this way, attempts were made to find a direct method for the determination of sulfate which should be generally applicable, exact, and require only small and easily determined corrections. We suggest the following procedure: To the solution (300 cc. for a precipitate to weigh 2 grams) add 50 cc. of concentrated hydrochloric acid, heat to boiling, and precipitate, stirring constantly, with a 10 per cent. solution of barium chloride. This should be added at such a

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[1] If the composition of the solution is not known, recourse must be had to the method in which all of the corrections are actually determined.

rate that about four minutes is required in running in the 22 cc. necessary; the rate is best regulated by attaching a suitable capillary tip to the buret containing the barium chloride solution. Evaporate the whole to dryness on the steam-bath (this may be done immediately after precipitation), take up with hot water, filter through paper, wash until the washings are free from chloride, ignite very carefully (so as to obviate reduction) and heat to constant weight over a Bunsen burner. The necessary correction is determined by a concurrent calibration of the method; that is, by dissolving an equivalent weighed amount of pure dry sodium (or potassium) sulfate in a medium such that the resulting solution is as nearly as may be of the same composition as the solution to be analyzed; the sulfate in this comparison solution is then determined precisely as above. The difference between the calculated amount of barium sulfate and that actually found is the correction to be applied to the weight of the precipitate obtained in the actual analysis.

This procedure, as compared with that advocated by Allen and Johnston, is easier and much more rapid; it is however not so generally applicable, but may be used whenever the composition of the solution containing the sulfate to be determined is known approximately; and, we believe, will yield results, accurate to ±0.05 per cent. of the total sulfate present, in most cases likely to occur in general analytical work.

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ARTIFICIAL CRYSTALLIZATION OF BARIUM SULFATE.[1]

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Barium sulfate has a conspicuous place in the literature of the artificial production of crystals, because it has been crystallized by several different methods. The largest crystals, some as long as 2 mm., were obtained by Manross[2] in Wöhler's laboratory, as a result of chemical change in the molten condition, *viz.*, by fusing potassium sulfate with an excess of barium chloride and lixiviating the cooled mass. De Schulten[3] obtained crystals by chemical change in aqueous solution, *viz.*, by very slow precipitation. Senarmont[4] got a similar result by heating barium sulfate with hydrochloric acid in a sealed tube at 250° for 60 hours. This has been considered (by Fock[5]) as a solution method, but it seems more likely that we have here to do with a reversible chemical reaction. Ad-

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[1] Presented at the December, 1910 (Minneapolis) meeting of the American Chemical Society, see *Science*, 33, 345.

[2] *Ann.*, 82, 349.

[3] *Bull. soc. franc. min.*, 26, 103; *Chem. Zentr.*, 1903, II, 845.

[4] *Ann. chim. phys.*, [3] 32, 155.

[5] Fock-Pope, "Introd. to Chem. Crystallography," Oxford, 1895, p. 77.