comes out as an integral part of the solid phase—inseparable from it even by perfect drainage.) For simplicity's sake, only those values of *n* are given in the table for which the values of y and x have a simple numerical ratio, and this ratio, y/x, is given in the top line of the table. I have called it the "inseparability "of the substances.

TABLE OF VALUES OF *n*.
"Inseparability" = y/x.
"Insolubility coefficient" of salt = x.

x.	$y/x = 0$.	10^{-3}.	10^{-2}.	10^{-1}.	0.2.	0.3.	0.4.	0.5.	0.6.	0.7.	0.8.	0.9.	0.99999.
10^{-2}.......	27.1	27.1	27.1	26.1	25.0	23.9	22.6	22.4	21.4	20.8	20.7	20.6	...
10^{-1}.......	11.1	11.1	6.8	6.4	6.0	5.7	5.4	5.1	4.8	4.5	4.4	4.2	3.2
0.2........	6.9	6.9	6.5	5.4	4.9	4.6	4.1	3.5	3.0	2.8	2.8	2.8	2.8
0.3........	5.7	5.7	4.9	4.3	3.8	3.5	3.2	2.9	2.6	2.4	2.4	2.4	2.4
0.4........	4.8	4.8	4.3	3.2	2.7	2.4	2.3	2.2	2.1	2.0	2.0	2.0	1.8
0.5........	4.5	4.5	4.1	2.8	2.3	2.1	2.0	1.9	1.8	1.6	1.6	1.6	1.6
0.6........	4.2	4.2	3.7	2.5	2.2	2.0	1.9	1.8	1.7	1.6	1.6	1.6	1.6
0.7........	4.0	3.9	3.5	2.3	2.1	1.9	1.8	1.7	1.6	1.5	1.5	1.5	1.5
0.8........	3.8	3.7	3.4	2.2	2.0	1.8	1.7	1.7	1.6	1.5	1.5	1.5	1.4
0.9........	3.6	3.5	3.3	2.1	1.9	1.8	1.7	1.6	1.5	1.5	1.5	1.4	1.3
0.99.......	3.5	3.4	3.2	2.0	1.9	1.7	1.6	1.5	1.4	1.4	1.4	1.3	1.3

$$\text{Values of } n = \frac{\log\left\{\dfrac{y + (1 - y)r'}{x + (1 - x)r'}\right\}}{\log\left\{\dfrac{y + (1 - y)r}{x + (1 - x)r}\right\}}, \text{ where } \begin{aligned} r &= 0.25 \\ r' &= 0.008 \end{aligned}$$

The value of x depends on the cooling interval and the slope of the solubility curve. The superiority of thorough drainage is relatively much greater in the case of those substances with flat, rather than steep, curves in the chosen temperature range and also for those systems where the proportion of the impurity that comes out with the salt is small. Thus the common practice of using only gravitational drainage in the case of rare earth and similar separations is shown to be well founded, since the extra time and trouble required for centrifugal drainage would more than outweigh the relatively small gain in efficiency. On the other hand, in the separation of very dissimilar substances, especially those with flat solubility durves, the attendant great increase in the speed of purification justifies almost any amount of pains taken in washing and drainage.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ILLINOIS.]

THE CONTAMINATION OF PRECIPITATES IN GRAVIMETRIC ANALYSIS: SOLID SOLUTION AND ADSORPTION *vs.* HIGHER-ORDER COMPOUNDS.

BY GEORGE MCPHAIL SMITH.

Received March 29, 1917.

Theoretical.—As is well known, many insoluble compounds which are precipitated in the course of analytical processes possess the property of carrying down and retaining certain soluble salts in such a manner that the latter oftentimes cannot be removed, even by prolonged washing. This property of the precipitated compounds is selective in character, and various explanations have at different times been advanced to account for it. Among these may be mentioned the following: (1) The mutual striving for saturation of basic and acidic compounds, *e. g.*, the tendency—even in the presence of ammonium salts—of the hydroxides of iron and aluminum to carry down magnesia, when precipitated by ammonia from solutions containing magnesium. (2) The formation of difficultly soluble double salts, *e. g.*, the contamination of barium sulfate by ferric iron is ascribed by P. Jannasch and T. W. Richards[1] to the presence in the precipitate of a double barium ferrisulfate. (3) The formation of difficultly soluble salts through the union of certain intermediate ions, *e. g.*, to explain the obstinate retention of barium chloride in precipitated barium sulfate and the evolution of free hydrochloric acid upon the ignition of such precipitates, G. A. Hulett and L. H. Duschak[2] suggest the formation of combinations, such as $(BaCl)_2SO_4$, $BaCl.HSO_4$, $Ba(HSO_4)_2$. (4) The presence in the insoluble compound of foreign salts in a state of solid solution, non-ionized soluble salt supposedly being dissolved by the precipitated compound at the instant in which the latter separates from the aqueous solution. In this way, T. W. Richards[3] accounts for the contamination of barium sulfate with ferric iron, the assumption being that there is a partition of the compound $FeSO_4.OH$ between the aqueous liquid and the solid barium sulfate. (5) The adsorption of soluble salts by the finely divided insoluble precipitate. In this connection, J. Johnston and L. H. Adams[4] make the following statements:

> "The occlusion[5] 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, 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."[6]

While recognizing the complexity of the problem, and without wishing

---

[1] *J. prakt. Chem.*, 39, 321 (1889).

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

[3] *Ibid.*, 23, 385 (1900).

[4] THIS JOURNAL, 33, 829 (1911); see also E. T. Allen and J. Johnston, *Ibid.*, 32, 588 (1910).

[5] The word "occlusion," as employed by Johnston and Adams, simply denotes contamination, regardless of its cause.

[6] It may be pointed out in this connection that Hulett and Duschak (*Loc. cit.*, p. 216) make the following statement: "Our original opinion that these phenomena might be due to surface adsorption and occlusion was abandoned in the course of the investigation on account of the contradictory evidence of several observations—." These observations are described and discussed in their paper.

to deny the possibility of other contributory causes, it nevertheless appears to the writer that the most general cause of contamination may well be sought in the formation of insoluble higher-order compounds which are to a certain extent stable under the analytical conditions. In that case the presence of impurity would not necessarily be due always to an inherent property of the precipitated compound itself, though of course this substance would in most instances be likely to take part in the formation of the respective higher-order compounds, and this then would readily account for the selective nature of the phenomenon.

The first three of the explanations listed above are in good agreement with the conception advanced in this paper, but such explanations have hitherto been applied only in special cases. In reality, however, many general cases may be gathered under this head—as, for example, the tendency of the hydroxides of the heavy metals to carry down appreciable quantities of sodium and potassium hydroxides when precipitated by these from aqueous salt solutions.[1] In view of the facts that the hydroxides of zinc, lead, tin, chromium, aluminium, etc., which are soluble in sodium hydroxide, are conceded to yield chemical compounds with the latter, and that the hydroxides of calcium, zinc, etc., are known to form insoluble compounds with hydrated manganese dioxide,[2] it should not appear unreasonable to suppose that the hydroxides of copper, nickel, ferric iron, etc., which show a marked tendency to carry down and retain alkali or alkali-earth hydroxide, are capable of uniting with these to form more or less insoluble hydroxo-salts of varying degrees of stability.[3]

The compound $[Zn(OH)_3]Na + nH_2O$, which has been obtained in

---

[1] Even ammonium hydroxide is probably carried down to some extent by the hydroxides of aluminum, chromium, and ferric iron; but since these precipitates are invariably ignited at a high temperature, no analytical error is introduced from this source.

[2] See F. P. Treadwell, "Lehrb. analyt. Chem.," **2**, 522 (1913).

[3] Corresponding to the hydroxo-zincates, plumbates, etc., of the water system, E. C. Franklin has discovered many (in liquid ammonia) difficultly soluble amido-salts, *e. g.*, the so-called ammono-zincate, -cadmiate, -nickelate, -barate, etc., of potassium, these being salts of the ammonia system of acids, bases and salts (cf. E. C. Franklin, *Am. Chem. J.*, **47**, 285 (1912); THIS JOURNAL, **29**, 1274(1907); **35**, 1455 (1913); **37**, 2295 (1915)).

In this connection, see the section on hydroxo-salts in A. Werner's "Neuere Anschauungen a. d. Gebiete d. anorg. Chemie," Braunschweig, **1913**; also A. M. Comey and C. L. Jackson, *Am. Chem. J.*, **11**, 145 (1889), and F. Foerster and O. Günther, *Z. Elektrochem.*, **6**, 302 (1899–00). Werner assigns to such compounds the formulas $[Sn(OH)_6]K_2$, $[Sn(NH_2)_6]K_2$, $[Zn(OH)_3]Na + nH_2O$, $[Zn(NH_2)_4]K_2$, etc., instead of $Sn(OK)_4$, $Sn(NHK)_2.4NH_3$, $Zn(ONa)_2$, etc., as commonly written. In confirmation of Werner's views, see the work on $[Pt(OH)_6]K_2$, $[Sn(OH)_6]K_2$, and $[Pb(OH)_6]K_2$, by I. Bellucci, *Z. anorg. Chem.*, **44**, 168 (1905); **45**, 142 (1905); and (with N. Parravano) *Gazz. chim. ital.*, **35**, 500, 509 (1905).

crystalline form by Comey and Jackson[4] and by Foerster and Günther,[1] dissociates in water largely into sodium and zinc hydroxides, and we should expect other similar compounds to do likewise.

Metallic halides readily unite with one another to form higher-order halo-salts; double sulfates and double sulfites[2] are well known, and exceedingly numerous; many fairly stable double nitrites are known; and metallic oxalates are frequently capable of uniting with one another to form more or less stable oxalo-salts.[3] In short, it is a general property of the simpler inorganic compounds to unite with one another, or with certain organic compounds to form higher-order compounds,[4] and, in view of the multitude of higher-order compounds which are capable of existence, it would indeed be a remarkable fact if many insoluble substances of this nature were not encountered in the ordinary processes of gravimetric analysis.[5]

---

[1] *Loc. cit.*

[2] It is of interest to note that in a recent study of the determination of lead as sulfite, by precipitation with $NaHSO_3$, G. S. Jamieson (*Am. J. Sci.*, 40, 157 (1915)) has found that, in the presence of calcium, the $PbSO_3$ precipitate carries down $CaSO_3$, although a calcium salt solution gave no precipitate with $NaHSO_3$ even after standing two days.

[3] Even calcium oxalate, when precipitated in the presence of sodium, for example, has a strong tendency to retain the alkali metal (cf. W. F. Hillebrand, "The Analysis of Carbonate and Silicate Rocks," U. S. Geol. Survey, *Bull.* 422, 119), probably in the form of a double oxalate or oxalo-salt; and the well-known tendency of calcium oxalate to carry down magnesium oxalate is probably due also to the same cause. The latter subject has been experimentally investigated in a thorough manner by T. W. Richards, C. T. McCaffrey and H. Bisbee (*Z. anorg. Chem.*, 28, 71 (1901)), who show that the presence of a large excess of ammonium oxalate greatly favors the separation of a precipitate which is free from magnesium; they ascribe this effect to the formation of easily soluble complex magnesium ammonium oxalates which are not occluded by (*i. e.*, which are insoluble in) calcium oxalate. Strangely enough they do not appear to have taken into consideration the equal possibility of the existence of an insoluble double oxalate of calcium and magnesium, although the existence of such a compound (analogous to dolomite) would furnish a somewhat more plausible explanation of the observed facts. Owing to mass action, the magnesium oxalate should be practically all removed by the large excess of ammonium oxalate, in the form of the soluble magnesium ammonium complex, and thus reduce to a minimum the quantity of the calcium magnesium complex in the precipitate; any ammonium oxalate carried down in combination with the calcium salt would of course be expelled upon ignition, and not be noted in the final residue.

[4] See A. Werner, "Neuere Anschauungen, etc."

[5] Many such difficultly soluble higher-order compounds are in fact actually made use of in analytical processes; of these it will suffice to mention only potassium chloroplatinate, potassium cobalti-nitrite, nickel dimethyl-glyoximine, and hydrated magnesium ammonium carbonate. It is further of interest in this connection to mention that, in reducing certain platinum residues by means of formic acid in ammoniacal solution, Dr. T. R. Ball of this laboratory a few months ago obtained, together with the main precipitate of platinum black, a considerable quantity of an insoluble green

Moreover, since higher-order compounds are formed in accordance with the law of mass action, the conditions which must frequently be observed in order to obtain reasonably pure precipitates—such as previous dilution to a large volume, dropwise addition of the precipitant, double precipitation, etc.—are precisely those under which a contaminating higher-order compound formed by the action of the precipitant would tend finally to be present in the minimum quantity; and, in case the desired precipitates were sufficiently less soluble than the contaminating higher-order compound, then the former would tend to separate, more or less quantitatively, in a fairly pure condition. At any rate, the danger of contamination through the formation and simultaneous precipitation of difficultly soluble higher-order compounds offers an explanation of the precautions which must in certain instances be observed in carrying out the operations of precipitation, which, to say the least, is in as good agreement with the experimental facts as are the more familiar theories of adsorption and solid solution, and which does not share the disadvantage of the latter in ascribing to barium sulfate, for example, the property of acting as a solvent for substances such as the chlorates, chlorides, and nitrates of barium and other metals, as well as for the basic sulfates, or other compounds of iron, chromium, aluminum, zinc, copper, etc. Furthermore, adsorption itself is very likely connected in an intimate manner with chemical forces—*e. g.*, through the coming into play of auxiliary valences—in which case it may be nothing other than the surface-formation of insoluble higher-order compounds. And, in case the solid adsorbing compound is not added to the solution in the solid condition, but is formed upon the addition of a given reagent as a precipitate in the solution, there is no reason to suppose that the so-called adsorption should be confined to the surface of the grains.

The theory of contamination through the agency of solid solution, or "occlusion," has been based primarily upon the work of E. A. Schneider,[1] who investigated the contamination of barium sulfate by ferric iron, and who, in consequence of his experimental results, drew the conclusion that we have to do here with a case of solid solution. It is for this reason that the contamination of barium sulfate by ferric iron furnishes an apt subject for the first paper of the present series; and it will be shown in the experi-

substance—the green salt of Magnus, $[Pt(NH_3)_4]PtCl_4$. This compound, which had in previous similar reductions been observed as a transitory intermediate product, persisted this time for several days in the hot reaction mixture, and disappeared only after the addition of a fresh quantity of ammonium formate. A portion of the chloroplatinic acid had evidently been reduced only to chloro-platinous acid, which is known to react with ammonia to give the green salt of Magnus (see Urbain and Sénéchal, "Chimie des Complexes," p. 230, Paris, 1913). No such difficulty was experienced when sodium hydroxide was substituted for ammonium hydroxide in this reduction.

[1] *Z. physik. Chem.*, 10, 425 (1895).

mental part that neither the hypothesis of solid solution, nor that of surface adsorption is capable of explaining the facts in this case.

Previous Investigations.—In 1889, P. Jannasch and T. W. Richards[1] investigated the determination of sulfuric acid, by precipitation with barium chloride, in the presence of iron. They observed that the ignited precipitate from a ferric salt solution, in spite of its iron content, weighs less than the barium-sulfate equivalent of the sulfuric acid originally present in the solution. They further found the loss in weight upon ignition of the well dried (at 250°?) precipitate to be approximately equal to the sulfur-trioxide equivalent of the ferric oxide contained in the ignited precipitate (two determinations). From these and other results, they concluded that the iron is precipitated in the form of a double compound with barium, as barium ferrisulfate, "probably containing a molecule of water of constitution which is not wholly expelled even at temperatures as high as 250°."

E. A. Schneider,[1] in 1895, was the first to consider the formation of solid solutions as an important factor in the contamination of inorganic precipitates; he believed the contamination of barium sulfate by iron, when precipitated in the presence of a ferric salt, to be a case in point. Schneider describes two series of experiments which in his opinion indicate that, at a given ferric-salt concentration, the amount of ferric sulfate which is carried down in solid solution by the barium sulfate is proportional to the quantity of the latter which is precipitated, and that, saturation of the barium sulfate having been reached, a further increase in concentration of ferric sulfate in the aqueous solution has no effect.[2]

F. W. Küster and A. Thiel,[3] in 1899, pointed out that the admixture of ferric salt in the barium sulfate is due to the simultaneous presence in the solution of ferric and sulfate ions, and they state that the addition of an oxalate gives rise to the formation of complex ferric ions and thereby tends to minimize such contamination. Ostwald,[4] in a favorable review of this paper, assumed a doubtful attitude as to the correctness of Schneider's assumption of a solid solution, and suggested the probable

---

[1] *Loc. cit.*

[2] Schneider's results are not, as he thought, necessarily incompatible with the formation of a double sulfate of iron and barium. Solutions of a given volume, such as were employed by Schneider, containing ferric chloride and hydrochloric acid at constant concentrations, and sulfuric acid in increasing amounts, should at a given temperature, owing to mass action, contain increasing amounts of sulfato-ferric acid—a compound at that time unknown, but which will be referred to in detail below; and we might in that case expect the quantities of iron carried down upon precipitation of the sulfuric acid with an excess of barium chloride to be roughly proportional to the quantity of the barium sulfate formed. It is unfortunate that Schneider did not describe in detail his analytical operations.

[3] *Z. anorg. Chem.*, **19**, 97 (1899).

[4] *Z. phys. Chem.*, **29**, 340 (1899).

formation of complex ferrisulfate ions, similar to those formed by the union of chromic and sulfate ions. In a somewhat later paper, Küster and Thiel[1] accepted this suggestion and assigned to the ferric compound the formula $Ba[Fe(SO_4)_2]_2$; they also state that precipitation in the cold yields a pure barium sulfate precipitate.[2]

Immediately after this, in 1900, T. W. Richards[3] published a paper in which he points out that Küster and Thiel have apparently overlooked the almost identical explanation of Jannasch and Richards, and also that they have ventured to assign an arbitrary formula to a substance, the exact composition, and mode of "occlusion" of which Jannasch and Richards did not make bold to explain. Richards then refers to Schneider's work, which, he says, renders it probable that the occlusion of the double salt or complex is the result of the formation of some sort of solid solution; he goes on to say that Schneider's experiments show that the degree of occlusion is roughly proportional to the increasing concentration of impurity in the solution, and that clearly we have in this instance to deal with a special case of partition;[4] *that in this case, however, partition can occur only in the instant of precipitation, since later the rigidity of the solid body hinders free diffusion.*[5] He compares the occlusion of hydrogen by palladium with the "uniform partition" of a dissolved substance from the solution into the solid precipitate, and suggests "*occlusion*" as the most appropriate name for the latter phenomenon also. By analogy with other cases of partition, he supposes the substances which are carried down by precipitates to consist rather of electrically neutral complexes than of ions. As to the nature of the electrically neutral group in this instance, however, Richards says that Küster and Thiel's assumption of $Ba[Fe(SO_4)_2]_2$ is entirely unproved; and that, while their comparison of ferric and chromic sulfates is a happy one, they have been unfortunate in their application of it to the case in question. He then points out that normal chromic sulfate upon hydrolysis yields free acid, and that this acid, at least to some extent, leads to the formation of chromi-sulfuric acid, more or less in accordance with the equation[6] $Cr_2(SO_4)_3 + H_2O = CrSO_4.OH + HCr(SO_4)_2$, and that, according to his own hypothesis regarding partition, the compound which is least dissociated should mainly be the cause

---

[1] *Z. anorg. Chem.*, **22**, 424 (1899).

[2] See, however, Series 3 of this paper.

[3] *Z. anorg. Chem.*, **23**, 383 (1900).

[4] In the case of an insoluble higher-order compound, however, we should have to deal here rather with the mass law, and with the relative solubilities and stabilities of certain compounds.

[5] The italics are the writer's.

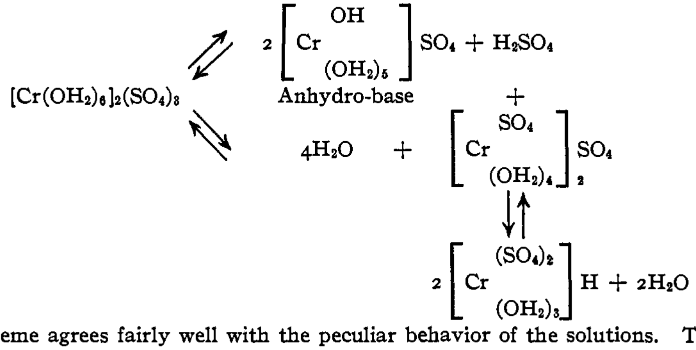
[6] The changes which take place upon heating a solution of chromic (or ferric) sulfate are certainly much more complex; in the light of Werner's theories, they may

of the occlusion in barium sulfate.[1] He says this is the basic complex, and that therefore he is inclined to believe it is mainly the basic complex ($FeSO_4.OH$) which is occluded by the precipitate. He further points out that the work of Küster and Thiel furnishes other grounds for the assumption of the presence of a basic complex in the precipitate, in that they show that acidification very much reduces the occlusion of the iron complex, for that according to the law of mass action the addition of acid must lessen the concentration of the basic complex in the solution, and therefore also, according to the partition law, the quantity which enters the precipitate.[2] Richards adds that still another, though less compelling ground to prove the basic nature of the complex is the fact that Jannasch and Richards found that the impure barium sulfate is able to hold back some water even at 250°; that although it is not impossible that this might be partially due to mechanical inclusion or to its presence as water of crystallization, one is nevertheless inclined to ascribe it partially to the existence of hydroxide in the precipitate.

In answer to Richards, Küster and Thiel[3] accept his explanation of the manner of formation of the complexion $[Fe(SO_4)_2]^-$, and say that he differs with them mainly in assuming that it is $FeSO_4.OH$, rather than $Ba[Fe(SO_4)_2]_2$, which is carried down by the precipitate. With respect to this question, however, they continue to prefer their own hypothesis.

---

more plausibly be represented by some such scheme as the following:



This scheme agrees fairly well with the peculiar behavior of the solutions. The basic substance present is a so-called anhydro-base, containing chromium (or iron) and water, *and it is not necessarily the least ionized of the compounds present.* (See Werner, "Neuere Anschauungen, etc.," sections on Hydrolysis and on the Theory of Bases.)

[1] This statement appears strange in view of the fact that the determining factor in the formation of a solid solution in this instance should undoubtedly be sought in the solubility of a compound in the barium sulfate. The least dissociated compound might be not at all soluble in barium sulfate, while the other compound might, in the non-ionized condition, conceivably be much more readily extracted by barium sulfate from the aqueous solution.

[2] In this connection it should especially be noted that Küster and Thiel allowed their precipitation mixtures to stand for 16 hours before filtration.

[3] *Z. anorg. Chem.*, 25, 319 (1900).

R. Silberberger,[1] who has more recently investigated this question, concludes that the complex which is precipitated along with the barium sulfate is $Ba_3[Fe(SO_4)_3]_2$. His argument is based partly upon analogy with trisulfato-aluminic acid, $H_3Al(SO_4)_3.3\frac{1}{2}H_2O$, which he prepared by heating a solution of aluminum sulfate in concentrated sulfuric acid,[2] and partly upon the equally good agreement of this formula with Jannasch and Richards' ignition data previously referred to.

Still more recently, R. F. Korte[3] has investigated the question with reference to the formation of a solid solution. He arrives at the conclusion that, while the precipitate of barium sulfate containing admixed ferric salt loses weight upon ignition, the ignition loss does not increase in proportion to the increasing concentration of iron in the aqueous solution, and that his experimental results only strengthen the opinion that we have to do here with a complication of physical and chemical processes, and that the observations of Schneider which led him to believe in the formation of a solid solution, find no support in these results. However, since Korte simply weighed the dried precipitates, before and after ignition, and drew conclusions as to their iron contents from the ignition losses, his results are of very questionable value; for the ignition losses do not necessarily indicate anything very definite regarding the iron contents of such precipitates.[4]

Finally, in 1911, Johnston and Adams[5] have investigated the barium sulfate precipitates obtained from solutions which respectively contained sulfate of sodium, lithium, potassium, copper, cadmium, zinc, nickel, manganese, aluminum, ferrous iron, and magnesium. Their data show that metals with soluble sulfates are in general carried down by barium sulfate, and that in each case the amount of contamination is of the same magnitude under identical conditions of precipitation, and is similarly affected by similar variation of the conditions.[6] They find that an in-

---

[1] *Monatsh.*, 25, 220 (1904).

[2] Silberberger, however, apparently overlooked the fact that E. Baud (*Compt. rend.*, 137, 492 (1903)) had previously obtained *di*sulfato-aluminic acid, $HAl(SO_4)_2.1^1/_2H_2O$, by heating a solution of aluminum sulfate in 75% sulfuric acid. Under analytical conditions, still more water is present, and, owing to mass action, it is very unlikely that the *tri*sulfato-acid should be formed.

[3] *J. Chem. Soc.*, 87, 1503 (1905).

[4] Proof of this statement will be found in Tables VI and VII of this paper. The same criticism is applicable to the work of H. J. M. Creighton (*Z. anorg. Chem.*, 63, 53 (1909)) on the contamination of barium sulfate precipitates by aluminum. Creighton, who did not actually determine the aluminum contents of his precipitates, nevertheless concludes from his data that there can hardly be a doubt that we have in this case an example of the solid solution of an aluminum salt in barium sulfate.

[5] *Loc. cit.*

[6] These facts in themselves, especially when viewed in the light of what is known about double sulfates, point strongly towards the formation of difficultly soluble sulfato-complexes.

crease in acidity causes a slow decrease in the amount of contamination; but, *in the light of the writer's results, attention should be drawn to the fact that they invariably allowed the precipitation mixtures to stand for 18 hours before filtering off the precipitates.*

From the foregoing detailed account of the previous work on this subject it may be seen that nothing definite has really been proved concerning the cause of the contamination of barium sulfate by ferric iron.

Experimental Part.

Introduction.—In previous studies of the determination of sulfuric acid in the presence of ferric salts, different investigators have in general made use of solutions belonging to one or more of the following types: (1) ferrous ammonium sulfate, oxidized, and acidified with hydrochloric acid; (2) a solution prepared from definite quantities of sulfuric acid and ferric chloride; (3) a solution of ferric sulfate acidified with hydrochloric acid; and (4) a solution of ferric ammonium alum acidified with hydrochloric acid.

Since the time of these investigations, however, a crystalline compound of ferric iron has been discovered, which, while undergoing dissociation into its constituents upon entering into aqueous solution, can not only be readily prepared and preserved in a state of purity, but which also is capable of serving as a convenient and suitable substance for the preparation of solutions for use in such studies. This is the ferri-sulfuric acid, $Fe_2(SO_4)_3.H_2SO_4.8H_2O$, of Recoura,[1] which was prepared and studied by him in 1903. According to Recoura, this compound is formed whenever ferric sulfate, in aqueous solution, is heated with free sulfuric acid; and the formula is constant, regardless of the quantity (within wide limits) of the concentrated sulfuric acid which is added. Recoura, who obtained the same compound also by treating solid ferric sulfate with hot hydrochloric acid, prepared and studied the ethyl ester of this acid, but, owing to the dissociation of the acid into its constituents upon the addition of water, he considered it useless to attempt the preparation of the corresponding alkali and alkali-earth salts.

Weinland and Ensgraber,[2] in 1913, have prepared this same acid, and in conformity with Werner's coördination theory, they have named it disulfato-ferric acid, and have assigned to it the formula $H[Fe(SO_4)_2].4H_2O$. Moreover, they have prepared the following salts: $K[Fe(SO_4)_2].H_2O$, $NH_4[Fe(SO_4)_2]$, and $C_5H_5NH\ [Fe(SO_4)_2].2H_2O$; also, $Na_3\ [Fe(SO_4)_3].3H_2O$, the sodium salt of a trisulfato-ferric acid.

These salts are prepared by heating the corresponding sulfates, in aqueous solution, with ferric sulfate and sulfuric acid, whereupon they separate in the form of colorless pulverulent crystals. In water, at 0°,

---

[1] *Compt. rend.*, 137, 118, 189 (1903).

[2] *Z. anorg. Chem.*, 84, 349 (1913).

they are very difficultly soluble, even to a concentration of 0.008 molal; the ammonium salt, for example, dissolves to this concentration only after several days' shaking at 0°, and even then the solution is identical with one of ferric alum. The salts of the sulfato-ferric acids—and the same is true of disulfato-ferric acid itself—are practically insoluble as such in water; upon going into aqueous solution they yield the corresponding alums,[1] and, upon the evaporation of the solutions at the ordinary temperature, characteristic crystals of the alums are deposited.[2]

The foregoing considerations indicate clearly that boiling hot solutions containing ferric sulfate and free acid, such as have been employed by previous investigators, invariably contain sulfato-complexes; and they are of the greatest interest in connection with the cause of the contamination of barium sulfate which has been precipitated in the presence of ferric iron.[3] Also, especially when taken in connection with the similar degrees of contamination which have been observed in this and in previous investigations, they serve to justify the use of the disulfato-ferric acid in the preparation of solutions for use in the present investigation.

The Preparation of Disulfato-ferric Acid.—265 g. of hydrated ferrous sulfate were dissolved in 400 cc. of hot water, with the addition of 30 cc. of sulfuric acid (sp. gr. 1.84) and 20 cc. of nitric acid (sp. gr. 1.42), the latter being added in small portions, with stirring, to the boiling solution. The mixture was repeatedly evaporated, with water, to a thick syrup, to completely expel the nitric acid. The ferric sulfate was then redissolved in a mixture of 135 cc. of sulfuric acid (sp. gr. 1.84) and 350–400 cc. of water, and, after filtration, the solution was heated for several hours on the steam bath, until the free acid separated in good yield.[4] The precipitate was filtered off with suction, in a Büchner funnel, and washed, first with a little ice-cold, dilute sulfuric acid, mixed with an equal volume of alcohol, and then with pure alcohol. It was dried on a porous plate, after

---

[1] These facts would seem to indicate that anhydrous ferric sulfate, which is white and which dissolves with extreme slowness in water, is really a ferric sulfato-ferriate, as $Fe[Fe(SO_4)_2]_3$, or $Fe[Fe(SO_4)_3]$. Anhydrous chromic sulfate behaves in the same way. Both of the hydrated salts are readily soluble in water.

[2] Weinland and Ensgraber (*Loc. cit.*) have carefully investigated these compounds, and the properties listed above have been determined by them.

[3] In this connection, see T. W. Richards and F. Bonnet (*Z. physik. Chem.*, 47, 42 (1904)). They find that the green sulfate of chromium (modified by heat) is carried down by barium sulfate about as ferric iron is, but that violet (unheated) chromium sulfate is carried down hardly at all. This behavior apparently coincides with that of ferric iron, which is carried down to a much greater extent in hot than in cold solutions, and is another point in favor of the view advanced in the present paper.

[4] If the ferric acid fails to separate in a resonable time, the process can be greatly hastened by the addition of concentrated sulfuric acid, in small portions, with stirring. Also, a better product is obtained if the mixture is stirred, on the steam bath, during the separation of the crystalline compound.

which it was allowed to stand for several days over concentrated sulfuric acid, in a desiccator.

The Analysis of the Disulfato-ferric Acid.—Sample I, which was used in the first two series of experiments, was analysed by the Zimmermann-Reinhardt method (*a*) after two days', and (*b*) after two weeks' preservation over concentrated sulfuric acid.

(*a*) 1.0155 g. = 32.05 cc. 0.1 *N* $KMnO_4$ .... 17.62% Fe
(*b*) 1.0540 g. = 33.30 cc. 0.1 *N* $KMnO_4$ .... 17.64% Fe

Sample II, which was used in all the other experiments, was analyzed after it had stood for more than six weeks in a cork-stoppered bottle.

(*a*) Z.-R. method, 1.1062 g. = 34.50 cc. 0.1 *N* $KMnO_4$ .... 17.42% Fe
(*b*) Precipitation with ammonia, 1.1290 g. = 0.2819 g. Fe_2O_3 .... 17.46% Fe
(*c*) Acid simply ignited, 1.0584 g. = 0.2629 g. Fe_2O_3 .... 17.39% Fe
1.0043 g. = 0.2492 g. Fe_2O_3 .... 17.35% Fe
Calculated for $HFe(SO_4)_2.4H_2O$ .... 17.39% Fe

Series 1.—Samples of disulfato-ferric acid of about 0.5 g. each were dissolved in 250 cc. portions of water, 3 cc. of hydrochloric acid (sp. gr. 1.12) were added to each, and the solutions were then treated with 20 cc. portions of 0.5 *N* barium chloride solution. After precipitation, 25 cc. of water were added to each solution, to allow for evaporation, and the mixtures were digested overnight, in covered beakers, on the steam bath. The precipitates were then filtered off, washed thoroughly, and ignited wet, to constant weight. The results are given in Table I.

TABLE I.—MIXTURES DIGESTED OVERNIGHT ON STEAM BATH.

	Precipitation mixture.						Grams of ignited ppt. from 1 g. of $HFe(SO_4)_2.4H_2O$.	
No.	Sample. G.	Water. Cc.	HCl (1.12). Cc.	$BaCl_2$ (0.5 *N*). Cc.	Temperature of solution and precipitant.	Wt. of ignited ppt. G.	Found. G.	Calcd. G.
1	0.4153	250	3	20	10°	0.6085	1.4652	1.4542
2	0.6308	250	3	20	Boiling	0.9088	1.4407	1.4542

Series 2.—In this series, portions of disulfato-ferric acid of about one gram each were dissolved in water, the solutions treated with hydrochloric acid in increasing quantities, and to these solutions 15 cc. portions of 1 *N* barium chloride solution were added slowly, with stirring. The mixtures were digested for 2½ hours on the steam bath, after which the precipitates were filtered off, washed free from chlorides, and ignited wet, to constant weight. The results are given in Table II.

TABLE II.—MIXTURES DIGESTED FOR $2^1/_2$ HOURS ON STEAM BATH.

	Precipitation mixture.						Wt. of ignited ppt. from 1 g. of $HFe(SO_4)_2.4H_2O$.	
No.	Sample. G.	Water. Cc.	HCl (1.12). Cc.	$BaCl_2$ (*N*). Cc.	Temp. of solution and reagt. ° C.	Wt. of ignited ppt. G.	Found. G.	Calcd. G.
3	0.9507	150	2	15	22	1.3818	1.4535	1.4542
4	0.7709	150	4	15	22	1.1174	1.4495	1.4542
5	1.0324	150	6	15	22	1.5028	1.4556	1.4542
6	1.0760	150	8	15	22	1.5593	1.4492	1.4542

Series 3.—In this series, the first three precipitations were carried out at room temperature, and the last three in solutions heated to a full boil. In all cases the barium chloride solution was run in cold, from a buret, in the course of about one minute, with stirring. All six mixtures were allowed to stand for 16 hours at the ordinary temperature. In each case, the supernatant liquid was then decanted through a filter, the precipitate washed once by decantation with 25 cc. of 2.5% hydrochloric acid, then with cold water (to avoid hydrolyzing the ferric chloride), and finally with hot water until free from chlorides.[1] The precipitates were then ignited wet to constant weight. The ignited precipitates were fused with 5 g. portions of pure sodium carbonate, the fusions extracted with hot water, and the residues analyzed for iron by solution in hydrochloric acid and double precipitation from carbonate-free solutions by means of pure ammonia.[2] The results are given in Table III.

TABLE III.—MIXTURES DIGESTED FOR 16 HOURS AT ROOM TEMPERATURE.

	Precipitation mixture.				Temp. of solution.	Wt. of ignited ppt.	Wt. of Fe_2O_3 found.	Wt. of ignited ppt. per g. of $HFe(SO_4)_2.4H_2O$.		Wt. of Fe_2O_3 per g. of ignited ppt.
No.	Sample. G.	Water. Cc.	HCl (1.12). Cc.	$BaCl_2$ (*N*). Cc.	° C.	G.	Mg.	Found. G.	Calcd. G.	Mg.
7	1.0107	84	2	15	*27*	1.4662	4.3	1.4507	1.4542	2.9
8	1.0072	82	4	15	*27*	1.4614	4.5	1.4510	1.4542	3.1
9	1.0079	80	6	15	*27*	1.4634	4.8	1.4519	1.4542	3.3
10	1.0023	84	2	15	*B. P.*	1.4383	9.8	1.4350	1.4542	6.8
11	1.0056	82	4	15	*B. P.*	1.4410	10.4	1.4330	1.4542	7.2
12	1.0029	80	6	15	*B. P.*	1.4376	10.2	1.4334	1.4542	7.1

Series 4.—In this series, and also in those which follow—since it was not so much a question of making sulfate determinations in the presence of iron, as of investigating the cause of the contamination of barium sulfate by ferric iron[3]—no attempt was made to determine the actual weights of the precipitates. The precipitates were simply dried, transferred for the most part to weighed platinum crucibles, and then treated as described under each series.

Each solution of this series was heated to a full boil, and then at once treated with 15 cc. of normal barium chloride solution, added cold from a buret, with stirring, in the course of about one minute. The mixtures

---

[1] In each case, although precipitated with barium chloride in excess, the chloride-free washings contained traces of ferric sulfate; they gave precipitates with the original filtrates, or with barium chloride solution. Küster and Thiel (*Loc. cit.*) called especial attention to this fact, but Richards (*Loc. cit.*) apparently considered it of minor importance. It will be considered later in the discussion.

[2] In all the experiments which follow, the precipitates were analyzed for iron according to this procedure. Although the ammonia used gave no turbidity with a freshly boiled solution of barium chloride, the first precipitates were invariably contaminated by baryta (see, for example, Table VII, footnote).

[3] This statement will serve also to explain the high concentration of the barium chloride solutions used in making the precipitations.

were allowed to stand for 8 hours on the desk, after which the precipitates were filtered off, washed once with 50 cc. of 2.5% hydrochloric acid, then with cold water, and finally with hot water until free from chlorides. The precipitates were dried for 4 hours at 120°, transferred from the filters to platinum crucibles, and ignited at a dull red heat for 5 minutes. They were then weighed, and analyzed for iron—5 g. portions of sodium carbonate being used in the fusions. The results are given in Table IV.

During the drying, the filters, which were placed in small beakers in the electric oven, were somewhat charred. Nos. 13–16 were very brittle, but Nos. 17–18 were less acted upon. It is of great interest in this connection to note that disulfato-ferric acid, when heated upon a filter paper at 120°, very soon chars the filter, as does also the potassium salt, $KFe(SO_4)_2.H_2O$, a sample of which was prepared according to the method of Weinland and Ensgraber,[1] especially for this test.

Table IV.—Mixtures Digested for 8 Hours at Room Temperature.

	Precipitation mixture.							
No.	Sample. G.	Water. Cc.	HCl (1.12). Cc.	$BaCl_2$ (*N*). Cc.	Temperature of solution.	Wt. of ppt. taken. G.	Wt. of Fe_2O_3 found. Mg.	Wt. of Fe_2O_3 per g. of ignited ppt. Mg.
13	2.004	168	4	15	Boiling	1.4043	9.2	6.5
14	2.007	164	8	15	Boiling	1.3940	9.0	6.5
15	2.001	160	12	15	Boiling	1.3982	7.8	5.6
16	2.003	156	16	15	Boiling	1.3989	7.2	5.1
17	2.004	148	24	15	Boiling	1.3968	4.4	3.1
18	2.003	140	32	15	Boiling	1.4085	4.4	3.1

Series 5.—In this series each solution was heated to a full boil, and then at once treated, as in Series 4, with 30 cc. of normal barium chloride solution, which was run in in the course of about 1½ minutes. The mixtures were in this instance allowed to stand for only 2½ hours. The precipitates were then freed from supernatant liquid by the direct decantation of the latter into the sink. Each precipitate was washed by decantation with two 25 cc. portions of 2.5% hydrochloric acid, and then with five 100 cc. portions of cold water, the washings being decanted into the sink. The precipitates obtained in this series were coarse, and they settled very rapidly; this was especially true of those at the end of the series, which were thrown down in the presence of relatively large quantities of acid. The precipitates were very readily separated from the mother liquids, and also (though less readily) from the washings, by decantation.

The washed precipitates were transferred to filters by means of a stream of distilled water; the washings which passed through were found to be free from chlorides, but to contain traces of ferric sulfate.[2] The precipi-

---

[1] *Loc. cit.*

[2] One portion gave a distinct precipitate with barium chloride acidified with a drop of hydrochloric acid, and, with potassium thiocyanate and hydrochloric acid, another portion gave a distinctly pink coloration. Needless to say, a blank test was applied to the hydrochloric acid.

tates were dried upon the filters, in small beakers, for 4 hours at 120°. All six filters were charred, increasingly from No. 19 to No. 24. The dried precipitates were transferred to platinum crucibles and analyzed for iron, 12 g. of sodium carbonate being used in each fusion.[1] The results are given in Table V.

TABLE V.—MIXTURES DIGESTED FOR $2^1/_2$ HOURS AT ROOM TEMPERATURE.

	Precipitation mixture.							
No.	Sample. G.	Water. Cc.	HCl (1.12). Cc.	$BaCl_2$ (*N*). Cc.	Temp. of solution.	Wt. taken of ppt. dried at 120°. G.	Wt. of Fe_2O_3 found. Mg.	Wt. of Fe_2O_3 per g. of dried ppt. Mg.
19	2.003	170	2	30	Boiling	2.799	14.6	5.2
20	2.000	168	4	30	Boiling	2.794	16.8	6.0
21	2.001	166	6	30	Boiling	2.804	17.1	6.1
22	2.003	164	8	30	Boiling	2.821	20.0	7.1
23	2.001	162	10	30	Boiling	2.776	22.2	8.0
24	2.002	160	12	30	Boiling	2.783	22.5	8.1

Series 6.—This series was carried out according to the procedure of Series 5, with the exception that the precipitates were washed with water alone—six times with 100 cc. portions. It will be noted that sulfuric acid was used, instead of hydrochloric acid, and that the quantity of barium chloride added was insufficient to precipitate all of the sulfate which was present.

In this case also the precipitates settled very rapidly, but only in the original solutions; when treated with water, they became much finer in texture, and still more time was consumed in the washing. The last washings were free from chlorides, but they contained traces of ferric sulfate. The precipitates when transferred to the filters were very slimy in appearance, although originally they were coarse grained; upon drying they shrank together. These facts, which point unmistakably to chemical action between the precipitates and the wash-water, will be referred to again in the discussion.

The precipitates were dried on the filters for 10 hours at 120°, whereby the filters were badly charred. After separation from the filters, the precipitates were further dried in platinum crucibles for 2½ hours at 120°. They were then weighed, further dried for 18 hours at 160°, and again weighed. Finally they were placed in a cold electric muffle furnace, heated to 950°, and kept at that temperature for one hour; after cooling in a desiccator, they were again weighed. The ignited precipitates were of a bright salmon color, and appeared to the naked eye to be entirely

---

[1] It will perhaps be of interest to note that in Experiments 19 and 24, in which 2 cc. and 12 cc. of 24% hydrochloric acid were respectively present, the aqueous extracts from the fusions were examined for chlorides by acidification with nitric acid and treatment with silver nitrate. In Experiment 19 only a slight turbidity was produced in the solution, while in Experiment 24 the silver chloride obtained was found to weigh 36.1 mg.

homogeneous; they were fused with 17 g. portions of sodium carbonate, and analyzed for iron. The results are given in Table VI.

TABLE VI.—MIXTURES ALLOWED TO STAND FOR 1/2 HOUR.

	Precipitation mixture.				Wt. taken of ppt. dried at 120°.	Loss in 18 hrs. at 160°.	Further loss at 950°.	Wt. of Fe_2O_3 found.	Ign. loss (120–950°) divided by wt. of Fe_2O_3.	Wt. of Fe_2O_3 per g. of ppt. dried at 120°.
No.	Sample. G.	Water. Cc.	H_2SO_4 (0.992 *N*). Cc.	$BaCl_2$ (*N*). Cc.	G.	Mg.	Mg.	Mg.		Mg.
25	2.001	167	3.1	30	3.2042	1.9	78.2	26.7	3.0	8.3
26	2.000	164	6.2	30	3.5639	2.4	104.0	32.4	3.3	9.1
27	2.000	158	12.5	30	3.6100	5.1	140.3	39.1	3.7	10.3
28	2.000	151	18.7	30	3.5567	6.3	136.0	33.0	4.3	9.3
29	2.000	145	25.0	30	3.5912	7.2	131.3	26.9	5.2	7.5
30	2.000	139	31.2	30	3.2523[1]	8.4	114.0	20.8	5.9	6.4

Series 7.—In this series each solution was heated to a full boil, and then at once treated with 30 cc. of normal barium chloride solution, which was suddenly poured into the hot reaction mixture, with stirring, from a small beaker into which it had previously been measured from a buret. The precipitation mixtures were in each case allowed to stand for ½ hour, after which the supernatant liquids were decanted into the sink. The precipitates, with the remaining liquid, were transferred to 50 cc. glass centrifugal tubes, the last portions being washed into the tubes by means of a little 2.5% hydrochloric acid, and the mixtures were then centrifuged at high speed in an electrical centrifuge. The liquid portions were then decanted, and each precipitate was washed three times as follows: 25 cc. of 2.5 % HCl were added to the precipitate, the precipitate was loosened with a glass rod, then it was shaken with the liquid to a milky mixture, and finally the mixture was centrifuged and the liquid decanted. After 30-40 seconds on the centrifuge the clear liquid could be easily and completely decanted without danger of losing any of the precipitate. The total time required in each case, including the ½ hour standing after precipitation, was 45 minutes. Finally the precipitates were dried for 18 hours at 120° in the glass tubes, and quantitatively transferred to platinum crucibles as follows: the solid cake was removed as far as possible onto a watch glass, the remainder was washed into the crucible with a little hydrochloric acid, and the latter driven off by evaporation on the steam bath; the bulk of the precipitate was then transferred to the crucible from the watch glass, and the whole dried for two hours at 120°. After weighing, the crucibles and their contents were heated up to 950° in an electric muffle, and kept at that temperature for one hour. After cooling they were again weighed, and then the precipitates were analyzed

---

[1] This precipitate, after being quickly weighed, was allowed to stand for 10 minutes upon the balance pan: in this time it increased in weight by 1.6 mg. This tendency of the precipitates dried at 120° to absorb moisture from the air had already been noted in many of the preceding experiments.

for iron, 12 g. portions of sodium carbonate being used in the fusions. In this way the precipitates were rapidly prepared for analysis, and during the drying operation there was no loss of iron, due to its absorption by a filter paper, as was probably the case in Series 4, 5, and 6.

The results will be found in Table VII. And in Fig. 1 the mgs. of Fe_2O_3 found per g. of dried precipitate are plotted as ordinates, with the cc. of 26% H_2SO_4 as abscissas. It will be noted that the free sulfuric acid from 2 g. of sulfato-ferric acid is equivalent in amount to 1 cc. of 26 % H_2SO_4, and since this compound dissociates almost completely upon going into solution, this additional 1 cc. has in each instance been added to the quantity shown in the table. It is further worthy of mention that, in Expt. 31, in which no additional sulfuric acid was added to the precipitation mixture, the walls and bottom of the beaker in which the precipitation was carried out were coated with a mirror of basic ferric sulfate. And, even in spite of this fact, the quantity of iron per 1 gram of dried precipitate was less than in any of the following three experiments. This in itself would seem to indicate clearly that the contamination is not due to the

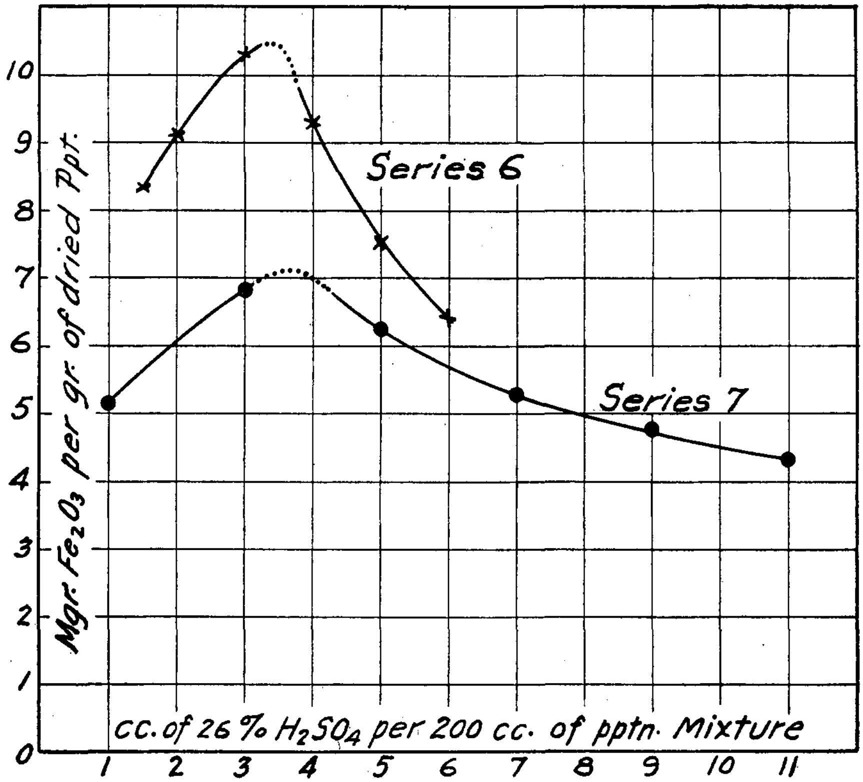


Fig. 1.

presence in the precipitate of a basic ferric sulfate in a state of solid solution.

TABLE VII.[1]—PRECIPITATION MIXTURES ALLOWED TO STAND FOR 1/2 HOUR, AND WASHING COMPLETED IN 1/4 HOUR.

	Precipitation mixture.								
No.	Sample. G.	Water. Cc.	H_2SO_4 (26%). Cc.	$BaCl_2$ (*N*). Cc.	Wt. taken of ppt. dried at 120°. G.	Ign. loss at 950°. Mg.	Wt. of Fe_2O_3 found. Mg.	Ign. loss (120–950°) divided by wt. of Fe_2O_3.	Wt. of Fe_2O_3 per g. of ppt. dried at 120°. Mg.
31	2.000	172	0	30	2.9166	28.5	14.9	1.91	5.16
32	2.000	170	2	30	3.5272	69.7	24.0	2.90	6.80
33	2.000	168	4	30	3.5016	74.2	21.9	3.39	6.25
34	2.000	166	6	30	3.4686	57.3	18.3	3.13	5.27
35	2.000	164	8	30	3.5145	60.1	16.8	3.58	4.78
36	2.000	162	10	30	3.5016	46.9	15.1	3.11	4.31

Attempts to Prepare Pure Sulfato-ferriates of the Alkali-earth Metals.—Upon heating freshly prepared barium sulfate with ferric chloride or sulfate, in the presence of hydrochloric or sulfuric acid, the barium sulfate was found to become somewhat largely contaminated with ferric iron, though the bulk of the precipitate remained barium sulfate even after heating the mixture for several days. Experiments carried out under various conditions with calcium sulfate gave similar results, in spite of the much greater relative solubility of this salt. Since however magnesium sulfate is a very soluble salt, it was hoped that more definite results might be obtained with it than with the sulfates of barium and calcium, and with that end in view the following experiments were carried out:

(A) 3 g. $MgSO_4.7H_2O$ and 7 g. $HFe(SO_4)_2.4H_2O$ (approximately equivalent amounts) were dissolved in a mixture of 12 cc. of conc. H_2SO_4 and 50 cc. of water. The filtered solution was evaporated on the steam bath to about one-half the original volume, and the crystals filtered off and washed with alcohol and dried for several days in a desiccator over sulfuric acid. The crystals, which resembled in appearance the free sulfato-ferric acid, were analyzed with the following results:

I. 2.0170 g. subst. yielded 0.4660 g. Fe_2O_3, 2.9157 g. $BaSO_4$, and 0.0256 g. $Mg_2P_2O_7$.

II. 2.0409 g. subst. yielded 0.4735 g. Fe_2O_3, 2.9610 g. $BaSO_4$, and 0.0236 g. $Mg_2P_2O_7$.

That is, 16.15 and 16.22% Fe, 59.49 and 59.70% SO_4, and 0.28 and 0.25% Mg, respectively.

(B) 20 g. $MgSO_4.7H_2O$ and 10 g. H $Fe(SO_4)_2.4H_2O$ (equivalent ratio, about 5 : 1) were dissolved in a mixture of 20 cc. of conc. H_2SO_4 and 100 cc. of water. The mixture was heated on the steam bath until crystals began to appear at a few points, when 5 cc. more of conc. H_2SO_4 were added with stirring; the heating was continued with

---

[1] In the case of this series, the Na_2CO_3 fusions, after extraction with water and thorough washing with Na_2CO_3 solution and then with water, were dissolved in HCl and precipitated in the absence of CO_2 with NH_4OH (volume in each case = about 100 cc.). The precipitates were washed 6 times with boiling water, redissolved in HCl, and the iron precipitated with NH_4OH. The original six filtrates from the second precipitation were united, acidified with HCl and the barium precipitated with H_2SO_4. The $BaSO_4$ obtained weighed 0.0486 g. That is, in the first precipitation of the iron, in about 600 cc. of solution containing about 12 g. of barium and 0.0777 g. of iron, the 148 mg. of $Fe(OH)_3$ retained after washing 35.6 mg. of $Ba(OH)_2$.

frequent stirring for 15 minutes. The crystals were then filtered off, transferred to a porous plate and allowed to drain, then quickly washed in a beaker with alcohol, and rapidly filtered off with suction; they were preserved over conc. sulfuric acid in a desiccator for five weeks. Upon analysis they gave the following results:

I. 0.6656 g. subst. yielded 0.1694 g. Fe_2O_3, 1.0755 g. $BaSO_4$, and 0.0252 g. $Mg_2P_2O_7$.

II. 0.9996 g. subst. yielded 0.2517 g. Fe_2O_3, 1.6129 g. $BaSO_4$, and 0.0360 g. $Mg_2P_2O_7$.

That is, 17.80 and 17.61% Fe, 66.50 and 66.40% SO_4, and 0.83 and 0.81% Mg, respectively.

While the attempts to obtain a pure sulfato-ferriate of magnesium did not meet with success—doubtless owing to the greater stability and insolubility of the free sulfato-ferric acid—it will nevertheless be seen that, in accordance with the law of mass action, the percentage of magnesium in the crystals was increased several times by increasing the proportion of magnesium sulfate in the original solution. And one would hardly care to maintain that the contamination of this small amount of magnesium sulfate (itself a very soluble salt), with so much ferric sulfate could be due to the presence of the latter in the former in a state of solid solution. Considered in connection with the marked percentage increase of SO_4 found in the second experiment, it is very likely that we have to do here with a mixture of disulfato-ferric acid and a triple compound of magnesium sulfate, ferric sulfate, and sulfuric acid, such, for example, as $Fe_2(SO_4)_3.MgSO_4.2H_2SO_4.nH_2O$, *i. e.*, $MgH_4[Fe(SO_4)_3]_2.nH_2O$, an acid magnesium salt of trisulfato-ferric acid. The correctness of this formula is strongly supported by the data of the experiments just described, as may be seen from the following calculations:

I. Analysis gave: 16.18% Fe; 59.60% SO_4; 0.265% Mg. As $MgH_4[Fe(SO_4)_3]_2.nH_2O$, 0.265 part by weight of Mg would require 1.30 parts of Fe and 6.28 of SO_4; there would therefore be left 14.88 parts by weight of Fe and 53.32 of SO_4, or, in atomic proportions, Fe : SO_4 = 1.00 : 2.08.

II. Analysis gave: 17.70% Fe; 66.45% SO_4; 0.82% Mg. In the same way, 0.82 part by weight of Mg would require 3.76 parts of Fe and 19.43 of SO_4; *i. e.*, there would remain 13.94 parts of Fe and 47.02 of SO_4, or, in atoms, Fe : SO_4 = 1.00 : 1.96.

Assuming the presence in the crystals of $MgH_4[Fe(SO_4)_3]_2.nH_2O$, both sets of data agree in indicating the existence in the mixture of another compound in which the atomic ratio is Fe : SO_4 = 1 : 2, the ratio in which these substances are present in $HFe(SO_4)_2.4H_2O$.

As to the number of water molecules in the magnesium salt, a calculation based upon the data of Expt. A (H_2O = 23.91%), after subtraction of the $HFe(SO_4)_2.4H_2O$, gives a value, n = 23.98; *i. e.*, 24 molecules. The data of Expt. B, on the other hand, give upon calculation a quantity of water (H_2O = 14.90%) which is slightly insufficient for the salt $HFe(SO_4)_2.4H_2O$; but, in addition to having stood for five weeks over concentrated sulfuric acid, the crystals in Expt. B were originally separated at a somewhat higher concentration of sulfuric acid. These facts might readily account for the different water contents found in the two cases.

Discussion of the Results.

The results obtained in the first three series of experiments serve to illustrate the influence exerted by ferric salts upon the determination of sulfuric acid. It will be seen from Tables II and III that (as Küster and Thiel pointed out) fairly good analytical results may be obtained in the presence of ferric iron, provided the precipitation with barium chloride is carried out in the cold; but that the precipitates thus formed are, contrary to the statement of Küster and Thiel, not free from iron (Table III). The data in these three series agree very well with data previously obtained by Küster and Thiel, and other investigators, and they are introduced here mainly in order to show that solutions made from disulfato-ferric acid behave in this respect also like ordinary mixtures of ferric sulfate and free acid, and to justify their use in this investigation.

The results obtained in Series 4, in which the precipitates were allowed to stand for 8 hours in the mother-liquids, are in good agreement with the analogous data of Küster and Thiel; taken alone, they seem to indicate that increased acidification very rapidly reduces the quantity of iron which is carried down by the precipitates. Taken in connection with the data obtained in Series 5 and 6, however, in which the precipitation mixtures were allowed to stand for $2^1/_2$ hours and for $^1/_2$ hour, respectively, and also in connection with the fact (also observed by Küster and Thiel), that the washings from these precipitates invariably contain traces of sulfuric acid and ferric iron, it is readily seen that the analytical data cannot be relied upon to furnish the actual composition, *at the time of their formation*, of such precipitates. What we analyze is a product which always has been more or less transformed, depending upon the length of time it has stood in contact with the mother-liquid, the composition of the latter, the time consumed in the washing, the composition of the wash-liquid, etc. However, the data contained in Tables IV–VII lead clearly to the conclusion that, contrary to the view of Richards, acidification actually increases the quantity of the iron complex which is carried down, but that, if the precipitate is allowed to stand for a long time in contact with the mother-liquid, the iron complex is removed at a rate which increases with the concentration of the acid in the solution. The complex is not, therefore, as Richards argues, a basic sulfate of iron. On the contrary, it is apparent that sulfuric acid—or hydrogen ion from hydrochloric acid—by mass action, increases the concentration of the disulfato-ferric acid in the solution, and therefore that of the iron complex in the impure precipitate, at the time that the latter is formed.

The results of Series 5 and 6 also lead to the conclusion that the iron content of the precipitates is not due to surface adsorption on the grains of the precipitate. The coarseness of the grains of the precipitates plainly increased in both series with the acid concentration of the precipitation mixtures, and we have already seen that acidification also increases the quantity of iron which is carried down. If the iron were carried down by surface adsorption, then the quantity should of course decrease with increasing coarseness of the grains.

Series 7, in which the results are similar to those of Series 6 (12.5 cc. 0.992 N H_2SO_4 = 2 cc. 26% H_2SO_4), differs from it mainly in that the precipitates were much more rapidly prepared for analysis, the washing being accomplished with the aid of a high speed centrifuge in about 15 minutes.

The manner of preparation and properties of disulfato-ferric acid, and of its alkali salts, as well as the results obtained in this investigation in attempting to prepare the alkali-earth salts, point unmistakably to the true cause of contamination in the case of these precipitates; and this conclusion is materially strengthened by the fact, apparently noted for the first time in this paper, that upon drying such precipitates on paper filters the latter are charred at temperatures as low as 120°. Disulfato-ferric acid itself, as well as its potassium salt, when heated in the dry condition upon a paper filter at 120°, very soon chars the filter. The sulfatoferriates containing water of crystallization evidently dissociate to a certain extent at this temperature, yielding free sulfuric acid, and this it is which chars the paper. Basic salts would show no such tendency. It is also doubtless due to this free acid that precipitates which have been dried at 120° tend to increase in weight upon being left in contact with the air (Table VI, footnote).

It will be noted that in Series 6 and 7 sulfuric acid was used instead of hydrochloric acid in the preparation of the precipitation mixtures. Assuming the iron complex carried down to be the barium salt of a sulfatoferric acid, then, on the one hand, owing to mass action, we should expect that with the use of sulfuric acid instead of hydrochloric acid larger amounts of this salt, and therefore of iron, would be found in the precipitates. On the other hand, however, owing to the greater concentration of sulfate ion in these solutions, we should expect that, upon precipitation with a deficiency of barium chloride, precipitates containing even a lower concentration of the iron complex might result. In reality, each of these factors seems to be able to exert a determining influence upon the composition of the precipitate, depending upon the concentration of the sulfuric acid; the quantity of iron carried down at first increases with the concentration of the free sulfuric acid in the mixture, reaches a maximum, and then decreases. This is plainly shown in Fig. 1, in which are plotted as ordinates the milligrams of Fe_2O_3 per gram of dried precipitate, and as abscissas the cubic centimeters of 26% H_2SO_4 present in a given volume of the precipitation mixture.

While in some of the completely washed precipitates of Series 6 a somewhat higher concentration of iron was found to be present than in any of those of Series 5 (in which hydrochloric acid was used), the precipitates were in Series 6 much more difficult to prepare for analysis. Although, like the precipitates of Series 5, they were coarse-grained and quick to settle in the precipitation mixtures, they became fine-grained and slow to settle during the washing, and at the last, on the filters, they were extremely slimy and impervious to the wash-water. This behavior, while unexpected, is nevertheless in good agreement with the conclusion that the iron is carried down in the form of a complex barium sulfato-ferriate. It has already been pointed out that the iron complex in these impure barium sulfate precipitates is slowly dissociated by water in the sense of the equation

$$Ba[Fe(SO_4)_2]_2.nH_2O + \text{Water} = BaSO_4 + Fe_2(SO_4)_3.mH_2O.$$

This dissociation takes place during the washing, and the barium sulfate formed in this way is, as we should naturally expect, very fine-grained and slow to settle. Again it should be emphasized, that analyses of the completely washed precipitates are incapable of furnishing accurate data as to their composition at the time of their actual formation.

One other point should be especially noted in connection with these precipitates, and that is that their losses in weight upon ignition do not of necessity bear any relationship to their iron contents. The truth of this assertion is plainly borne out by the data of Tables VI and VII.

Conclusion.

Barium sulfate precipitates which have been thrown down in solutions containing ferric iron, carry down the latter in varying quantities, not in the form of a solid solution of basic ferric sulfate or other compound, nor adsorbed on the surface of the grains, but in the form of a hydrated complex sulfato-ferriate of barium (or other cation), which is present in intimate mechanical admixture with the barium sulfate.

URBANA, ILL.

[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION OF WASHINGTON.]

THE TERNARY SYSTEM $H_2O-K_2SiO_3-SiO_2$.

BY GEORGE W. MOREY.

(MICROSCOPIC STUDY BY C. N. FENNER.)

Received April 2, 1917.