

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

THE SYSTEM, $\text{Fe}_2\text{O}_3\text{-SO}_3\text{-H}_2\text{O}$

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Introduction

This paper treats of the general¹ equilibrium relations in the system, $\text{Fe}_2\text{O}_3\text{-SO}_3\text{-H}_2\text{O}$, from 50° to 200° and comprises the determination of the compositions and properties of the solid phases, as well as the compositions of the solutions in equilibrium with the various solid and vapor phases within the above temperature range.

The list of recorded ferric sulfate salts is long,² and includes some of very complex composition. However, only a few of them are properly defined and represent single crystalline substances; the majority, especially the basic salts, are described as "amorphous" substances, and undoubtedly are mixtures. The reason for the apparent chemical complexity of many of them may easily be found in the general way in which such products had been formed as well as in the difficulty with which many of them are known to crystallize. It will be seen from this paper that all the ferric sulfate salts decompose more or less slowly in contact with water and the atmosphere, and are stable only in contact with solutions of certain concentrations, temperatures and pressures. The preparation of pure substances could, therefore, be attained only under definitely controlled conditions. The great majority of the synthetic products which have been recorded, however, were formed by precipitation, hydrolysis, or partial evaporation of ferric sulfate solutions, conditions under which no equilibrium could have been reached, and which resulted mostly in the formation of mixtures. The slow reactivity with water gave rise to the assumption that these products were definite stable compounds, while in reality their stability was only apparent. We shall not discuss in detail the recorded preparations, as pertinent references will be given below. Special mention should, however, be made of three papers embodying attempts to deal with the problem according to the phase rule.

Cameron and Robinson² prepared a number of samples by saturating ferric sulfate solutions of various strengths with freshly precipitated ferric hydroxide, and shaking them at 25° for 4 months. At the end of this time they found that the specific gravities of the solutions had become

¹ Certain special problems, to which time could not well be given, still need to be worked out.

² See Dammer, "Handbuch der anorganischen Chemie," III, 332. Cameron and Robinson, *J. Phys. Chem.*, 11, 641 (1907). Dana, "System of Mineralogy," J. Wiley and Sons, 1906.

constant. The solutions as well as the solids with adhering mother liquor were analyzed. From the results obtained they concluded (1) that there are no definite basic ferric sulfates formed at this temperature, but that the stable solid phase up to a concentration of about 25% sulfuric acid is one of a series of solid solutions containing ferric oxide, sulfuric acid and probably water; (2) that the normal salt with 10 molecules of water is stable with solutions containing between 25 and 28% of sulfuric acid; and (3) that above this concentration the stable solid phase is an acid sulfate of the composition, $\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 10\text{H}_2\text{O}$. This deduction that solid solutions are the stable solid phase in contact with solutions containing up to about 25% of sulfuric acid will be disproved and the existence of definite basic salts shown. The water content of both the normal and the acid salt mentioned by those authors is erroneously stated, and the curves representing the solutions with which these solids are in equilibrium are not exact.

Better progress in the study of ferric sulfates has been made by Wirth and Bakke³ who also worked at 25°. These authors were unable to establish the solid phases which are in equilibrium with solutions containing less than about 26% of sulfuric anhydride. However, they prepared and determined the saturation curve of the basic salt, $2\text{Fe}_2\text{O}_3 \cdot 5\text{SO}_3 \cdot 17\text{H}_2\text{O}$, which is known as a mineral, copiapite, and claimed to have confirmed the existence of Scharizer's β -copiapite. The latter is probably erroneous and will be discussed below. Further, Wirth and Bakke determined the isothermal saturation curve at 25° for the normal ferric sulfate, $\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 9\text{H}_2\text{O}$, as well as the acid salt, $\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$. It required much time and a considerable number of experiments to obtain these results. The difficulty lay chiefly in the sluggishness with which equilibrium was reached in the viscous solutions.⁴

The results which the previous authors obtained with solutions containing less than about 25% of sulfuric anhydride are not surprising and are probably accounted for by the procedure which they used. It consisted in treating precipitated ferric oxide with ferric sulfate solutions of various concentrations, in which it dissolves to a certain extent, according to a statement by Maus.⁵ Ferric oxide probably dissolves to the extent of forming a saturated solution of the basic salt which should be stable in contact with a solution of this particular acidity. However, the conversion of the ferric oxide added in excess of that amount into the basic

³ Wirth and Bakke, *Z. anorg. Chem.*, **87**, 13 (1914).

⁴ Very recently a paper has been published by Applebey and Wilkes [*J. Chem. Soc.*, **121**, 337 (1922)] dealing with the system, $\text{Fe}_2\text{O}_3\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$, at 18° and 25°. These authors do not mention the work of Wirth and Bakke and have apparently entirely overlooked it. Their own work, however, is not appreciably in advance of that of Wirth and Bakke and therefore need not be further discussed.

⁵ Maus, *Pogg. Ann.*, **11**, 75 (1827).

salt probably proceeds exceedingly slowly at 25° on account of the rather inert character of ferric oxide. This is apparent from the observation of Wirth and Bakke,⁸ who state that in these particular experiments equilibrium was apparently not established and the solids were slowly undergoing a change. Cameron and Robinson² probably did not allow sufficient time to observe such changes. The fact that the sulfate contents of the solids varied to a certain extent with the acidity of the solution suggested to them the existence of solid solutions. It is probable that the adsorption of sulfate by the finely divided ferric oxide used in the experiments was largely responsible for this.

Our interest in this system had a geologic background and was concerned primarily with the conditions relating to the formation of anhydrous and hydrated ferric oxides. However, it seemed to be of sufficient interest to extend the work to the whole system.

Experimental Methods

Two preparations of domestic "Analyzed Chemicals" were used for the experiments. One was labeled "Ferric sulfate" and the analysis showed the following composition: 29.02% Fe₂O₃, 43.59% SO₃, water by difference 27.39%. The other preparation was labeled "Basic ferric sulfate" and had the following composition: 33.61% Fe₂O₃, 42.12% SO₃, and by difference, 24.27% water. Both were extremely fine-grained and could not for that reason be definitely identified microscopically. However, the composition of the first indicates that it is probably partly dehydrated normal ferric sulfate 9-hydrate, while the second in composition is close to the basic salt 2Fe₂O₃·5SO₃·17H₂O. These two preparations with suitable additions of sulfuric acid and water were sufficient to prepare all the necessary initial solutions, that is, to prepare mixtures which in equilibrium would contain the solid and a saturated liquid phase.

The total amount of the mixture was usually about 25 g., except when dealing with the rather dilute solutions in which case sufficient amounts (about 100 g.) were taken to permit accurate analyses. The mixture was sealed in a Jena glass tube, which it about half filled. With the exception of the experiments which were made at 50° and in which the sealed tubes were placed directly in an air thermostat, each tube was heated by means of a resistance furnace within a steel bomb described in a previous paper from this Laboratory.⁶ The temperature of these furnaces was kept constant within about 5° and the tubes were left in the furnace for various times depending on the temperature of the experiment. Those at higher temperature did not require more than a week or 10 days to reach equilibrium, while those at lower temperature required much more time; at 50° the tubes were left in the furnaces for 2 months or at

⁶ Allen, Crenshaw, Johnston and Larsen, *Am. J. Sci.*, **33**, 172 (1912).

least 6 weeks. The establishment of equilibrium at the various temperatures was judged by the presence of well defined crystalline solids, and concordant points for their saturation curves. When the solid did not crystallize properly, as was the case in the very dilute and the very acid solutions, approximately the same time was allowed for the establishment of the equilibrium as that required for solutions from which well defined crystals had been obtained at the corresponding temperature. In general the tubes were left in the furnace for a considerably longer period than was necessary. Except, therefore, for two or three experiments, no difficulties on this account were experienced in the whole course of this investigation.

After the tubes had been left in the furnace sufficiently long, the bombs were taken out and rapidly cooled to room temperature by plunging them into a vessel with running cold water. To prevent appreciable displacement of the equilibrium by prolonged contact at the lower temperature between the liquid and solid in the tubes the solid was separated as soon as possible.⁷ The separation was rapidly accomplished by the use of a strong water suction pump in conjunction with an alundum filtration crucible, and samples for analysis and microscopical examination were usually ready about 15 minutes after the bomb had been removed from the furnace. Of this time from 4 to 6 minutes were required for the cooling of the bombs to room temperature. The fact that concordant and reproducible results were obtained, and that the microscopical examination revealed no significant etching except in the case of very small crystals indicates that these results closely represent true equilibria.

Each experiment required the establishment of the composition of the liquid and solid phases. No difficulties present themselves in determining the composition of the liquid, for which a suitable amount, depending on the concentration of the solution, was weighed out as soon as it was freed by filtration of the solid and then analyzed. The possible effects of the condensation of vapor from the upper part of the tube were considered. Taking account of the relative volumes of the liquid and the vapor space, and of the shape of the saturation curves it appears that the effect at most would raise the third significant figure of the recorded values of ferric oxide and sulfur trioxide one or two units. The establishment of the composition of the solid phase required the use of both chemical and microscopical methods and varied somewhat to meet the different conditions. After the compounds encountered in this system were established the optical identification was usually relied upon, as this eliminated a great deal of analytical work. However, it was not always possible to apply it, as the solids were often in a condition of very fine subdivision and either

⁷ With few exceptions the amount of dissolved substance decreased with increasing temperature.

could not be identified properly or could not be freed from the adhering mother liquid without decomposition. Two samples of the solid were usually taken: one with adhering mother liquid and the other after the preparation had been washed. Both were examined microscopically to make sure that the treatment did not result in decomposition. Alcohol was generally used for washing, as it sufficiently removed the mother liquid and did not attack the salts nearly so much as would water. However, the more basic salts and large crystals of the other salts could be and occasionally were washed with water without appreciable decomposition. The washing was always carried out rapidly with the aid of an alundum filtration crucible and a strong suction pump. If water had been used it was usually followed by alcohol, and the alcohol was removed with ether. Only when practically no decomposition could be observed microscopically by comparison of such air-dry preparations with the corresponding ones in the mother liquid, were they utilized for chemical or microscopical determinations.

The chemical identification was accomplished by analyzing either the air-dry sample or the one with adhering mother liquid. The latter is possible by the well-known method of "residues" which was first pointed out by Schreinemakers.⁸ This method is based on the fact that if the composition of the solid with adhering mother liquid is plotted in a triangular diagram this point will always lie on the straight line connecting the composition of the liquid with that of the solid phase. Now, if at least two experiments are made (irrespective of the temperature) in which the same solid phase is in equilibrium with liquids of varying composition and the two liquids and the corresponding solid with adhering mother liquid are analyzed and the results plotted, the straight lines drawn through those points will come to an intersection at a point representing the composition of the pure solid. The determination of the composition of the solid by this method is exact provided the analytical results are sufficiently accurate. However, it must be remembered that this method is only applicable if the solid consists of only one phase of constant composition. Here the microscopical examination of the solid in the mother liquid proves very useful. It may be pointed out in this connection that the results of Wirth and Bakke,⁹ who used this method without definite microscopical control throughout their investigation, are in many cases unsatisfactory, probably because the solid was not homogeneous on account of not having come completely to equilibrium with the liquid,—provided, of course, that their analytical results were reliable.

The analytical methods used were very simple. The weighed samples in most cases were dissolved in a suitable amount of water and a sufficient

⁸ Schreinemakers, *Z. physik. Chem.*, **11**, 76 (1893). Bancroft, *J. Phys. Chem.*, **6**, 179 (1902); *Z. anorg. Chem.*, **40**, 148 (1904).

amount of the solution taken for the analysis. The iron was reduced in a practically neutral solution with sulfur dioxide and afterwards titrated in the usual way with potassium permanganate. The sulfate was determined as barium sulfate after the iron had been removed by double precipitation with ammonia water.⁹ Water was usually taken by difference; in one or two instances when it was directly determined the Penfield method¹⁰ was used and the substance mixed with a sufficient amount of calcium oxide.

In the microscopical determinations chief reliance was placed upon refractive index measurements made in standardized media. For obtaining *optical dispersion* a graphical method was used as follows. Along the right margin of a cross-section paper refractive indices from 1.520 to 1.870 were written so that readings as close as 0.001 could be made. A line was drawn across the paper through the middle at 45°; along this line the refractive index n_D of each liquid¹¹ was marked; above and below each such point were placed points, suitably spaced for interpolation, marking the index of the liquid for other wavelengths; points representing a given wavelength were connected.

Two (or more) refractive indices of a salt under investigation were found with the aid of a monochromatic illuminator, and placed on the plot. The dispersion was read from a straight line through these points. Table IV gives the results. The errors probably do not exceed ± 0.002 .

The error of interpolation in this series of salts is less than 0.001; the errors in the standard liquids should not exceed 0.001; the error in matching the grain and the liquid depends upon several factors,¹² such as shape and size of grain and, especially for these salts, the character of the surface.¹³ Under favorable conditions by this method there is no difficulty in observing differences of 0.0002 in refractive index between liquid and grains, and by approaching from both directions the wavelength at which matching occurs, differences of 0.0001 can be detected.

The difficulty of holding minute lath-shaped crystals in any desired position was overcome by having them supported in the liquid by powdered glass, quartz, etc., having about the refractive index of the crystals.

⁹ See Allen and Johnston, *THIS JOURNAL*, **32**, 588 (1910), where directions for the exact determination are given.

¹⁰ See Hillebrand, "Analyses of Silicate and Carbonate Rocks," *U. S. Geol. Survey Bull.*, **1910**, 422.

¹¹ Dispersion must increase regularly. The liquids used were: (1) mixtures of bromonaphthalene with liquid petrolatum and with methylene iodide; (2) a saturated solution of certain iodides in methylene iodide [see *J. Wash. Acad. Sci.*, **3**, 36 (1913)].

¹² For central illumination the opening in the substage diaphragm should be less than 1 mm. if very close matching is desired.

¹³ Even very thin films of liquid on grains of an apparently dry powder, or films of reaction products formed during washing, may lead to errors greater than 0.005.

For refractive indices above 2.2 immersion media made of sulfur, selenium, arsenic iodide, arsenic selenide and tellurium were used.

The Solid Phases

Ferric Oxide—Anhydrous and Hydrated

Fe₂O₃ (Hematite and Turgite).—Hematite appeared as a dark red powder, usually very fine-grained (0.002 mm. or less in diameter). Distinct double refraction indicated a crystalline substance having very strong birefringence. Observed refractive indices were higher than 2.7. These properties are characteristic of hematite.¹⁴ But little tendency for these minute particles to form aggregates was observed, in contrast with a very strong tendency in the case of the hydrated oxide. (In one case tabular crystals about 0.01 mm. in diameter were obtained.) For discussion of stability relations see "Description of solid model."

Turgite appeared in red radial fibrous aggregates 0.05 mm. and less in diameter. The fibers were negatively elongated, strongly doubly refracting, with α about 2.6. It was formed from very dilute solutions from about 130° to 150°. The possibility that these aggregates were dehydrated fibrous goethite was considered and discarded because some of the aggregates were much larger than any fibrous goethite produced, and the elongation of the constituent fibers negative instead of positive, as we have found in dehydrated fibrous goethite. In a paper previously published by us,¹⁵ it has been suggested that turgites are possibly solid solutions of ferric oxide and goethite, but that part of their water content is enclosed or adsorbed. X-ray experiments made recently by one of the authors, and which are still unpublished, indicate that turgites have the same ultimate structure as hematite and the two are in this sense probably identical. The water content of turgites must, therefore, be ascribed to their fibrous structure.

Fe₂O₃.H₂O (Goethite and Limonite).—In the paper just referred to the question of the composition of the hydrated ferric oxides was investigated. A brief summary of the results will be given here.

It was found that no *series* of hydrates of ferric oxide exists among the natural minerals, and the only existing hydrate is ferric oxide monohydrate. This substance occurs in nature in two crystalline forms, goethite and lepidocrocite, and also in an indefinite "amorphous" condition, with a considerable excess of water. The latter is commonly known under the name limonite.¹⁶ Goethite is often fibrous, and then may contain several per cent. excess of water and other substances held in capillaries among the fibers.

¹⁴ Wülfing measured the dispersion of hematite, *Tschermak's mineralog. petrog. Mitt.*, **15**, 71 (1896).

¹⁵ Posnjak and Merwin, *Am. J. Sci.*, **47**, 311 (1919).

¹⁶ Powders of some of these limonites, as well as some synthetic preparations made in the course of the present investigation, were recently studied by us by means of X-rays. The spectra obtained could not be distinguished from those of goethite.

The similarity between the synthetic and the natural hydrated ferric oxides in respect to their composition was discussed. It appeared at that time that no definitely crystallized synthetic hydrated ferric oxide had been prepared, and further, that only two kinds of "amorphous" hydrated ferric oxide seemed to exist, of which one was yellow and the other reddish-brown. The yellow one appeared to be essentially ferric oxide monohydrate and similar to the natural limonite. The reddish-brown substance, on the other hand, appeared according to van Bemmelen¹⁷ and to Foote and Saxton¹⁸ to hold its water in either an adsorbed or dissolved condition and did not represent a definitely hydrated compound.

It has been found in the course of the present investigation that crystalline ferric oxide monohydrate identical microscopically with certain natural fibrous goethites¹⁹ can be prepared synthetically. In several preparations the material has appeared in individual or clustered yellow spherical grains less than 0.01 mm. in diameter which showed the characteristics of radial fibrous aggregates of a crystalline substance having double refraction of about 0.06, and positive optical elongation. The mean refractive index of the most typical material was 2.14. This, like the natural material, contained only about 83% of ferric oxide against 89.86% in pure goethite. The deficiency in this case is due to excess of water and sulfur trioxide. Less typical material was less distinctly spherulitic, the spherules were smaller and often so closely aggregated that they showed no distinct double refraction,²⁰ refractive indices were less and the content of water and sulfur trioxide higher. The upper part of Table I shows the results of the studies of several preparations. Refractive index follows ferric oxide content.

Nowhere in this series can a division be made, on one side of which the material can be called non-crystalline. All the preparations listed in the upper part of the table were in the furnace for several weeks and had become compact or granular. The precipitates which formed when the tubes were first filled were flocculent and showed no evidence of crystallinity. As heating progressed nuclei formed in the solution, not only within the limits of the tube occupied by the precipitate but, especially at higher temperatures, above the original precipitate. The nuclei became centers of spherulites which, especially at higher temperatures, grew to determinable sizes or disappeared while larger ones grew.²¹

These spherulites of ferric oxide monohydrate did not appear above the temperature 130°. It is of interest to compare this temperature with temperatures at which various samples of natural goethite and

¹⁷ van Bemmelen, *Z. anorg. Chem.*, **20**, 185 (1899).

¹⁸ Foote and Saxton, *THIS JOURNAL*, **39**, 1103 (1917).

¹⁹ Ref. 15, p. 320.

²⁰ Crusts viewed edgewise often showed some birefringence.

²¹ Slight fluctuations of temperature in our furnaces were favorable to the growth of larger at the expense of smaller grains.

limonite decomposed when heated slowly in dried air.²² The apparent stability, especially of well-crystallized goethite, at a considerably higher temperature, is noteworthy.

In the lower part of Table I are shown the results of some preliminary experiments in which ferric oxide monohydrate was produced in a few

TABLE I
PROPERTIES AND COMPOSITION OF SOME PREPARATIONS OF FERRIC OXIDE MONOHYDRATE

Expt.	Temp. °C.	Mean ref. ind.	Solid phase			Liquid phase			Time Weeks
			Fe ₂ O ₃ %	SO ₃ %	H ₂ O %	Fe ₂ O ₃ %	SO ₃ %	H ₂ O %	
61	50	1.99	70.18	12.00	17.82	0.90	1.53	97.57	...
123	50	..	73.14	8.16	18.70	0.39	0.79	98.72	10
60	50	2.00	73.44	7.98	18.58	0.38	0.79	98.83	8
48	75	2.01	73.49	9.18	...	0.34	1.00	98.66	...
109	50	2.06	75.89	5.89	18.22	0.14	0.39	99.47	...
74	110	2.11	76.53	8.10	...	0.33	1.31	98.46 ^a	...
78	110	2.11	77.87	7.25	...	0.15	1.19	98.66 ^a	...
116	110	2.12 ^b	0.08	0.83	99.09	10
115	110	2.14	82.24	3.24	...	0.01	0.53	99.45	...
112	130	2.14	82.95	2.94	...	0.01	0.42	99.47	10
35	130	2.15	0.12	1.36	98.52	...
F2	25	1.87	70.99	7.47	21.54
F21	ca.100	1.98	76.58	6.98	16.44
F27	ca.100	2.13	82.64	3.15	14.21

^a Equilibrium has not been reached.

^b Fe₂O₃·H₂O and 3Fe₂O₃·4SO₃·9H₂O were both present, but the index measurements were made on separate grains of the former.

hours or days instead of several weeks. The precipitates were not definitely crystalline (spherulitic), and thus resembled natural limonite.²³ In Expt. F2 a liter of water containing 50 g. of ferrous sulfate was allowed to oxidize and hydrolyze at room temperature while vigorously stirred. The precipitate was washed for a few minutes. In Expt. F21 a solution of ferric sulfate was hydrolyzed on a steam-bath and the precipitate washed a few minutes. Expt. F27 is like Expt. F21 except that the precipitate was extracted with hot water in a Soxhlet extractor for 2 days. Comparing the refractive indices of materials used for Expts. F2 and 61, which have about the same content of ferric oxide, the effect of long heating in consolidating the material is very evident. After once being consolidated further changes are slow (cf. Expts. F27 and 115).

Some natural limonites²⁴ which show no other special microscopical characteristics of crystalline substances have been observed to have birefringence as high as 0.040. This leads one to inquire what amount of

²² Ref. 15, p. 328.

²³ In the restricted sense in which we have used the term in preceding paragraphs.

²⁴ Most specimens are almost isotropic.

birefringence may be developed in substances which are not microscopically crystalline. We have observed that many organic materials such as wool, cotton, silk, linen, have double refraction comparable with or even twice as great as that of limonite. Experiments made in this connection show that rubber can be made to show birefringence somewhat greater than 0.040. A tension of only about 350 g. per sq. mm. produces birefringence of 0.010. It is, therefore, not improbable that limonite may be strained sufficiently to account for its birefringence.

Adsorption Phenomena.—It was mentioned above that certain preparations which resembled limonite and fibrous goethite microscopically contained considerable amounts of sulfate. Inasmuch as the nature of these preparations was not clear, a study of the variation in the composition of the solid with that of the liquid phase of all the ferric oxide monohydrate preparations was made. The tubes in some of these experiments were taken out for a short time every few days and thoroughly shaken. They were left in the furnace for a period of 10 weeks except that in Expt. 123, which was a duplicate of Expt. 60, heating was for only 8 weeks to ascertain whether sufficient time was allowed. As will be seen (Table II), the two experiments are in good agreement and show that these results are reproducible.

TABLE II
VARIABILITY IN COMPOSITION OF THE SOLID. TEMPERATURE, 50°

Expt.	Liquid phase			Solid phase		
	Fe ₂ O ₃ %	SO ₃ %	H ₂ O %	Fe ₂ O ₃ %	SO ₃ %	H ₂ O %
109	0.14	0.39	99.47	75.89	5.89	18.22
123	0.39	0.79	98.82	73.14	8.16	18.70
60	0.38	0.79	98.83	73.44	7.98	18.58
61	0.90	1.53	97.57	70.18	12.00	17.82
96	1.44	2.30	96.26	65.77	16.35	17.48 ^a

^a The solid consists of Fe₂O₃·H₂O and fine crystals, probably the basic salt 3Fe₂O₃·4SO₃·9H₂O.

The experiments show that the sulfur trioxide content in the solid phase is not constant, but increases continuously with its increase in the liquid phase.²⁵ Thus, presumably, the solid is not a definite compound, and the possibility of solid solution may be considered.

The question then arises as to the nature of the end members of such possible solid solution. The assumption that they are the simple components of the complete system, ferric oxide-sulfuric trioxide-water, or ferric oxide-sulfuric acid, is not probable and need not be considered seriously.²⁶ It is more likely that they are the two most nearly related

²⁵ It is of interest to note that the water content stays fairly constant.

²⁶ Cameron and Robinson (Ref. 2) stated that in "a solution containing less than about 25% of sulfuric acid (SO₃), the stable solid is one of a series of solid solutions con-

compounds. These two substances are ferric oxide monohydrate²⁷ and the basic salt $3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$.

To examine such cases²⁸ it is best to present them graphically. We may do this as shown in Fig. 1 by plotting the concentration of sulfur trioxide in solution and the sulfur trioxide of the solids. Experiments having the basic salt, $3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$, for the solid phase are represented by points on the horizontal line, which indicates that the composition of the solid phase does not change with increasing content of sulfur trioxide in solution. The occurrence of two phases (Expt. 96) indicates that the two solids do not form a complete series of solid solutions and,

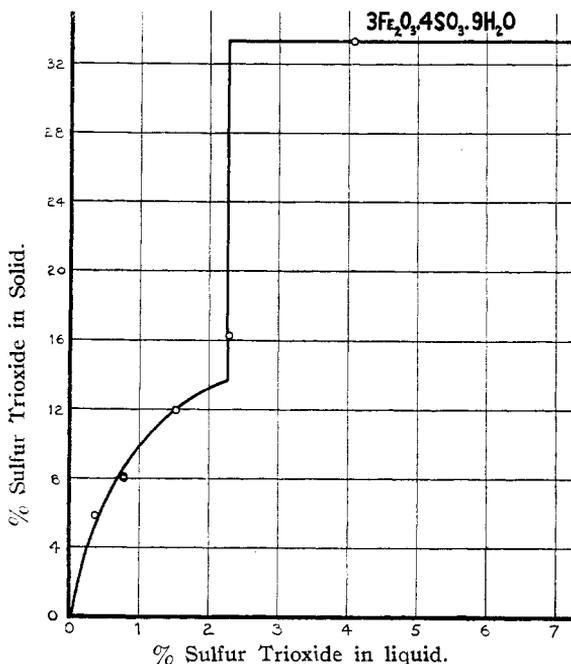


Fig. 1.—Change in the composition of solid phase with that of liquid.

as the composition of the mother liquor in the presence of two solids will be constant independent of their proportion in the mixture, all such mixtures containing ferric oxide, sulfuric acid and probably water.” As will be seen from the present paper definite basic salts and not such “solid solutions” are the stable phases in the greater portion of the region indicated. The region in which the nature of the solid is at present under discussion is that of the first few per cent. of sulfuric acid; and even in such a restricted area it is improbable that such different substances could form solid solutions (mix-crystals).

²⁷ Ferric oxide monohydrate must appear as a solid phase in this system because it undoubtedly is a solid phase in the binary system, ferric oxide-water.

²⁸ See Miller and Kendrick, *J. phys. Chem.* 7, 259 (1903), for a general discussion of such cases.

tures will lie on the vertical line drawn in the diagram. Now the points representing the solids of variable composition seem best to fit a curved line (Fig. 1) which intersects the vertical one representing the mixtures.

The assumption of a solid solution does not agree with the fact that the experiments are best represented by a curved line, for in case of solid solution a straight inclined line would be expected. The character of the curve and the observed decrease in the sulfate in the solid phase with increasing temperature suggest adsorption phenomena. As seen from Fig. 2, the experiments at 50° are satisfactorily expressed by the adsorption isotherm.²⁹

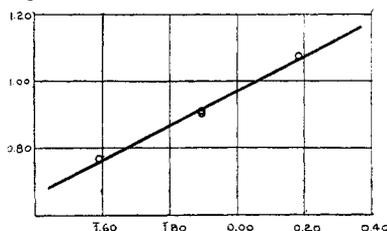


Fig. 2.—The logarithmic values of the sulfur trioxide content in the solid and liquid phases.

crystalline compound of this composition exists within the investigated range of temperatures. However, substances of variable composition but approximating the one ascribed to glockerite may readily be formed under suitable conditions.

In this connection it may be of interest to mention that a substance of the approximate composition, $2\text{Fe}_2\text{O}_3 \cdot \text{SO}_3 \cdot 6\text{H}_2\text{O}$, has been described as a mineral under the name of glockerite. Cornu³⁰ expressed his belief (no experimental data are given) that this substance is probably an adsorption compound. The present investigation shows clearly that no

Basic Ferric Sulfates

Three series of basic ferric sulfates have been encountered in this investigation, and it appears that they are the only types of basic ferric sulfates. However, other hydrates than those to be described may exist. The type ratios of Fe_2O_3 to SO_3 are 3:4, 1:2, and 2:5. Of the first type only one hydrate, $9\text{H}_2\text{O}$, appeared. Of the second type, two hydrates, $1\text{H}_2\text{O}$ and $5\text{H}_2\text{O}$, were found, but two others, amarantite with $7\text{H}_2\text{O}$ and fibroferrite with $10\text{H}_2\text{O}$, have been described as well-defined minerals; and still another, castanite, with $8\text{H}_2\text{O}$, may exist. Descriptions of these minerals, except the important optical properties, may be found in mineralogical texts. These properties have been studied recently, partly on somewhat ill-defined material, by Larsen.³¹ His results are recorded here for comparison.

Only one hydrate of the third type of basic ferric sulfate is known, $2\text{Fe}_2\text{O}_3 \cdot 5\text{SO}_3 \cdot 17\text{H}_2\text{O}$. This corresponds to the well-known mineral copiapite.

²⁹ Freundlich, "Kapillarchemie," Akademische Verlagsgesellschaft, 1909, p. 92.

³⁰ Z. Koll. Chem., 4, 295 (1909).

³¹ Larsen, U. S. Geol. Survey, Bull., 679 (1921).

		α	β	γ	
$\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot 7\text{H}_2\text{O}$	amarantite	1.51	1.605	1.611	} α and β , pale orange-yellow; γ , orange-yellow
$\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot 8\text{H}_2\text{O}?$	castanite?	1.526	1.532	1.533	
$\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot 10\text{H}_2\text{O}$	fibroferrite	1.525	1.54	1.565	} α and β , nearly colorless; γ , orange-yellow
		1.533	1.534	1.575	

All of these 7 basic sulfates are alike in having a yellowish color, and in having the same type of absorption, that is, the ray that is most refracted is most deeply colored. The same is true of the two forms of the anhydrous normal salt. Hematite and the hydrated oxides have similar absorption.

$3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$.³²—Rhombohedral, $c = 1.14$: habit, rhombs (with a very small base) which are nearly cubes: $\omega = 1.816$, $\epsilon = 1.728 \pm 0.002$: ω , deep yellow; ϵ , light yellow; color of fine powder, orange-yellow; no good cleavage. See Table III. The same value for c was obtained microscopically as was later found goniometrically from the angle $c \wedge r = 52^\circ 45' \approx 10'$.

TABLE III

	Expt.	Limits observed	Mean	Calc.	
$\{001\} \wedge \{011\}$	11	$71^\circ 12' - 71^\circ 34'$	$71^\circ 24'$	$71^\circ 24'$	} Includes reduced measurements of \angle between the dome and the prism zone
$\{001\} \wedge \{13.0.\bar{1}\}$	15	$52^\circ 0' - 52^\circ 15'$	$52^\circ 9'$	$52^\circ 9'$	
	? 16	$73^\circ 23' - 75^\circ 4'$	$74^\circ 4'$	$74^\circ 5'$	
$(110) \wedge (1\bar{1}0)$				$78^\circ 14'$	
Various prism angles	35	$78^\circ 44' - 89^\circ 36'$			
Between bases of twins on $\{30\bar{1}\}$	10	$12^\circ 0' - 13^\circ 2'$	$12^\circ 42'$	$13^\circ 0'$	
Between bases of twins on $\{20\bar{3}\}$	11	$66^\circ 50' - 67^\circ 12'$	$67^\circ 2'$	$67^\circ 6'$	

Athanasesco³³ prepared this salt by heating a 25% solution of ferric sulfate at 150° . He describes it as pale yellow, nearly cubical rhombohedrons, and states that an analogous aluminum salt appears in similar but colorless rhombohedrons. Both the salts closely resemble crystallographically members of the alunite-jarosite group of minerals³⁴ and the ferric salt is almost identical in color, pleochroism and refractive indices³⁵

³² Recently Saxén has described from Otravaara the mineral borgströmite, to which the formula $\text{Fe}_2\text{O}_3 \cdot \text{SO}_3 \cdot 3\text{H}_2\text{O}$ is ascribed. *Medd. Geol. Fören. Helsingfors*, 1919-1920, p. 20. This may be the 3:4:9 compound slightly contaminated with limonite.

³³ Athanasesco, *Compt. rend.*, 103, 271 (1886).

³⁴ The formula for jarosite is $3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot \text{K}_2\text{O} \cdot 6\text{H}_2\text{O}$. See Schaller, *Am. J. Sci.* 32, 359 (1911) for discussion.

³⁵ According to measurements on jarosite by Larsen, Ref. 31.

with jarosite. A pronounced basal cleavage, a tendency toward tabular habit, and sometimes optical anomalies are, however, found in the alunite-jarosite group.

Early analyses of a mineral called carphosiderite seemed to indicate the formula of this ferric salt, but later analyses³⁶ show a large alkali content as in jarosite.

It will be seen from our experiments that this is the most basic ferric sulfate and that it is stable in contact with solutions of certain concentrations from ordinary temperature up to about 170°. It crystallizes readily and crystals 1 mm. in diameter may be easily obtained above about 75°. Following are two analyses which establish the composition of the crystals.

Calc.: Fe₂O₃, 49.84; SO₃, 33.30; H₂O, 16.86. Found: Fe₂O₃, (I) 50.06, (II) 50.05; SO₃, (I) 33.29; H₂O, (II) 16.55.

Fe₂O₃ · 2SO₃ · H₂O.—Orthorhombic: habit, fibrous crusts and rough prisms; $\alpha = 1.782 \pm .003$, $\beta = 1.806 \pm .005$, $\gamma = 1.918 \pm .003$; elongation = γ . In prisms 0.03 mm. in diameter γ is clear yellow, α and β colorless. See Table III. A slightly compressed mass of such crystals is orange-yellow. The crystals are slowly affected by exposure.

This compound has been previously mentioned only by Maus³⁷. Its stability in the system extends from above about 75° throughout the investigated temperature region. The analysis of the crystals was as follows.

Calc.: Fe₂O₃, 47.28; SO₃, 47.39; H₂O, 5.33. Found: Fe₂O₃, 46.84; SO₃, 47.49.

Fe₂O₃ · 2SO₃ · 5H₂O.—Monoclinic, $a:b:c = 0.858:1:1.358$, $\beta = 71^\circ 24'$. Usually the grains were microscopic diamond-shaped, with a transverse zone of twinning. In one preparation somewhat larger single stout prismatic crystals were accompanied by groups of 3 intergrown. Fair goniometric signals were obtained from each of about 20 crystals and groups. The single crystals were bounded by base, prism, minute unit clinodome, and a large, very steep positive orthodome. Curiously, the prism faces,

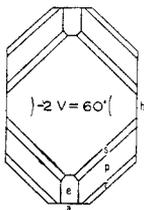


Fig. 3.—Orthorhombic form of anhydrous ferric sulfate, p. 1981.

though closely in zone and flat and usually four on each crystal, varied so much in position that no satisfactory value of a could be obtained from them; therefore a was sought by an indirect method based on twinning. The groups were too minute to sketch but they could be mounted so as to give a zone of signals in which the following sequence of angles was observed: $100^\circ 5'$ to $101^\circ 20'$, 12° to 13° , $66^\circ 50'$ to $67^\circ 10'$. These signals were found to come entirely from the bases of the three constituent individuals. The identi-

³⁶ Lacroix, *Minér. France*, 4, 145 (1911).

³⁷ Ref. 5, p. 77.

fication of the bases was made easy by the presence of the clinodome; thus the twinning planes were shown to be normal to the symmetry plane. Six possible twinings had to be considered to give the above sequence of angles, and at the same time various values of a , which was still unknown, had to be tried and one value selected which would be consistent with the twinning. The possible twinning planes were drawn on a b -pinacoid section with $c = 1.358$. Finally 3 planes, $\{30\bar{1}\}$, $\{20\bar{3}\}$, $\{40\bar{3}\}$, were obtained which fitted when $a = 0.858$. Of these the two with the smallest indices³⁸ are sufficient and are chosen as most probable.

The measurements are summarized in Table III. $\alpha \wedge c = 19^\circ \pm 2^\circ$ in acute angle β ; $\gamma = b$; α is colorless, β faint yellow, and γ light yellow; $\alpha = 1.588$, $\beta = 1.678$, $\gamma = 1.749$; good basal cleavage.

No previous record of this compound could be found. It is stable in contact with its saturated solutions only below about 100° ; its lower limit of stability lies below 50° and was not determined. Crystals analyzed as follows.

Calc.: Fe_2O_3 , 38.97; SO_3 , 39.06; H_2O , 21.97. Found: Fe_2O_3 , 38.80; SO_3 , 39.13.

$2\text{Fe}_2\text{O}_3 \cdot 5\text{SO}_3 \cdot 17\text{H}_2\text{O}$ (Copiapite).—Orthorhombic, $a:b:c = 0.81:1:?$; tabular with maximum observed dimensions of artificial crystals about 0.01 by 0.04 by 0.05 mm.; cleavage good $\parallel b$ and probably $\parallel c$; $a = \gamma$, $b = \beta$, $c = \alpha$; $\gamma = \text{Bx}_a$; $+2V = 52^\circ \pm 5^\circ$ (measured); dispersion very small; α colorless, β light grayish-yellow, γ bright yellow; in mass light greenish yellow; $\alpha = 1.531$, $\beta = 1.546$, $\gamma = 1.597$, all ± 0.003 . See Table IV. Scharizer's³⁹ description of this salt, though not so complete, is otherwise similar. The crystals often have a decidedly monoclinic appearance due to the unequal development of boundaries which correspond to the prism faces (110), (120), and ($1\bar{1}0$), ($1\bar{2}0$).

The crystals may undergo considerable dehydration without changing the general microscopical appearance of the tables but the refractive indices may be 0.04 greater.

Natural copiapite essentially identical with the artificial salt has been described recently by McCaughey.⁴⁰ Some earlier (1918) samples differing notably among themselves in composition⁴¹ had similar refractive indices⁴² which were about 0.002 less than for the artificial salt.⁴¹ In

³⁸ The occurrences of twinning planes having index numbers greater than 3 are almost vanishingly small. We have noted the following in Dana's Mineralogy: annerödite {530}; enstatite {014}; barite {601}; {9.11.0?}; tridymite {1016}, {3034}; humite group {017}, {037}, {107}, {305}; feldspar?; quartz?.

³⁹ Scharizer, *Z. Kryst. Mineralog.*, **46**, 432, 442 (1909).

⁴⁰ McCaughey, *Am. Mineral.*, **3**, 162 (1918). The refractive indices are 0.003 lower.

⁴¹ The question of solid solution comes in here. Al_2O_3 replacing Fe_2O_3 would lower refractive indices, but other factors must enter in this case. See discussion by Scharizer, *Z. Kryst. Mineralog.*, **52**, 385 (1913).

⁴² Manasse, *ibid.*, **54**, 205 (1915) abs.

still earlier descriptions⁴³ certain minor details differ, and in one case crystals were measured goniometrically and described as monoclinic.⁴⁴ If the optical orientation of these crystals with respect to cleavage and habit is considered, it seems likely that the crystals were identical with those since described, which appear to be definitely orthorhombic. The measured crystals were very small and had to be remounted several times for measurement on a one-circle goniometer. Furthermore, faces in the zone essential to the definite determination of symmetry were wholly lacking, except one. Probably *b* and *d* of Linck's crystals correspond respectively to *c* and *b* of those here described.

Scharizer⁴⁵ prepared this salt and wrote its formula $(\text{HO})\text{Fe}_4(\text{SO}_4)_5 + 17 \text{ aq.}$ He believed he had also another⁴⁶ slightly different compound $(\text{HO})\text{Fe}_3(\text{SO}_4)_4 + 13 \text{ aq.}$ The former he called α - and the latter β -copiapite. The terms thus applied do not conform to any established usage. He came to his conclusion concerning the supposed β -copiapite chiefly on the basis of "solubility" experiments in alcohol, but it is quite obvious that his methods of preparation produced mixtures, and that his conclusion is erroneous. Unfortunately, Wirth and Bakke⁴⁷ evidently found Scharizer's work acceptable and tried to substantiate it. While pointing out that a solution of normal ferric sulfate is unlikely to deposit by crystallization a basic, a neutral, and an acid salt, these authors presume to confirm the existence of Scharizer's α - and β -copiapites. However, confirmation was not based on the preparation of the pure substance and the determination of its properties, but was wholly dependent on the indirect method of establishing the composition of solids, that is, the corresponding analyses of the saturated solution and the solid with the adhering mother liquid. Even so, the results are not convincing as the lines drawn through the determined points give various points of intersection besides the one corresponding to the so-called " β -copiapite." It may also be stated that the solids appear not to have been examined microscopically to establish their homogeneity. The best interpretation of Wirth and Bakke's experiments in respect to the " β -copiapite" is that equilibrium had not been established and that mixtures of copiapite and the normal ferric sulfate were present.

Copiapite is stable in contact with its saturated solutions only below about 90°.

Our analysis was as follows: Fe_2O_3 , 30.75%; SO_3 , 39.28%; H_2O , (29.97)%; mol. ratios, 1.00, 5.10, and 17.30, respectively. This analysis indicates

⁴³ For example see Weinschenk, *ibid.*, **44**, 75 (1908).

⁴⁴ Linck, *ibid.*, **15**, 14 and Plate I (1889). For discussion of these measurements see Scharizer, Ref. 41, p. 38.

⁴⁵ Scharizer, *Z. Kryst. Mineralog.*, **43**, 125 (1907).

⁴⁶ Scharizer, Ref. 43, p. 441.

⁴⁷ Ref. 3, p. 16.

that the composition of copiapite is $2\text{Fe}_2\text{O}_3 \cdot 5\text{SO}_3 \cdot 17\text{H}_2\text{O}$. The amount of water held by this compound had not been known definitely, but the basis of certain analyses was usually assumed to be 18 mols. It was thought that our preparation may have been somewhat dehydrated in view of the fact that it was washed with alcohol and ether. However, an indirect analysis on the basis of the following data also indicates 17 mols. of water: the mother liquid showed 20.71% of Fe_2O_3 , and 28.40% of SO_3 , while the solid with some mother liquid gave Fe_2O_3 25.52%, and SO_3 33.80%.

While our data indicate that copiapite probably contains 17 mols. of water, we do not consider this certain, and it would require a more careful study to establish this point definitely.

Normal Ferric Sulfates

The best known normal ferric sulfate is the one which contains 9 mols. of water ($\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 9\text{H}_2\text{O}$), the mineral coquimbite. It is rhombohedral, $\omega = 1.549$, $\epsilon = 1.556$, approximately. According to Wirth and Bakke⁴⁷ this compound is stable at 25° ; however, Applebey and Wilkes⁴ state that at 18° and 25° the normal salt containing 7 molecules of water is stable. Following are the salts obtained by us at higher temperatures.

$\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3$.—This compound appears in two crystalline forms⁴⁸ one rhombohedral, the other orthorhombic. Usually both have been present together in our preparations, and both retain their optical properties when heated dry for a few moments to a temperature at which sulfur trioxide is given off; therefore their relative stability relations are not known. Both hydrate slowly on exposure.

The *rhombohedral* form occurs in somewhat flattened rhombs, with narrow prism faces over all the lateral edges, and rhombohedral cleavage. Out of several crystals examined two were found which had fairly good faces giving $r \wedge r = 93^\circ 15'$ to $93^\circ 40'$ and $c \wedge r = 57^\circ 28'$, from which $c' = 1.35 \pm 0.01$. $\omega = 1.770$, $\epsilon = 1.760$.

A grayish-yellow color is scarcely noticeable except in grains more than 0.1 mm. diameter. The color of the fine powder is light grayish-yellow. See Table IV.

The *orthorhombic* form of similar color appears in thick tables flattened parallel to the base. Several crystals were mounted and reflections observed. Only one gave signals suitable for measurement, although most of the crystals had faces about as sketched in Fig. 4. The bounding angles of several measured microscopically were $87\frac{1}{2}^\circ$ and $92\frac{1}{2}^\circ$. The same angles calculated from the completely measured crystal were $87^\circ 40'$ and $92^\circ 20' \approx 30'$. The other measurements and calculations follow.

⁴⁸ See statement by Recoura, *Compt. rend.*, **144**, 1427 (1907).

$$a:b:c = 0.957:1:1.357$$

	Calc.	Obs.(mean)
$c \wedge s$ (112)	44°31'	44°50'
$c \wedge p$ (111)	63° 1'	62°41'
$c \wedge r$ (771)	85°50'	85°47'
$c \wedge e$ (101)	54°48'	54°21'
(110) \wedge ($\bar{1}\bar{1}$ 0)	87°30'	

$\alpha = 1.802$, $\beta = 1.814$, $\gamma = 1.818$; $\alpha = c$, $\beta = a$, $\gamma = b$; $-2V$ is about 60°. See Table IV.

Following is an analysis of the crystals and data for an indirect analysis.

		Calc.	Mother liquid	Solid with some mother liquid
Fe ₂ O ₃	40.41	39.95	0.08	28.88
SO ₃	59.53	60.05	74.95	64.37

Fe₂O₃·3SO₃·6H₂O.—Monoclinic, slender, colorless laths elongated $\parallel c$ and flattened $\parallel \{010\}$; $\alpha \wedge c = 22^\circ$ for red and 26° for blue; $\beta = b$; $\alpha = 1.605$, $\beta = 1.635$, $\gamma = 1.657$. The fine-grained powders available were all practically colorless. See Table IV.

No previous record of this substance could be found. It crystallizes readily and is stable in contact with its saturated solutions from somewhat above 50° to about 150° . The crystals analyzed as follows.

Calc.: Fe₂O₃, 31.45; SO₃, 47.27; H₂O, 21.28. Found: Fe₂O₃, 31.30; SO₃, 47.06.

Fe₂O₃·3SO₃·7H₂O.—Monoclinic, colorless laths elongated $\parallel c$ and flattened $\parallel \{010\}$ $\alpha \wedge c = 20^\circ \pm 2^\circ$; $\gamma = b$; polysynthetic twinning traces show on $\{010\}$ parallel to the elongation; $\alpha = 1.572 \pm 0.003$, $\beta = 1.586 \pm 0.003$, $\gamma = 1.640 \pm 0.002$. See Table IV.

A faint rose-pink color was seen in coarser-grained powders. Crystals a few millimeters in diameter would be distinctly colored, but not predominantly yellow like the anhydrous normal salt and the basic salts. It is possible, however, that γ is yellow, in which case flattening in some plane parallel to γ would give a faint yellowish color to powders. Compare with the 1:4:9 salt.

This hydrate of the normal ferric sulfate is stable in contact with its saturated solutions only below about 80° ; the lower limit was not ascertained, but according to Applebey and Wilkes, it is stable at 25° and 18° .⁴⁹ The analysis of the crystals was as follows.

Calc.: Fe₂O₃, 30.43; SO₃, 45.74; H₂O, 23.83. Found: Fe₂O₃, 29.77; SO₃, 44.71.

As it was doubtful from this analysis whether this substance contained 7 or 8 mols. of water and it was found difficult to free the crystals from the mother liquid without some decomposition taking place, the indirect

⁴⁹ Wirth and Bakke (Ref. 3), however, state that the normal salt with 10 molecules of water is stable at 25° .

method was used and gave the following results which, when plotted, confirmed the formula as stated.

	Mother liquid		Solid with some mother liquid	
	Fe ₂ O ₃	SO ₃	Fe ₂ O ₃	SO ₃
(1)	8.56	32.52	17.84	37.87
(2)	10.26	31.91	19.11	37.97

Acid Ferric Sulfates

Fe₂O₃ · 4SO₃ · 3H₂O.⁵⁰—This appeared only in exceedingly small needles with apparently parallel extinction, and elongation γ . It could not be separated from the highly acid mother liquid sufficiently well to allow determination of refractive indices, or to be used for direct analysis. The indirect analyses are given below. This is probably the salt which Recoura⁵¹ obtained. It is stable in contact with its saturated solutions from ordinary temperatures to about 140°.

	Mother liquid		Solid with some mother liquid			Mother liquid		Solid with some mother liquid	
	Fe ₂ O ₃ %	SO ₃ %	Fe ₂ O ₃ %	SO ₃ %		Fe ₂ O ₃ %	SO ₃ %	Fe ₂ O ₃ %	SO ₃ %
1	0.07	62.34	6.42	61.80	4	0.15	59.80	11.81	59.79
2	0.07	75.37	4.24	73.33	5	0.07	59.20	15.04	59.43
3	0.09	67.54	10.47	64.99	6	0.19	56.25	8.94	57.44

Fe₂O₃ · 4SO₃ · 9H₂O (Rhomboclase).⁵²—Orthorhombic; $a : b : c = 0.563 : 1 : 0.940$; lozenge-shaped tables with base and unit pyramid as prominent forms, unit prism and b -pinacoid usually present;⁵³ eminent basal cleavage and fibrous prismatic cleavage; flexible; $\alpha = 1.533$, $\beta = 1.550$, $\gamma = 1.635$; +2V small; $\alpha = c$, $\beta = a$, $\gamma = b$; γ and β are very light yellow, α is very light purple; fine powder is white, but coarse powder is very light rose. See Table IV. The crystals deliquesce slowly.

Some crystals obtained were a centimeter long. Five crystals were measured. The prism angle ($m \wedge m''$) from good faces varied from 57°52' to 59°3' (mean and calculated 58°45'); and $c \wedge p$ varied from 62°22' to 62°43' (mean and calculated 62°27').

This compound is stable in contact with its saturated solutions from

⁵⁰ Scharizer applies this formula to well defined crystals approximating this composition, but which were reddish and contained about half as many mols. of ferrous as of ferric oxide. *Z. Kryst. Mineralog.*, **56**, 377 (1921).

⁵¹ Recoura, *Compt. rend.*, **137**, 189 (1903).

⁵² The mineral was described as to composition, habit, and basal cleavage by Krenner in 1891 and 1910 (*Mineralog. Mag.*, **15**, 429).

⁵³ Scharizer's measurements are too few to determine symmetry or axial ratios. *Z. Kryst. Mineralog.*, **56**, 354 (1921). Orientation according to R. Scharizer for microscopic crystals, *ibid.*, **35**, 345 (1902). This salt was obtained by Recoura, Ref. 51, p. 118.

ordinary temperature up to nearly 140°. It crystallizes very readily and an analysis gave the following result.—

Calc.: Fe₂O₃, 24.88; SO₃, 49.87; H₂O, 25.25. Found: Fe₂O₃, 24.31; SO₃, 49.66.

TABLE IV
OPTICAL DISPERSION AND COLOR

	3Fe ₂ O ₃ .4SO ₃ .9H ₂ O		Fe ₂ O ₃ .2SO ₃ .H ₂ O			Fe ₂ O ₃ .2SO ₃ .5H ₂ O			
	ω	ϵ	α	β	γ	α	β	γ	
F	1.865	1.755	1.814	1.844	1.968	1.603	1.702	1.787	
Tl	1.836	1.739	1.796	1.821	1.940	1.594	1.688	1.765	
Na	1.816	1.728	1.783	1.804	1.918	1.588	1.678	1.749	
C	1.799	1.718	1.772	1.790	1.897	1.581	1.669	1.735	
Li	1.797	1.716	1.770	1.788	1.894	1.580	1.667	1.733	
Color	a* 19 h to 19'		19 e to 19 f			21" f			
	b 17 h		18 d to 17' c			17" b			
	2Fe ₂ O ₃ .5SO ₃ .17H ₂ O			Rhombohedral		Fe ₂ O ₃ .3SO ₃ Orthorhombic			
	α	β	γ	ω	ϵ	α	β	γ	
F	1.542	1.559	1.620	1.809	1.798	1.844	1.857	1.861	
Tl	1.536	1.552	1.606	1.786	1.775	1.819	1.831	1.835	
Na	1.531	1.546	1.597	1.770	1.760	1.802	1.814	1.818	
C	1.527	1.541	1.589	1.756	1.746	1.787	1.799	1.803	
Li	1.526	1.540	1.587	1.754	1.744	1.785	1.797	1.801	
Color	a* 25 f		21" f			21" f			
	b		17" b						
	Fe ₂ O ₃ .3SO ₃ .6H ₂ O			Fe ₂ O ₃ .3SO ₃ .7H ₂ O			Fe ₂ O ₃ .4SO ₃ .9H ₂ O		
	α	β	γ	α	β	γ	α	β	γ
F	1.624	1.656	1.618	1.585	1.603	1.666	1.545	1.564	1.657
Tl	1.613	1.644	1.667	1.578	1.593	1.651	1.538	1.556	1.644
Na	1.605	1.635	1.657	1.572	1.586	1.640	1.533	1.550	1.635
C	1.598	1.627	1.648	1.566	1.579	1.631	1.529	1.545	1.626
Li	1.597	1.626	1.646	1.565	1.578	1.629	1.528	1.544	1.625

* a and b refer to Ridgway's color system for powder having grains about 0.005 to 0.050 mm. and 0.05 to 0.50 mm. diameter, respectively.

General Experimental Results

Altogether 12 crystalline phases were encountered in the investigation of the system, ferric oxide-sulfur trioxide-water, between 50° and 200°. The establishment of their stability relations required a considerable number of experiments which consumed much time. As mentioned before, the experiments were made in sealed glass tubes so that a definite equilibrium pressure existed for each temperature and concentration. The pressures were of wholly subsidiary interest and were not measured.

The experimental results are tabulated below. On account of greater simplicity at elevated temperatures, they are arranged in order of descending temperature. The polybaric isotherms are also presented graphically.

Polybaric Isotherms

The Isotherm at 200° (Table V).—Only 3 solid phases are stable at this temperature in contact with the various liquid and vapor phases: Fe_2O_3 , the basic salt $\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot \text{H}_2\text{O}$ and the normal salt $\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3$.

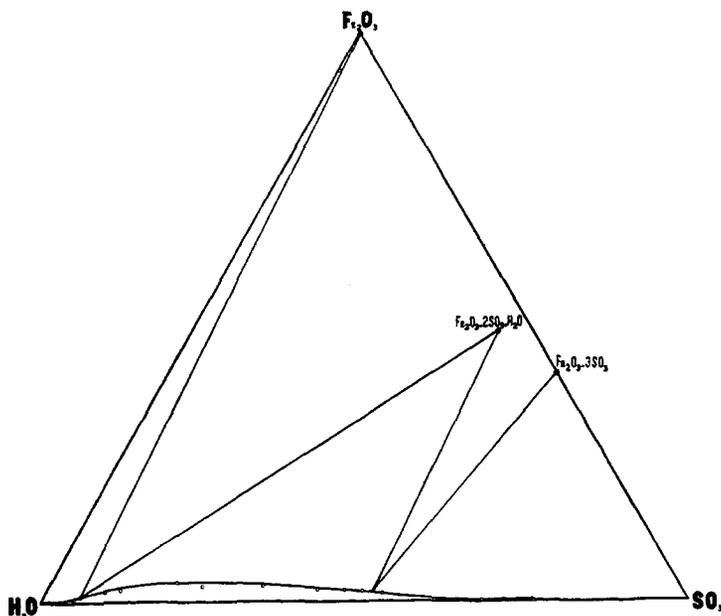


Fig. 4.—200° isotherm.

TABLE V
THE ISOTHERM AT 200°
SO₃
Fe₂O₃
Solid phase
in solution

Expt.	Composition of liquid phase			SO ₃ Fe ₂ O ₃ in solution	Solid phase
	Fe ₂ O ₃ %	SO ₃ %	H ₂ O %		
9	0.56	4.90	94.54	17.4	Fe ₂ O ₃
25	0.63	5.58	93.79	17.6	Fe ₂ O ₃ and Fe ₂ O ₃ ·2SO ₃ ·H ₂ O
10	1.61	9.08	89.31	11.52	
1	1.69	11.39	86.92	13.45	Fe ₂ O ₃ ·2SO ₃ ·H ₂ O
2	3.50	19.43	77.07	11.08	
3	2.40	23.78	73.82	19.77	
184	2.59	33.14	64.27	25.53	
18	2.00	41.87	56.13	41.78	
185	2.00	45.05	52.95	44.9	
11	1.91	48.94	49.15	51.0	
186	1.35	52.12	46.53	77.0	Fe ₂ O ₃ ·3SO ₃
26	0.85	53.44	45.71	125.	
188	0.08	68.14	31.78	170.	
27	0.05	73.54	26.41	...	
189	0.03	74.88	25.09	...	
33	0.04	76.17	23.79	...	

The quadruple point in which $\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot \text{H}_2\text{O}$ and $\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3$ co-exist at this temperature was not determined experimentally, but the liquid phase must have approximately the following composition: % Fe_2O_3 , 1.5; % SO_3 , 50.5; % H_2O , 48.0.

The Isotherm at 140° (Table VI).—With decreasing temperature the isotherms become more complicated. At 140° five solid phases are present: Fe_2O_3 , the basic salt $3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$ and the normal salts $\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3$. Only one quadruple point was experimentally determined. The composition of the liquid phase is estimated for the other quadruple points as follows.

Liquid phase			Solid phase
Fe_2O_3 %	SO_3 %	H_2O %	
0.8	3.5	95.7	Fe_2O_3 and $3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$
11.5	19.0	69.5	$3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$ and $\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot \text{H}_2\text{O}$
15.5	31.5	53.0	$\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot \text{H}_2\text{O}$ and $\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 6\text{H}_2\text{O}$

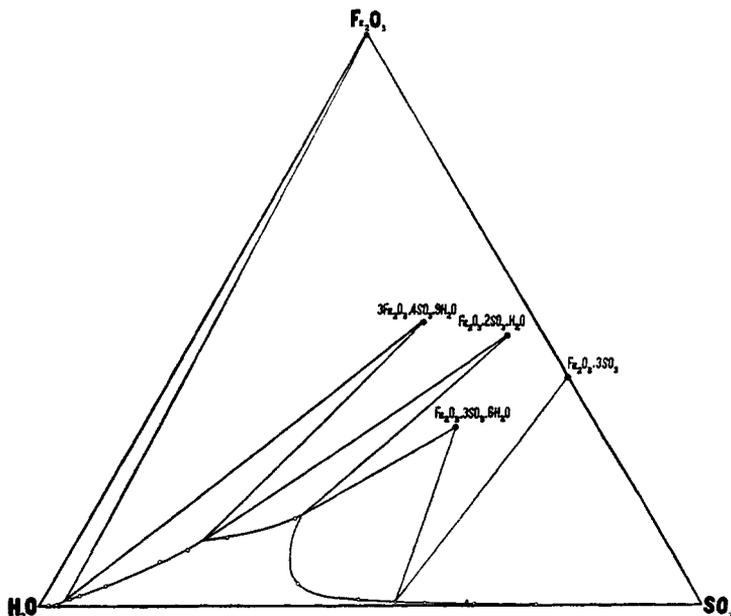


Fig. 5.—140° isotherm.

It will be seen by comparison with the isotherm for 200° that the isothermal saturation curve for this temperature contains considerably more dissolved substance. The amount of ferric oxide in solution rises rapidly with increasing acidity until ferric sulfate hexahydrate becomes the stable solid phase. From this point the ferric oxide content in solution falls off sharply.

TABLE VI
THE ISOTHERM AT 140°

Expt.	Composition of liquid phase			SO ₃ Fe ₂ O ₃ in solution	Solid phase
	Fe ₂ O ₃ %	SO ₃ %	H ₂ O %		
72	0.01	0.82	99.17	215.	Fe ₂ O ₃
36	0.03	1.34	98.63	89.	
37	0.05	2.60	97.35	89.	
20	1.18	4.06	94.76	6.87	
21	1.71	5.25	93.04	6.13	3Fe ₂ O ₃ .4SO ₃ .9H ₂ O
13	3.51	8.25	88.24	4.69	
14	7.78	14.31	77.91	3.67	
28	9.84	17.65	72.51	3.58	Fe ₂ O ₃ .2SO ₃ .H ₂ O
15	12.05	22.39	65.56	3.71	
17	15.35	30.88	53.77	4.01	Fe ₂ O ₃ .3SO ₃ .6H ₂ O
29	3.71	37.10	59.19	19.9	
22	1.02	47.67	51.31	93.3	Fe ₂ O ₃ .3SO ₃ .6H ₂ O and Fe ₂ O ₃ .3SO ₃
30	0.64	53.31	46.05	166.	
164	0.36	58.00	41.64	321.	Fe ₂ O ₃ .3SO ₃
23	0.16	61.01	38.83	...	
165	0.11	65.49	34.40	...	
73	0.08	74.95	24.97	...	

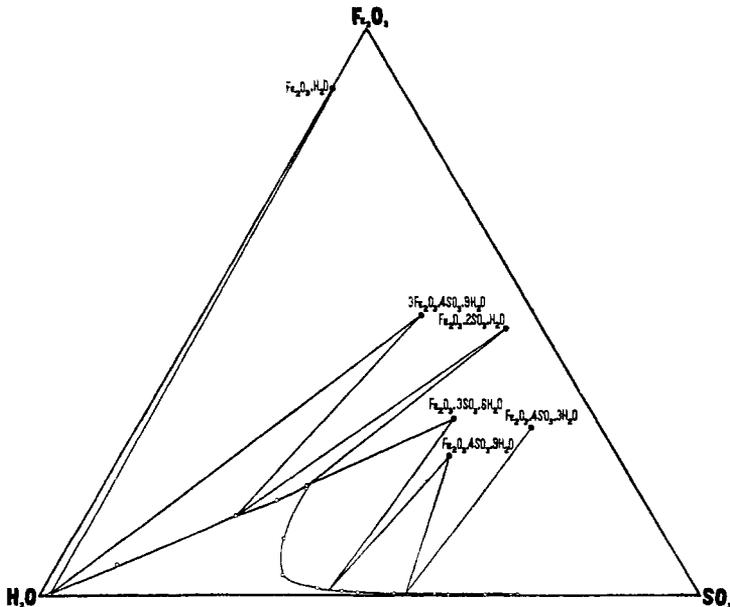


Fig. 6.—110° isotherm.

The Isotherm at 110° (Table VII).—Six solid phases are now present Fe₂O₃.H₂O, the basic salts 3Fe₂O₃.4SO₃.9H₂O and Fe₂O₃.2SO₃.H₂O, the normal salt Fe₂O₃.3SO₃.6H₂O and the acid salts Fe₂O₃.4SO₃.9H₂O

and $\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 3\text{H}_2\text{O}$. As compared with the isotherm at 140° we notice the following changes: (1) ferric oxide monohydrate replaces the anhydrous ferric oxide which was found only above about 130° , and (2) the two hydrates of the acid ferric sulfate have become stable at this temperature. In general, however, the shape of this isotherm is similar to the one at 140° .

TABLE VII
THE ISOTHERM AT 110°

Expt.	Composition of liquid phase			$\frac{\text{SO}_3}{\text{Fe}_2\text{O}_3}$ in solution	Solid phase
	Fe_2O_3 %	SO_3 %	H_2O %		
115	0.01	0.53	99.45	70.	$\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (both crystalline and amorphous)
116	0.08	0.83	99.09	20.	$\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (crystalline) and $3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$
76	5.58	8.93	85.49	3.20	$3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$
77	14.31	22.71	62.98	3.17	$3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$ and $\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot \text{H}_2\text{O}$
132	17.08	27.42	55.50	3.20	$\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot \text{H}_2\text{O}$
147	19.74	30.80	49.46	3.11	
161	19.04	30.97	49.99	3.24	$\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 6\text{H}_2\text{O}$
181	10.22	32.03	57.75	6.25	
158	3.47	35.07	61.46	20.1	$\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$
44	1.26	41.38	57.36	65.5	
159	0.81	45.45	53.74	112.	$\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$
83	0.43	48.03	51.54	223.	
45	0.48	53.45	46.07	...	$\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 3\text{H}_2\text{O}$
85	0.15	59.80	40.05	...	
46	0.13	61.96	37.91	...	$\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 3\text{H}_2\text{O}$
84	0.09	67.54	32.37	...	
47	0.06	72.50	27.44	...	

As may be seen from Table VII, only two quadruple points were experimentally determined. An estimate of the composition of the liquid phase at the remaining points is given below.

Liquid phase			Solid phase
Fe_2O_3 %	SO_3 %	H_2O %	
20.0	31.0	49.0	$\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot \text{H}_2\text{O}$ and $\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 6\text{H}_2\text{O}$
1.0	43.0	56.0	$\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$
0.3	56.0	43.7	$\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$ and $\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 3\text{H}_2\text{O}$

The Isotherm at 75° (Table VIII).—The number of solid phases has increased to 8: $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$, the basic salts $3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$, $\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot 5\text{H}_2\text{O}$ and $2\text{Fe}_2\text{O}_3 \cdot 5\text{SO}_3 \cdot 17\text{H}_2\text{O}$, the normal salts $\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 7\text{H}_2\text{O}$ and $\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 6\text{H}_2\text{O}$ and the acid salts $\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$ and $\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 3\text{H}_2\text{O}$. The amount of dissolved substance continuously increases

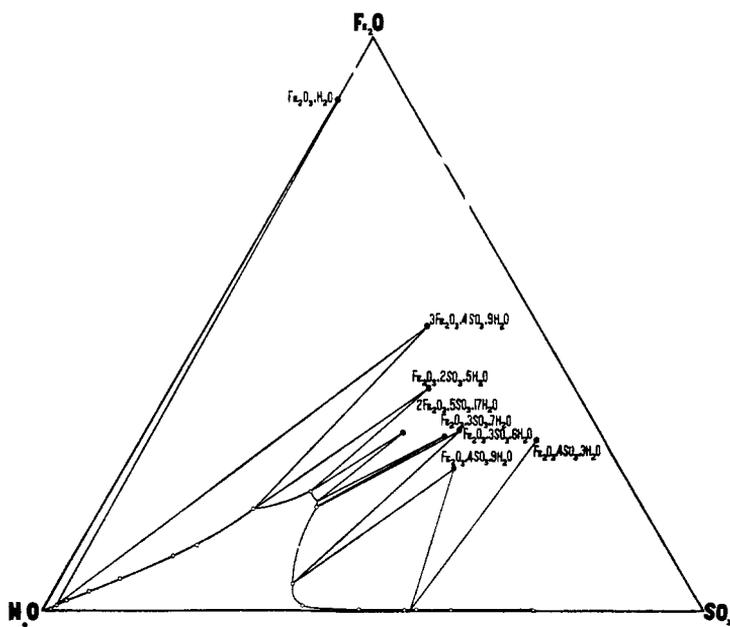


Fig. 7.—75° isotherm.

TABLE VIII
THE ISOTHERM AT 75°

Expt.	Composition of liquid phase			SO ₃ Fe ₂ O ₃ in solution	Solid phase
	Fe ₂ O ₃ %	SO ₃ %	H ₂ O %		
48	0.34	1.00	98.66	5.89	Fe ₂ O ₃ .H ₂ O
88	0.93	1.62	97.45	3.49	Fe ₂ O ₃ .H ₂ O and 3Fe ₂ O ₃ .4SO ₃ .9H ₂ O
89	1.72	2.79	94.49	3.23	3Fe ₂ O ₃ .4SO ₃ .9H ₂ O
50	3.40	5.24	91.36	3.08	
51	5.54	8.88	85.57	3.20	
49	9.46	14.95	75.59	3.16	
52	11.23	17.73	71.04	3.15	
148	17.78	23.10	59.12	2.58	3Fe ₂ O ₃ .4SO ₃ .9H ₂ O and Fe ₂ O ₃ .2SO ₃ .5H ₂ O
149	20.93	30.11	48.96	2.87	Fe ₂ O ₃ .2SO ₃ .5H ₂ O and 2Fe ₂ O ₃ .5SO ₃ .17H ₂ O
54	18.13	32.32	49.55	3.56	Fe ₂ O ₃ .3SO ₃ .7H ₂ O and Fe ₂ O ₃ .3SO ₃ .6H ₂ O
91	4.59	35.51	59.90	15.4	Fe ₂ O ₃ .3SO ₃ .6H ₂ O and Fe ₂ O ₃ .4SO ₃ .9H ₂ O
55	0.71	38.68	60.61	108.	Fe ₂ O ₃ .4SO ₃ .9H ₂ O
56	0.15	47.61	52.24	633.	
57	0.12	54.63	45.25	...	
154	0.12	56.25	43.63	...	
58	0.07	61.73	38.20	...	
59	0.07	74.14	25.79	...	Fe ₂ O ₃ .4SO ₃ .3H ₂ O

with decreasing temperature, but in general the shape of the isothermal saturation curve remains the same. The third type of the basic salts, $2\text{Fe}_2\text{O}_3 \cdot 5\text{SO}_3 \cdot 17\text{H}_2\text{O}$, which for the first time appears in this isotherm, has a very sharply defined saturation curve which falls off in the direction of greater acidity. The curves of the other two basic salts are different in this respect in that they rise in this direction. However, it will be readily observed that the saturation curve of the intermediate basic salt shows a considerably smaller rise than the more basic one, and for that reason the character of the saturation curve of the salt $2\text{Fe}_2\text{O}_3 \cdot 5\text{SO}_3 \cdot 17\text{H}_2\text{O}$ is not surprising.

Of the 7 quadruple points on this isotherm 5 were experimentally determined. The composition of the liquid in respect to the other points is estimated as follows.

Liquid phase			Solid phase
Fe_2O_3 %	SO_3 %	H_2O %	
19.0	32.2	48.8	$2\text{Fe}_2\text{O}_3 \cdot 5\text{SO}_3 \cdot 17\text{H}_2\text{O}$ and $\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 7\text{H}_2\text{O}$
0.1	55.5	44.4	$\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$ and $\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 3\text{H}_2\text{O}$

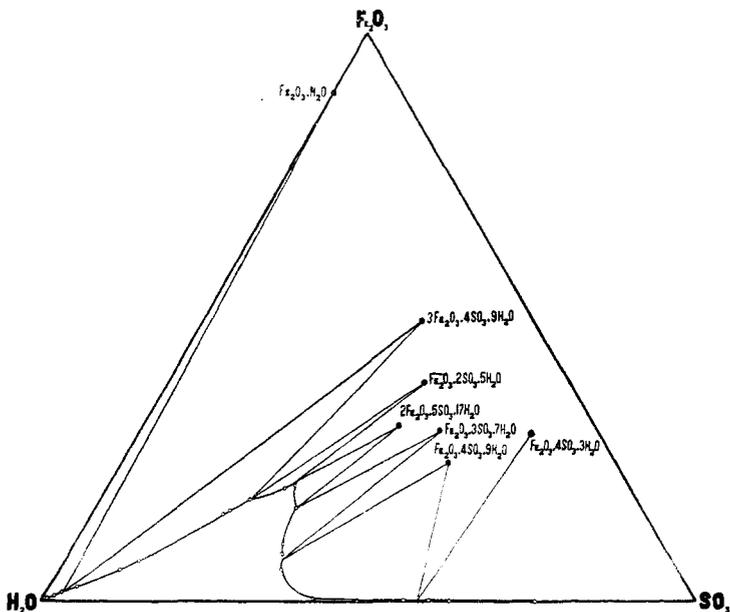


Fig. 8.—50° isotherm.

The Isotherm at 50° (Table IX).—This isotherm differs but little from the one at 75°. The solid phases are: $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$, the basic salts $3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$, $\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot 5\text{H}_2\text{O}$ and $2\text{Fe}_2\text{O}_3 \cdot 5\text{SO}_3 \cdot 17\text{H}_2\text{O}$, the nor-

mal salt $\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 7\text{H}_2\text{O}$ and the acid salts $\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$ and $\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 3\text{H}_2\text{O}$. The following is an estimate of the composition of the liquid at the undetermined quadruple points.

Liquid phase			Solid phase
Fe_2O_3 %	SO_3 %	H_2O %	
21.0	28.2	50.8	$\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot 5\text{H}_2\text{O}$ and $2\text{Fe}_2\text{O}_3 \cdot 5\text{SO}_3 \cdot 17\text{H}_2\text{O}$
7.5	33.0	59.5	$\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 7\text{H}_2\text{O}$ and $\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$
0.7	57.0	42.3	$\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$ and $\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 3\text{H}_2\text{O}$

TABLE IX
THE ISOTHERM AT 50°

Expt.	Composition of liquid phase			$\frac{\text{SO}_3}{\text{Fe}_2\text{O}_3}$ in solution	Solid phase
	Fe_2O_3 %	SO_3 %	H_2O %		
109	0.14	0.39	99.47	5.62	$\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$
123	0.39	0.79	98.82	4.15	
61	0.90	1.53	97.57	3.40	
96	1.44	2.30	96.26	3.19	$\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ and $3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}(?)$
63	2.59	4.08	93.33	3.14	
64	5.71	9.09	85.20	3.17	$3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$
99	7.19	11.19	81.62	3.11	
107	15.43	20.08	64.49	2.60	
130	16.09	20.81	63.10	2.58	
170	17.96	22.96	59.08	2.55	
169	20.13	27.18	52.69	2.69	$3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$ and $\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot 5\text{H}_2\text{O}$
151	20.70	28.40	50.90	2.74	$\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot 5\text{H}_2\text{O}$
101	16.78	30.72	52.50	3.66	$2\text{Fe}_2\text{O}_3 \cdot 5\text{SO}_3 \cdot 17\text{H}_2\text{O}$
168	10.26	31.91	57.83	6.21	$2\text{Fe}_2\text{O}_3 \cdot 5\text{SO}_3 \cdot 17\text{H}_2\text{O}$ and $\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 7\text{H}_2\text{O}$
167	8.56	32.52	58.92	7.58	
108	5.55	33.96	60.49	12.2	$\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$
67	0.34	41.18	58.48	240.	
68	0.10	48.44	51.46	...	
69	0.09	55.34	44.57	...	
103	0.07	59.20	40.73	...	
70	0.08	62.34	37.58	...	$\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 3\text{H}_2\text{O}$
71	0.07	75.37	24.56	...	

Miscellaneous Temperatures.—Table X gives a few additional points which were determined at different temperatures. Expt. 5 is of interest because it shows that the basic salt $\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot \text{H}_2\text{O}$ is still stable at 300° . The following four experiments at 150° indicate the rapid expansion of the field of $\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot \text{H}_2\text{O}$ as compared with its stability in the 140° isotherm. Finally, the last two experiments in this table are cited to

indicate the temperature limit at which ferric oxide monohydrate is stable; above about 130° anhydrous ferric oxide becomes stable.

TABLE X
EXPERIMENTS AT MISCELLANEOUS TEMPERATURES
Composition of liquid phase Solid phase

Expt.	Temp. °C.	Composition of liquid phase			Solid phase
		Fe ₂ O ₃ %	SO ₃ %	H ₂ O %	
5	300	1.70	24.42	73.88	Fe ₂ O ₃ .2SO ₃ .H ₂ O
197	150	3.95	13.83	82.22	
173	150	4.81	15.79	79.40	
174	150	6.43	22.52	71.05	
163	150	6.29	30.97	62.74	
112	130	0.01	0.42	99.47	Fe ₂ O ₃ .H ₂ O (both crystalline and amorphous)
35	130	0.12	1.36	98.52	Fe ₂ O ₃ .H ₂ O

Description of the Solid Model

On the basis of the experimental results a solid model was constructed. It is represented within the space of a triangular prism in which the components of the system are placed at the points of the triangle and the temperature is represented along the edges of the prism. In this way the variation in composition with change of temperature is shown.

Inasmuch as many quadruple points were definitely known, the fields within which each solid is stable could readily be marked off by connecting the corresponding quadruple points. The extension of such lines to the intersection with lines drawn through neighboring quadruple points gives the approximate location of the quintuple points, that is, points in which 3 solid phases are stable in contact with the same solution and the same vapor phase. While none of these points was experimentally determined, an approximate estimation of the temperatures at which they occur may be given.

The relations and the fields of stability of the various solids may be seen from this model, and are as follows.

Ferric oxide monohydrate is stable only in very dilute solutions and its field narrows down with increasing temperature, giving way to anhydrous ferric oxide at higher temperatures. In the direction in which the sulfur trioxide increases, it adjoins the field of the basic salt, 3Fe₂O₃.4SO₃.9H₂O. The intersection of the three surfaces representing these solids takes place at about 130°.

The basic salt, 3Fe₂O₃.4SO₃.9H₂O, occupies an extensive field. It is stable up to approximately 170° at which temperature lies the invariant point, 3Fe₂O₃.4SO₃.9H₂O, Fe₂O₃, Fe₂O₃.2SO₃.H₂O, liquid and vapor.

Adjoining the field of the basic salt, 3Fe₂O₃.4SO₃.9H₂O, in the direction of increasing sulfur trioxide content, lie the fields of the basic salts of the

composition, $\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot 5\text{H}_2\text{O}$ and $\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot \text{H}_2\text{O}$. The invariant point for the 3 salts lies at approximately 110° .

Adjoining the fields of the basic salts with the ratio of $\text{Fe}_2\text{O}_3:2\text{SO}_3$ lies, at the lower temperatures, the field of the third type of basic salt which has the composition, $2\text{Fe}_2\text{O}_3 \cdot 5\text{SO}_3 \cdot 17\text{H}_2\text{O}$. It is stable up to about 90° , at which temperature it may coexist with the basic salt $\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot \text{H}_2\text{O}$ and the normal salt, $\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 6\text{H}_2\text{O}$. At about 80° it may coexist also with the two hydrates of the basic salt, $\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot 5\text{H}_2\text{O}$ and $\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot \text{H}_2\text{O}$.

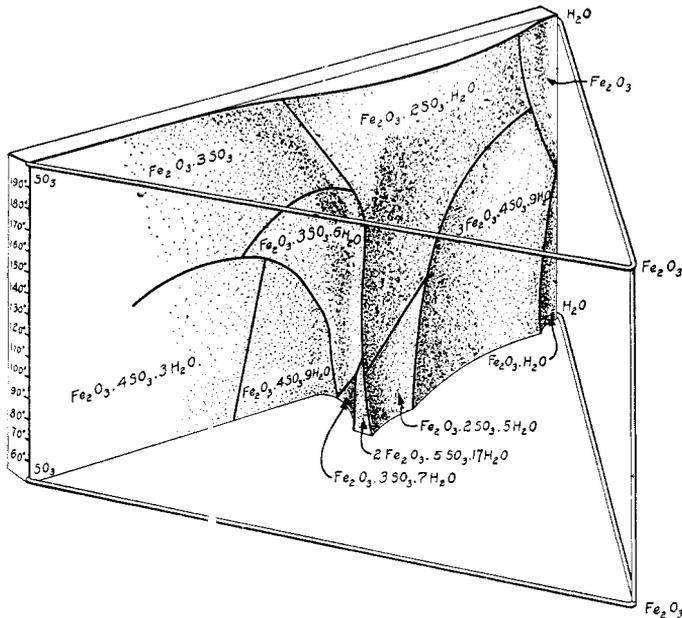


Fig. 9.—Solid model of the system, $\text{Fe}_2\text{O}_3\text{-SO}_3\text{-H}_2\text{O}$, from 50° to 200° .

With further increase of sulphur trioxide in solution the fields of normal ferric sulfates appear. The heptahydrate is stable up to about 75° and may coexist there with the normal hexahydrate and the basic salt, $2\text{Fe}_2\text{O}_3 \cdot 5\text{SO}_3 \cdot 17\text{H}_2\text{O}$. The ferric sulfate hexahydrate is stable to approximately 160° where the quintuple point, $\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot \text{H}_2\text{O}$, $\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 6\text{H}_2\text{O}$, $\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3$, liquid and vapor, occurs. At higher temperature and in more acid solutions only the anhydrous ferric sulfate is stable.

At the lower temperatures in more acid solutions the acid ferric sulfate, $\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$, and above a concentration of 55% SO_3 , $\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 3\text{H}_2\text{O}$, becomes stable. The temperatures of the invariant points in this region are: $\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 7\text{H}_2\text{O}$, $\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 6\text{H}_2\text{O}$, $\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$, liquid and vapor at about 50° ; $\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 6\text{H}_2\text{O}$, $\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$, $\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 3\text{H}_2\text{O}$, liquid and vapor at about 130° and $\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 6\text{H}_2\text{O}$, $\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3$, $\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 3\text{H}_2\text{O}$, liquid and vapor at about 135° .

Summary

The system, ferric oxide-sulfur trioxide-water, has been studied over the temperature range from 50° to 200°.

The following crystalline phases were encountered: Fe_2O_3 ; $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$; $3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$; $\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot \text{H}_2\text{O}$; $\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot 5\text{H}_2\text{O}$; $2\text{Fe}_2\text{O}_3 \cdot 5\text{SO}_3 \cdot 17\text{H}_2\text{O}$; $\text{Fe}_2\text{O}_3 \cdot \text{SO}_3$ (2 forms); $\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 6\text{H}_2\text{O}$; $\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 7\text{H}_2\text{O}$; $\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 3\text{H}_2\text{O}$ and $\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$.

The conditions under which these substances are formed, the ranges of their stabilities, and their relations to one another, also some of their crystallographic and optical properties, were determined. The data obtained are presented by means of tables, and graphically by means of curves and a solid model.

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THE CRYSTAL STRUCTURE OF SILVER MOLYBDATE

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Introduction

Crystals of silver molybdate, Ag_2MoO_4 , were obtained by the slow evaporation of ammonia from a solution of silver molybdate in ammonium hydroxide. From the best of these, most of which were flat, rather imperfect octahedral plates, 3 or 4 mm. across, a satisfactory reflection photograph was prepared. The Laue photographs, on the other hand, were made from a perfect appearing octahedron less than 1 mm. in greatest dimension. It is of interest to observe that such a small crystal can furnish satisfactory Laue photographic data. Optical examination showed these crystals to be essentially isotropic; no assignment to a particular class of symmetry on the basis of the ordinary crystallographic information appears ever to have been made.

The Crystal Structure of Silver Molybdate

This determination of structure was made by the generally applicable procedure which has previously been described.² Measurements of a comparison reflection photograph against the (111) face of silver molybdate and the (100) face of calcite, combined with an estimation of the density of the salt, showed that either 8 or 64 chemical molecules are to be

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² Wyckoff, *Am. J. Sci.*, **50**, 317 (1920). Wyckoff and Posnjak, *THIS JOURNAL*, **43**, 2292 (1921).