NOTE 1.—A similar article will shortly appear upon the rare earths contained in samarskite from Sankara Mica Mine of Mysore, India. The author desires to express his thanks to the Syndicate for their generosity in supplying him with a very large amount of this mineral.

NOTE 2.—It becomes necessary to correct another point with regard to the bromate method of fractionation. In order to observe how the separation of holmium and dysprosium is proceeding, one must convert into the nitrates before observing the absorption spectrum, and the solution should be concentrated. This work upon the Carolina monazite has shown that the bromate method is after all a very good one for the separation of these elements. It possesses the advantage that no hydrolysis takes place, as is the case with the ethyl sulfates, even when one uses great care.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY.]

THE ACTION OF SULFUROUS ACID UPON THE SULFIDES OF IRON, ZINC AND MANGANESE.

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It is a well known fact that the sulfides of iron, zinc, and manganese, when freshly prepared, are readily soluble in a concentrated solution of sulfur dioxide, while those of nickel and cobalt are difficultly soluble. As early as 1833, Berthier[1] employed this reaction as a means of freeing the hydrates of titanium and zirconium from ferrous sulfide, and Delffs[2] recommends the same process, although neither investigated the character of the reaction.

An inspection of the literature discloses the fact that while there are many references to the reaction, and a number of suggestions as to the products formed, there is little recorded experimental work relating to it. Mendelejeff[3] and Dammer[4] state that the product of the reaction is ferrous dithionate. Rammelsberg[5] says that when a stream of sulfur dioxide is conducted into a suspension of manganese sulfide in water, the products are the thiosulfate and sulfur. Guerout[6] expresses the opinion that the products are the thiosulfate and the sulfite, but records no experimental data and is not quoted in the handbooks.

In view of this uncertainty it seemed desirable to make a study of the reaction, especially as there is much confusion in regard to most of the thio acids and their salts and the reactions in which they are supposed to be formed, and many of them are in need of further study. The results of a preliminary investigation are recorded in the following pages.

[1] *Ann.*, 5, 246.

[2] *Jahresb.*, 1851, 174.

[3] "Principles of Chemistry," Vol. II, p. 171.

[4] "Anorg. Chem.," Vol. II, p. 564.

[5] *Pogg. Ann.*, 56, 305.

[6] *Compt. rend.*, 75, 1276.

First Procedure.—Convenient quantities of the sulfides of iron, zinc, and manganese were prepared as needed by precipitating a weighed quantity of a suitable salt with ammonium sulfide and washing by decantation with water containing a little ammonium sulfide. The freshly prepared sulfide was suspended in water in a round-bottomed flask provided with a two-holed stopper. Through one hole was inserted a tube for delivering sulfur dioxide, and through the other a short tube provided with a Bunsen valve for excluding air. When sulfur dioxide is passed into the suspension, the sulfide rapidly dissolves with rise of temperature, so that the flask was kept cool with ice-water. As the action proceeds a crystallin material separates as a heavy deposit on the bottom of the flask. This proved to be the sulfite of the metal. Its formation is in accord with the suggestion of Guerout, and may be represented by the equation

$$MS + H_2SO_3 = MSO_3 + H_2S.$$

If the current of sulfur dioxide is continued, the crystals of sulfite dissolve, forming the acid sulfite. When the solution of the acid sulfite is warmed, the normal sulfite is once more deposited, and if the heating is done carefully well-formed crystals of considerable size may be obtained. The sulfites are practically insoluble in water.

The solution, from which all of the sulfite has been removed by boiling, still gives a strong reaction for the metal, and when it is treated with acid liberates milky sulfur, indicating the presence of thiosulfate. This is easily accounted for. The hydrogen sulfide set free in the primary reaction in large part escapes under the conditions of the experiment. In part, however, it reacts with sulfur dioxide forming free sulfur and possibly other products known to be present in Wackenroder's solution.[1] Debus[2] has shown that the sulfur formed in such reactions is very reactive, and it at once acts upon the acid sulfite in solution, in accordance with the equation

$$M(HSO_3)_2 + S = MS_2O_3 + H_2O + SO_2.$$

Second Procedure.—To test the validity of this view the procedure was modified. A suspension of the sulfide was added in small portions at a time, and with constant stirring, to a concentrated solution of sulfur dioxide. Under these conditions the sulfur dioxide is always in great excess. Consequently nearly all of the hydrogen sulfide is oxidized to sulfur, and the sulfite is transformed into thiosulfate about as fast as it is formed, no solid sulfite being produced. The resulting solution contains the metal very largely as thiosulfate, together with a little acid sulfite, while a considerable deposit of sulfur occurs. The reaction can be formulated as follows:

$$2MS + 3SO_2 = 2MS_2O_3 + S.$$

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[1] *Ann.*, 60, 189.

[2] *J. Chem. Soc.*, 53, 278.

While the sulfur set free approximated the quantity required by the equation it never quite equaled it. This is accounted for (1) by the formation of some acid sulfite, (2) by the escape of some hydrogen sulfide, (3) by colloidal sulfur remaining in solution. Although the solution of thiosulfate filtered from the sulfur appeared to be perfectly clear, a beam of light from a lantern projected through the solution revealed a very considerable suspension of colloidal sulfur.

The Formation of other Thio Salts.—Since a number of thio-acids have been described as being formed in Wackenroder's solution (which results from the continued action of hydrogen sulfide upon sulfur dioxide in solution) attention was directed to the possible presence of other thionic salts, especially in view of the statements in the literature that the dithionate is the main product of the reaction. Ferrous sulfide was dissolved in both of the ways just described and the solution was made decidedly alkaline with barium hydroxide. This precipitates practically all iron, sulfites, sulfates, and thiosulfates, but would not precipitate the other thio-acids, the barium salts of which are described as soluble, and relatively stable. The excess of barium hydroxide in the filtrate was removed by carbon dioxide and the neutral solution evaporated to dryness. Practically no residue was obtained in any case, either with iron, zinc, or manganese. It is therefore certain that not more than traces of any other thio-salt are formed under the conditions described.

Isolation and Analysis of the Sulfites.—The solution of acid sulfites of iron, zinc, and manganese prepared according to the first procedure was placed in a water bath, the temperature of which was slowly raised. The normal sulfite gradually separates in well formed crystals, and in much more satisfactory condition than the descriptions in the literature indicate. The chief research upon the sulfites in recent years is that of Seubert and Elten[1] who prepared a long series of these salts by double decomposition of various metallic salts with sodium sulfite, the products being crystallin precipitates. It is much better to treat the metallic salt with a solution of sodium acid sulfite saturated with sulfur dioxide, and slowly warm the solution. The procedure is a perfectly general one as far as our experience goes, and a subsequent paper will be devoted to a review of the normal sulfites prepared in this way.

The normal sulfite of manganese is of the tint of pink characteristic of manganese salts in general; zinc sulfite forms large colorless crystals; ferrous sulfite is light green, or nearly white if the crystals are small. It is difficult to prevent the latter from oxidizing while in contact with the mother liquor and exposed to the air. The crystals should be filtered as rapidly as possible on a Buchner filter, and at once washed with freshly boiled water to which a little sulfur dioxide has been added. They are

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[1] *Z. anorg. Chem.*, 4, 44.

perfectly stable when dry. The analysis of the three salts is shown in the following table:

Salt.	Component.	Theoretical.	Found.		
$FeSO_3.3H_2O$	Fe	29.43	29.70	29.52	30.00
	S	16.88	17.17	17.08	16.70
	3 H_2O	28.50	28.44	28.60	28.55
$MnSO_3.3H_2O$	Mn	29.08	28.98	29.10	...
	S	16.95	17.01	17.04	17.12
	3 H_2O	28.58	28.40	28.29	28.47
$ZnSO_3.2^1/_2H_2O$	Zn	34.35	34.69	34.41	34.39
	S	16.81	16.80	16.80	16.65
	$2^1/_2$ H_2O	23.64	23.72	23.65	...

The Thiosulfates of Iron, Manganese and Zinc.—Attention was next directed to the solution obtained in the second procedure, in which qualitative experiments had indicated the presence of thiosulfates. Descriptions of a considerable number of thiosulfates are to be found in the literature. Those prepared by boiling a soluble base with sulfur are well known, while those containing a heavier metal have been very imperfectly described. For the most part the latter have been obtained by rubbing a suspension of the difficultly soluble barium thiosulfate with other sulfates in molecular proportions—a procedure which will always leave them contaminated with soluble sulfate. The solution obtained in this way has been brought to crystallization either by evaporation *in vacuo* or by adding a mixture of alcohol and ether which separates the thiosulfate as a liquid phase which is then allowed to crystallize spontaneously. (Vortmann and Padberg.[1]) All writers agree that these salts decompose with great ease in concentrated solution, and it would appear that all crystallin preparations have been of doubtful purity.

In view of these facts it was thought best to determin the ratio of the metal to sulfur in the solution before attempting to isolate the salts in crystallin form. Accordingly the solutions were boiled in a flask provided with a valve until all sulfite had been precipitated. The solution was rapidly filtered and measured portions were analyzed for the metal and sulfur. The results in the case of solutions containing iron and manganese were as follows:

	Wt. of metal.	Equivalent.	Wt. of sulfur.	Equivalent.	Ratio.
Mn	0.2613	0.004751	0.2991	0.00935	1 : 1.986
Mn	0.2617	0.004768	0.3024	0.00945	1 : 1.970
Fe	0.1277	0.002284	0.1469	0.00459	1 : 2.009

From these results it will be seen that if care is taken to exclude the air while removing the sulfur dioxide and sulfites, only the thiosulfate remains, the experiments already described having shown that no other thionic

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[1] *Ber.*, 22, 2637.

acids are present. If precautions for excluding air are neglected, a very considerable oxidation to sulfate occurs.

Attempts to Isolate Crystallized Thiosulfates.—A special form of apparatus was devised for evaporating the dilute solutions out of contact with the air and at moderate temperatures. A resistance heater was made out of a piece of alberene stone about six inches in diameter, by fastening metallic contacts diametrically opposit to each other, and covering the surface between them with kryptol. This heater was placed within a large bell desiccator, the leads being brought out through a tight-fitting stopper in the side tubulus. The dish containing the dilute solution was placed upon the heater, and the exit tube from the tubulus at the top of the bell was connected with a pump. The aqueous vapor was rapidly removed in this way and evaporation was quite rapid at 40°. With this apparatus it was found to be an easy matter to evaporate the solution to a syrupy consistency without any marked decomposition. If the evaporation goes beyond a certain point, a very rapid and complete decomposition occurs, the whole contents of the dish turning to a paste of sulfur, sulfate and sulfide. Apparently the salts can be concentrated until they are simply melted hydrates, further abstraction of water resulting in decomposition. The marked viscosity of the solution is very unfavorable to spontaneous crystallization, recalling the familiar case of ferric nitrate, and no crystallization was secured beyond the separation of a little sulfate, probably formed by spontaneous decomposition.

The salts were then separated from moderately concentrated solution by the addition of alcohol and ether, and many attempts were made to isolate a pure product from this source. Spontaneous crystallization was always accompanied by the formation of sulfate crystals, while the thiosulfate formed melts readily at room temperatures. Experiment showed that the sulfates of all three metals, as well as their thiosulfates, can be thrown out of their solutions as liquid phases by the addition of alcohol and ether, so that no separation of the two salts is effected in this way. It is possible to freeze the entire liquid phase but the resulting crystals always gave reactions for the sulfate as well as for the thiosulfate. A large number of analyses were made, and the largest ratio of metal to sulfur, obtained with the manganese salt, was 1 : 1.78, indicating the presence of a considerable percentage of sulfate.

The results described seem to leave no doubt as to the character of the reaction in which sulfides of iron, zinc, and manganese are dissolved in sulfurous acid. Lack of time prevented a further study of the thiosulfates, but a better method of preparing the pure salts is now under investigation, and work will be continued with the purpose of obtaining a series of these salts and making a study of their reactions.

Conclusions.—It has been shown: (1) that the primary action of sulfurous acid upon the sulfites of iron, zinc, and manganese is a double decomposition of the usual type; and (2) that in as far as the conditions of the reaction lead to the oxidation of the liberated hydrogen sulfide by sulfur dioxide, a corresponding quantity of thiosulfate is formed as a secondary reaction.

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ON EXTRACTION WITH LIQUEFIED GASES AND THE AMMONOLYSIS OF HYDRAZINE SULFATE.

BY FRITZ FRIEDRICHS.

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In connection with the choice of a solvent for use in extraction two considerations are of importance: first, the relative solubility of the substances to be separated; and second, the ease with which the solvent may be recovered without loss and without decomposition of the extract or of the residue. Since the removal of the solvent is usually effected by evaporation, a solvent with the lowest possible boiling point would normally be preferable, especially when the material to be extracted decomposes at relatively low temperatures, or possesses a high vapor tension. This leads at once to the application of liquefied gases in extraction in case the usual solvents can not be readily recovered after the operation is complete.

The reason that such comparatively inexpensive gases as ammonia, sulfur dioxide, hydrogen sulfide, methylamine, etc., have not found more frequent application as extracting media in scientific and industrial work lies in the fact that the solvent power of these substances, with the exception of ammonia, has not yet been thoroughly investigated, and further, that suitable apparatus for the purpose has not yet been designed. Various extractions, to be discussed in more detail later, have already been carried out by A. W. Browne, T. W. B. Welsh,[1] and A. E. Houlehan,[2] but the apparatus employed has not yet been completely developed for general use. The author of the present paper, in undertaking the continuation of the work, has consequently devised, on the basis of the work already done, the apparatus shown in the accompanying sketch.

The apparatus consists of three parts: (1) the extraction apparatus proper, D, (2) the container C, for the substance to be extracted, suspended in D from three glass projections, and (3) the condenser B, which is carefully ground to fit D. The extraction apparatus is modeled after the Landsiedl device except that the bulb F is provided with a small siphon and with a stopcock, G, through which the extract may be drawn off, and that the entire apparatus is insulated by means of a vacuum jacket.

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[1] THIS JOURNAL, 33, 1728–34 (1911).

[2] *Ibid.*, 33, 1734–42 (1911).