

Summary.

The solubility curves for hydrogen sulfide, boric acid, benzoic acid and salicylic acid in aqueous solutions of hydrogen chloride, and for the last three of the above mentioned weak acids in aqueous solutions of nitric acid, have been determined. The changes in the specific conductivities of the solvent acids, due to the presence of the weak acids in solution, have also been investigated.

The results obtained, together with those of previous investigators, have been critically discussed in connection with the rule, established in an earlier article, that compound formation between acids in pairs increases in extent with increasing diversity of acidic strengths. The predicted and observed solubility curves for systems of various types have been compared, and satisfactory agreement, in general, has been obtained. The conductivity results also fall into line in most cases. Further experimental work, however, is required to elucidate certain abnormalities in particular systems. To establish the rules here outlined upon a final basis, a better understanding of the part played by the third component—water—is also necessary.

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A MODIFIED METHOD FOR THE DETERMINATION OF IRON AND VANADIUM AFTER REDUCTION BY HYDROGEN SULFIDE.¹

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I. Introduction.

Some time ago the authors had occasion to determine whether uranyl compounds suffered reduction when their ammoniacal solutions were saturated with hydrogen sulfide and then slightly acidified with sulfuric acid and boiled. Experiments were accordingly carried out which demonstrated that while there was no reduction of uranium, some compound was formed in sufficient amount to consume appreciable quantities of a potassium permanganate solution. It was suspected that this reduction was occasioned by polythionic acids which had been formed during the course of the reactions and it was realized that if such was the case, the observation would be of importance in operations dealing with sulfide reductions in general and those of iron and vanadium in particular.

¹ Published by permission of the Director of the Bureau of Standards.

A search of the literature revealed considerable differences in the methods recommended for hydrogen sulfide reductions and in three researches direct evidence was found that the method was subject to error. The conclusions reached in these researches have been practically buried because one research was published under the broad title "The Determination of Iron in Iron Ores" in a foreign journal, another appeared under the title "Contributions to the Volumetric Determination of Antimony, Tin, Titanium, Iron and Uranium" in a privately printed doctorate dissertation, while the third was unpublished.

II. Historical.

Fresenius-Cohn² specify that the cold ferric solution containing a liberal excess of sulfuric acid be reduced by hydrogen sulfide in a flask two-thirds filled until the color disappears and the passage of gas be then continued for at least 10 minutes. The solution is boiled until reduced to $\frac{1}{2}$ its first volume, and finally diluted with cold water until the flask is nearly filled.

Treadwell-Hall³ outline two procedures as follows.

(1) The solution of the ferric sulfate containing 10% (by volume) of sulfuric acid is boiled, reduced with hydrogen sulfide until colorless, and the boiling then continued as a current of carbon dioxide is swept through to expel the hydrogen sulfide. (2) The cold sulfuric acid solution (acidity not stated) is saturated with hydrogen sulfide, heated to boiling, and filtered into a flask containing carbon dioxide. The filtrate is boiled as a current of carbon dioxide is passed through and the solution finally cooled in a stream of the gas. In addition it is stated on page 609, "By means of the latter (hydrogen sulfide) the ferric salt is completely reduced, independent of how little or how much free acid is present in the solution."

Gooch⁴ directs that the acidified iron solution be boiled, treated to complete reduction with hydrogen sulfide, and the gas expelled by boiling with carbon dioxide.

Scott⁵ advocates the use of the filtrate from the hydrogen sulfide group separation, after boiling out hydrogen sulfide.

Mellor⁶ merely states that "hydrogen sulfide can be used for reducing the iron," and is obviously not enthusiastic concerning its use.

Washington⁷ specifies that the gas be passed through the cold sulfuric acid solution, (acidity not defined), the solution filtered, boiled while carbon dioxide is passed through, and cooled under the same gas.

² Fresenius-Cohn, "Quantitative Chemical Analysis," John Wiley and Sons, 1, p. 326 (1904).

³ Treadwell-Hall, "Analytical Chemistry," John Wiley and Sons, 4th Ed., 2, pp. 99, 115.

⁴ Gooch, "Representative Procedures in Quantitative Chemical Analysis," John Wiley and Sons, 1st Ed., p. 142.

⁵ Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Co., 2nd Ed., p. 215.

⁶ Mellor, "A Treatise on Quantitative Inorganic Analysis," C. Griffin and Co., 1, p. 191 (1913).

⁷ Washington, "The Chemical Analysis of Rocks," John Wiley and Sons, 3rd Ed., pp. 163-165.

Hillebrand⁸ directs that the cooled solution containing 1.5 to 2.5% by volume of sulfuric acid be treated with hydrogen sulfide, boiled with continued passage of the gas until the sulfur is coagulated, cooled during continued passage of the gas, filtered, treated again with hydrogen sulfide, then boiled and cooled while a current of carbon dioxide is passed through the solution.

R. Fresenius⁹ in an article on the determination of iron in iron ores by the Reinhardt method, noted that filtrates from the hydrogen sulfide separation of copper from iron were apt to give high values when subsequently titrated with permanganate. He reached the conclusion that satisfactory results could be obtained by the complete oxidation with permanganate of the hydrogen sulfide filtrate, followed by reduction with stannous chloride and final titration in accordance with the Reinhardt method.

Boller¹⁰ quoted a private communication from Dr. Herrmann to Dr. Treadwell to the effect that values obtained by Hillebrand's method were too high. Work subsequently done by Boller demonstrated that 500 cc. of 1*N* sulfuric acid solution, treated with 1.0 cc. of a saturated sulfur dioxide solution and then as in Hillebrand's method required 2.9 cc. of 0.01 *N* permanganate solution; practically the same values were obtained with sulfur present as with sulfur filtered off. Boller demonstrated by experiments with purified sulfur treated under like conditions that the reducing compounds obtained above were not entirely due to polythionic acids formed by the action of hydrogen sulfide on sulfur dioxide. Further tests of the method carried on with a standard solution of ferric chloride in hydrochloric acid with final titration in the presence of Zimmermann-Reinhardt solution gave results which averaged 0.1040 g. of iron with no filtration of sulfur, 0.1041 g. of iron with filtration of sulfur through paper, and 0.1040 g. of iron with filtration of sulfur through a Gooch crucible, as against a true value of 0.1020 g. of iron.

McBride,¹¹ in a series of experiments dealing with the reduction of iron by hydrogen sulfide, arrived at the following conclusions.

"It should be noted that the limits of acidity at the time of reduction are given as 2.00 to 2.5%. Any variation from these limits introduces an error. If more than 2.5% volume of free sulfuric acid is present the iron cannot be completely reduced. The use of less than 2.0% by volume of free acid, however, is not permissible, as with the less strongly acidified solution, some compounds having a reducing action on potassium permanganate are formed which are not removable by the boiling with carbon dioxide before titration. The smaller the amounts of free acid, the higher the amount of iron indicated by the titration."

The above citations, particularly the last three, demonstrated the need of an investigation of the hydrogen sulfide reduction and full publicity of the results obtained. This is all the more important since the method is often recommended and widely used on account of such considerations as enumerated by Washington.⁷ "This (hydrogen sulfide) commends itself on account of its certainty and rapidity of action, its easy and complete removability, and still more by the fact that it has no reducing action on the titanous and platinous sulfates that are always present (in rock analysis);" and "Hydrogen sulfide is much more readily obtainable than sulfur dioxide—a minor, but practically important consideration."

⁸ "The Analysis of Silicate and Carbonate Rocks," U. S. Geol. Survey, *Bull.* 700, pp. 119-120.

⁹ R. Fresenius, *Z. anal. Chem.*, 53, 595 (1914).

¹⁰ Wilhelm Boller, "Beiträge zur titrimetrischen Bestimmung des Antimons, Zinns, Titans, Eisens und Urans," Zurich, 1915, p. 32.

¹¹ McBride, unpublished work carried on at the Bureau of Standards.

III. Experimental.

Preliminary experiments demonstrated that compounds which were removed neither by filtration nor by prolonged boiling in a stream of carbon dioxide, and which subsequently reduced potassium permanganate, were formed in either hot or cold solutions: (1) when a dilute solution of sulfurous acid was treated with hydrogen sulfide; (2) when a freshly-prepared ammonium sulfide solution containing a very small amount of polysulfide was acidified with sulfuric acid; and (3) when a sulfuric acid solution of potassium permanganate was treated with hydrogen sulfide. That the reduction was not due to sulfur dioxide or hydrogen sulfide was demonstrated by the fact that aliquot portions of the solutions did not react with 0.1 *N* iodine solution.

It seemed entirely probable that similar reducing compounds would be formed in any reduction involving the use of hydrogen sulfide. Table I presents data which show the results that are to be expected in hydrogen sulfide reductions of iron carried out under varying conditions of acidity, volume of solution, temperature, and time of reduction.

Counterpoised weight burets were used throughout and corrections made in the usual manner for reagents and end-points. The iron solution was prepared from highest purity ferrous ammonium sulfate and its iron titer taken as an average of closely agreeing values found by reduction with sulfur dioxide, reduction in a Jones reductor, double gravimetric precipitations by ammonia with final correction for silica and precipitation with cupferron followed by silica correction. The permanganate solution was prepared with the necessary precautions and standardized by means of the Bureau of Standards sodium oxalate by the method of McBride.¹² The hydrogen sulfide used was passed through solutions of sodium hydrogen carbonate and blank runs demonstrated that it contained no products which subsequently consumed permanganate. Reductions were performed in glass wash-bottles in order that no organic material might be introduced.

All reduced iron solutions were tested with potassium thiocyanate and in Table I reductions were complete unless otherwise indicated. Since preliminary experiments demonstrated that sulfur alone in sulfuric acid solution was without effect on permanganate, titrations were performed in its presence unless otherwise specified.

A study of the data presented in Table I demonstrates that: (1) The hydrogen sulfide reduction method for iron ordinarily gives high values in completely reduced solutions. This holds true in all acidities, in reductions in cold or boiling solutions and in the presence or absence of sulfur. The high values are not in direct ratio to the quantity of iron

¹² McBride, *THIS JOURNAL*, 34, 393 (1912).

TABLE I.—DETERMINATION OF IRON BY ORDINARY HYDROGEN SULFIDE METHODS.

Iron.		Error. G.	Volume of solution. Cc.	H ₂ SO ₄ . % by volume.	Duration of H ₂ S treatment in minutes.			CO ₂ passed into boil- ing sol. Minutes.
Taken. G.	Found. G.				Cold.	Warming.	Boiling.	
0.0288	0.0295	+0.0007	200	0.2	0	0	60	60
0.0782	0.0799	+0.0017	350	0.6	95	0	0	"
0.1074	0.1099	+0.0025	300	0.6	30	15	60	60 ^b
0.1646	0.1673	+0.0027	200	0.8	0	0	60	60
0.1042	0.1054	+0.0012	100	1.0	0	0	70	60
0.0938	0.0980	+0.0042	250	1.0	0	0	75	60 ^c
0.1060	0.1075	+0.0015	350	2.0	20	15	45	60
0.0105	0.0108	+0.0003	100	2.5	30	15	30	60 ^d
0.1735	0.1741	+0.0006	100	2.5	30	15	30	60 ^d
0.0780	0.0786	+0.0006	350	2.5	120	0	0	"
0.0124	0.0130	+0.0006	300	2.5	30	15	30	30 ^f
0.1012	0.1027	+0.0015	350	3.0	20	15	60	60
0.1702	0.1733	+0.0031	300	5.0	30	15	0	30
0.1006	0.1018	+0.0012	350	5.0	20	15	60	60
0.00935	0.00955	+0.0002	100	5.0	30	15	0	30
0.0105	0.0113	+0.0008	100	5.0	40	25	0	30 ^f
0.1787	0.1794	+0.0007	100	5.0	40	25	0	30 ^f
0.0283	0.0280	-0.0003	100	5.0	15	15	0	30 ^g
0.1331	0.1335	+0.0004	100	5.0	15	15	0	30 ^h
0.0992	0.0881	-0.0111	350	7.5	0	15	60	60 ^g
0.1018	0.1003	-0.0015	350	7.5	30	25	0	60 ^g
0.1029	0.1031	+0.0002	350	8.0	20	15	55	60
0.0933	0.0936	+0.0003	350	10.0	20	15	60	60
0.0984	0.0969	-0.0015	350	10.0	20	15	60	60 ⁱ
0.0780	0.0733	-0.0047	100	10.0	120	0	0	" j

^a CO₂ passed into cold sol. for 100 min. and into boiling sol. 30 min.

^b Titrated with K₂Cr₂O₇ solution. Sulfur filtered off before final reduction.

^c Not reduced at end of 55 min., cooled in H₂S for 10 min., and reboiled in H₂S for 10 min.

^d Sulfur filtered off before final reduction.

^e CO₂ passed into cold sol. for 145 min. and into boiling soln. for 45 min.

^f Sulfur filtered off before final reduction.

^g Reduced sol. contained Fe₂(SO₄)₃.

^h Reduced sol. contained no Fe₂(SO₄)₃.

ⁱ Reduced sol. contained Fe₂(SO₄)₃.

^j CO₂ passed into cold sol. for 145 min. and into boiling sol. for 45 min. Reduced sol. contained Fe₂(SO₄)₃.

involved. (2) A low initial volume (100 cc.) and moderate acidity (2 to 2.5% by volume) is desirable. (3) Complete reduction in cold solution is slow, and in boiling solutions impossible in acidities much over 1%, especially in solutions of large volume. A favorable procedure consists in reduction in cold solution for 30 minutes, followed by warming to the boiling point for 15 minutes. (4) Complete reduction can sometimes be had

by the latter procedure in sulfuric acid concentrations as high as 10% by volume. Complete reduction in 5% by volume is easily attained.

Table II lists determinations carried out under the following conditions which were based for the most part on a study of the experiments listed in Table I: volume of solution, 100 cc.; acidity, 2.5% sulfuric acid by volume; hydrogen sulfide reduction 30 minutes in cold solution and 15 minutes as solution is heated to boiling; addition of 15 cc. of sulfuric acid (1:1); boiling for 30 to 60 minutes to a volume of approximately 50 cc. as a stream of carbon dioxide is bubbled through; cooling under the same conditions; dilution to 200 cc. with cold distilled water; and titration with standard permanganate solution. In some cases the separated sulfur was filtered off after the hydrogen sulfide treatment and after the reduced solution was cooled somewhat. The filtrate was then again treated with hydrogen sulfide for 10 minutes before proceeding as above described. The modified method differs from the method given by Hillebrand¹³ in that the volume of the solution is fixed at 100 cc., the solution is not boiled as hydrogen sulfide is bubbled through and the acidity of the solution is raised before the expulsion of the hydrogen sulfide. The method differs from that advocated by McBride¹⁴ in the latter two respects and also by the expressed limitation of the solution to small volume.

TABLE II.—DETERMINATION OF IRON BY THE MODIFIED HYDROGEN SULFIDE METHOD.

Iron.		Error.	CO ₂ passed into the boiling sol. (minutes).	Remarks.
Taken.	Found.			
G.	G.	G.		
0.0129	0.0132	+0.0003	30	
0.1765	0.1766	+0.0001	30	Acidity at end of boiling was 25%.
0.00748	0.00756	+0.00008	60	Acidity at end of boiling was 33%.
0.0266	0.0267	+0.0001	60	Acidity at end of boiling was 33%.
0.1253	0.1253	0.0000	50	Sulfur filtered off before final reduction.
0.00442	0.00455	+0.00013	60	Sulfur filtered off before final reduction.
0.0254	0.0256	+0.0002	60	Sulfur filtered off before final reduction.
0.1310	0.1313	+0.0003	60	Sulfur filtered off before final reduction.

The data in Table II demonstrate that while the modified method still gives values which are slightly high, determinations by the method are sufficiently accurate for most purposes. Incidentally, it is seen that ferrous sulfate is not oxidized upon boiling in a solution containing 33% (by volume) of sulfuric acid. The authors did not carry out experiments

¹³ Hillebrand, "The Analysis of Silicate and Carbonate Rocks," U. S. Geol. Survey, *Bull.* 700, pp. 119-20.

¹⁴ Unpublished.

dealing with slight variations of the modified method on account of the ease with which the specified conditions can be met.

Table III presents data obtained in the determination of vanadium by the ordinary hydrogen sulfide reduction and also by the modified method. The vanadium solution was standardized by sulfur dioxide reduction and also by reduction in a Jones reductor with ferric alum and phosphoric acid in the receiver.

TABLE III.—DETERMINATION OF VANADIUM BY THE ORDINARY AND BY THE MODIFIED HYDROGEN SULFIDE METHOD.

Vanadium.		Error. G.	Volume of solution cc.	H ₂ SO ₄ (% by Volume).	Remarks.
Taken. G.	Found. G.				
0.0469	0.0482	+0.0013	250	0.5	Ordinary Method.
0.0419	0.0428	+0.0009	250	0.5	Ditto, sulfur filtered off.
0.0430	0.0431	+0.0001	100	2.5	Modified Method.
0.0469	0.0469	0.0000	100	2.5	Ditto.

It is apparent that high results are to be expected in ordinary hydrogen sulfide reductions of vanadium and that satisfactory values are obtained with the modified method. Hillebrand¹⁵ has noted the former and states "One or two checks (on vanadium) are always to be made by reducing again (after titration of the solution reduced by hydrogen sulfide) by means of a current of sulfur dioxide, boiling this out again and repeating the titration. The latter results are apt to be a very little lower than the first and are to be taken as the correct ones." The higher value in the first titration was ascribed by Hillebrand to the extraction of oxidizable matter from the filter paper used to filter off sulfur and sulfides, as noted by McBride and Scherrer,¹⁶ and recently, under more severe conditions, by Myhill.¹⁷

As sulfur alone is without effect on permanganate and the sulfur in Expt. 2 was filtered off on a filter paper freshly washed with acid it is certain that the higher values cannot be ascribed entirely to oxidizable extracts from filter papers.

IV. Conclusions.

Published methods for the reduction of iron by hydrogen sulfide are faulty in either of two respects: (1) complete reduction is impossible or, (2) when reduction is complete, other oxidizable compounds are formed

¹⁵ *Op. cit.*, p. 186.

¹⁶ McBride and Scherrer, *THIS JOURNAL*, 39, 928 (1917).

¹⁷ Myhill, *Chem. Age*, 4, 151 (1921).

which cause high values.¹⁸ The second statement also applies to the determination of vanadium.

The hydrogen sulfide method for iron or vanadium as herein modified is sufficiently accurate for all ordinary work.

In case the highest accuracy is desired, the sulfur dioxide method is recommended. Sulfur dioxide reduces vanadium to the quadrivalent condition and does not reduce quadrivalent titanium. Unfortunately it reduces platinum to the bivalent condition and also reduces various members of the hydrogen sulfide group; consequently when platinum (as is usually the case in rock analysis, owing to the platinum ware employed) or other members of the hydrogen sulfide group are present, a modification of the method already used in the determination of vanadium by Hillebrand¹⁹ is called for, namely, precipitation with hydrogen sulfide in acid solution, separation of sulfides by filtration, boiling out of hydrogen sulfide in the filtrate, complete oxidation by 10% permanganate solution and final reduction with sulfur dioxide gas. The following notes and precautions, taken for the most part from the work of Hillebrand²⁰ are of interest in the later operation.

The direct use of a solution of sulfur dioxide or of an alkali sulfite is inadmissible unless these have been freshly prepared, for after a lapse of time they contain other oxidizable bodies than sulfurous acid or a sulfite.

Sulfur dioxide is most conveniently obtained from a cylinder of the liquefied gas or, in default of this, by heating a flask containing a solution of sulfur dioxide, or of a sulfite to which sulfuric acid has been added.

Reductions with this gas require low initial acidities, and hydrochloric-acid—chloride solutions are reduced more rapidly than sulfuric-acid—sulfate solutions; in the former case a titration with permanganate requires previous addition of titrating solution as in the Zimmermann-Reinhardt method.

Reduced solutions containing sulfur dioxide should not be allowed to stand for over 24 hours lest other oxidizable bodies be formed.

The expulsion of the last trace of sulfur dioxide is said to be accomplished more effectively by boiling with simultaneous passage of a rapid current of carbon dioxide.

The authors have not made any serious attempts to isolate and identify the oxidizable compound or compounds which are formed in hydrogen

¹⁸ It is to be borne in mind that these oxidizable compounds are quite stable and consequently may cause trouble in any quantitative operation calling for a final oxidation as, for instance, where the hydrogen sulfide solution is boiled to expel the gas and then reduced by stannous chloride or in a Jones reductor preliminary to titration with dichromate or permanganate. The obvious remedy lies in complete oxidation before the final reduction.

¹⁹ Hillebrand, *op. cit.*, p. 168.

²⁰ Hillebrand, *ibid.*, p. 186.

sulfide reductions. It is believed that they are polythionic acids and it has been noted that (1) they are quite stable upon boiling with sulfuric acid in concentrations as high as 33% by volume; (2) they are volatile upon prolonged boiling; (3) the volatilized compounds do not react with iodine solution; and (4) their dilute solutions give with silver nitrate solution a yellowish-brown coloration.

V. Summary.

1. The determination of iron or of vanadium by reduction with hydrogen sulfide followed by titration with permanganate or dichromate ordinarily gives high values.

2. These high values are not due to the presence of sulfur and persist in spite of the complete expulsion of hydrogen sulfide and the avoidance of organic matter extracted from filter paper. They may be ascribed to polythionic acids which are not destroyed by boiling in moderately conc. sulfuric acid solution and which are volatilized slowly from dilute and more rapidly from concentrated solutions.

3. Reasonably accurate determinations may be made by restricting the original solution to 100 cc. and proceeding by the described modified method.

4. For accurate determinations of iron and vanadium in solutions containing platinum (as in rock analysis) a preliminary separation of the hydrogen sulfide group, followed by expulsion of the gas, complete oxidation with permanganate and reduction with sulfur dioxide is recommended.

The authors desire to express to Dr. W. F. Hillebrand their sincere appreciation of his aid and counsel.

WASHINGTON, D. C.

{CONTRIBUTION FROM THE CHEMICAL LABORATORY OF CLARK UNIVERSITY,
No. I, 6.}

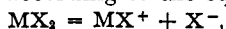
THE CONDUCTANCE OF SOLUTIONS OF TERNARY ELECTROLYTES IN PROPYL ALCOHOL.

BY CHARLES A. KRAUS AND JOHN EGBERT BISHOP.

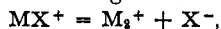
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I. Introduction.

Our knowledge of the ionization process of ternary electrolytes in non-aqueous solvents is very limited and even in the case of aqueous solutions the nature of the ionization process for these substances is uncertain. If intermediate ions are formed according to the equation



which, in turn, break down according to the equation



then it is not possible to determine the equilibrium in the solution by means