

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

THE VOLUMETRIC DETERMINATION OF SULFIDE BY OXIDATION TO SULFATE.

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In the usual iodometric oxidation of hydrogen sulfide to sulfur only two equivalents of oxygen are required, whereas if it is oxidized to sulfuric acid, eight equivalents are necessary. It would obviously be a distinct advantage to use the latter process instead of the former, if it could be as readily accomplished. Of the methods suggested for this purpose only three can be considered as reasonably accurate. Feit and Kubierschky¹ added to the sulfide excess of standard bromate solution, acidified with sulfuric acid, boiled off the bromine liberated in the reaction and titrated the excess of bromate iodometrically. Dean² oxidized hydrogen sulfide with a large excess of standard iodate solution in a solution containing sufficient hydrochloric acid to form iodine chloride and titrated the excess with standard *iodide* solution. Kolthoff³ added an excess of standard bromine solution and determined the excess iodometrically. The first and last methods have several obvious disadvantages and the second one requires a high concentration of hydrochloric acid, which is somewhat inconvenient, since alkaline solutions must be used to absorb hydrogen sulfide. In connection with the use of hypobromite in the determination of ammonia⁴ it seemed desirable to investigate the use of this reagent (and also hypochlorite) for the oxidation of sulfide to sulfate. It was found that if the solution is sufficiently alkaline the oxidation goes very rapidly according to the equation, $4 \text{ NaBrO} + \text{Na}_2\text{S} = 4 \text{ NaBr} + \text{Na}_2\text{SO}_4$. The excess of hypobromite is easily determined by adding potassium iodide, acidifying, and titrating the liberated iodine by means of thio-sulfate. The same reaction occurs with hypochlorite, but less readily.

Preparation of the Standard Hypobromite Solution.

A solution of convenient concentration was prepared by adding 100 g. of bromine slowly and with constant stirring to a solution of 60 g. of pure sodium hydroxide in 1600 cc. of water, keeping the solution well cooled. Such a solution is about 0.6 *N* and 1 cc. corresponds to approximately 2.4 mg. of sulfur. Since the presence of traces of iron, copper and other metals increases enormously the rate of decomposition of the solution, it is advisable to let the hydroxide solution stand for a day or two and filter or siphon off the clear liquid, before adding the bromine. It should be kept in the dark; but even with pure materials the rate of decomposition is appreciable.⁴ Fleury⁵ has shown that this

¹ Feit and Kubierschky, *Chem. Ztg.*, **15**, 351 (1891).

² Dean, *THIS JOURNAL*, **40**, 619 (1918).

³ Kolthoff, *Pharm. Weekblad*, **56**, 143 (1919).

⁴ Willard and Cake, *THIS JOURNAL*, **42**, 2646 (1920).

⁵ Fleury, *Compt. rend.*, **171**, 957 (1920).

may be greatly decreased by adding to each liter of solution 1 g. of potassium iodide or iodate. This suggestion was tried, with contradictory results. One solution changed rapidly to bromide and bromate, the total oxygen remaining unchanged. Another, more dilute in hypobromite but containing relatively more alkali, showed almost no change. The reason for this difference in behavior is being investigated.

Preparation of the Standard Hypochlorite Solution.

A hypochlorite solution made from sodium hydroxide purified as described above is much more stable. It was prepared by passing into a cold solution of 90 g. of sodium hydroxide in 1500 cc. of water sufficient dry chlorine to give an increase in weight of about 35 g. Table I shows the rate of change of this solution when kept in the dark at about 22°.

TABLE I.

Date.	Cc. of 0.1 N thiosulfate sol. equivalent to 10 cc. of hypochlorite sol.
Nov. 7	69.16
8	69.06
12	68.96
26	68.67
Dec. 3	68.34
8	68.18
25	67.57

Procedure.

In the experiments described the procedure was as follows. To the alkaline sulfide solution was added sufficient standard hypobromite or hypochlorite solution so that not over two-thirds of it was reduced by the sulfide. After standing for 3 to 5 minutes, 2 to 3 g. of potassium iodide was added and the solution diluted to 4 or 5 times the original volume. The solution was neutralized with conc. hydrochloric acid (the color of the iodine acts as an indicator) and 3 to 5 cc. in excess was added. The iodine was then titrated with standard thiosulfate solution.

Effect of Varying the Concentration of Sodium Hydroxide.

Unless a certain minimum concentration of sodium hydroxide is present the oxidation is incomplete. This is shown in Table II. To 50 cc. of sodium hydroxide solution of the concentration given were added 5 cc. of standard sodium sulfide solution and 10 cc. of standard hypobromite or hypochlorite solution; the excess was titrated as described above. The theoretical value as determined by an iodine titration is 9.86 cc.

TABLE II.

Conc. of NaOH solution, N.	Cc. of NaClO reduced.	Cc. of NaBrO reduced.
1	7.05	8.11
2	9.45	9.50
3	9.68	9.82
4	9.73	9.82
5	9.83	9.86
6	9.85	9.86

It was found, using 2 *N* sodium hydroxide solution, that, in the case of hypochlorite, heating to 45° for 5 minutes reduced the error a little, but standing for 30 minutes at room temperature had no effect. From this it is evident that, when using hypobromite, the concentration of sodium hydroxide during the reaction must be at least 2.5 *N* and when using hypochlorite, 4 *N*. Practically, therefore, only hypobromite would be used, but experiments were made with both reagents.

The first experiments were made with a solution of sodium sulfide prepared by absorbing about 2 g. of hydrogen sulfide in 16 g. of sodium hydroxide dissolved in a liter of water. Ten cc. of this solution was pipetted into a flask, 10 cc. of 10 *N* sodium hydroxide solution added, then 20 cc. of standard hypobromite solution. After standing for 5 minutes 100 cc. of water was added and 3 g. of potassium iodide. The solution was acidified with conc. hydrochloric acid, 5 cc. in excess being added. The iodine was titrated with thiosulfate. The results are shown in Table III.

TABLE III.

S found. G.	S present by iodine titration. G.
0.0193	0.0195
0.0195	
0.0194	
0.0195	
0.0196	

The same procedure was followed, using hypochlorite, except that twice as much sodium hydroxide was added. Another solution of sodium sulfide was used.

TABLE IV.

S found. G.	S by iodine titration. G.
0.0150	0.0150
0.0151	
0.0150	

This method was found to be rapid and accurate for the determination of sulfur in steel. The steel was dissolved in hydrochloric acid in the usual way, the hydrogen sulfide absorbed in sodium hydroxide and titrated as described above. The other gases, such as hydrocarbons and phosphine, either were not absorbed or did not reduce the oxidizing solution.

Procedure for Steels.

Weigh out 5 g. of the steel into a 250-cc. flask through which hydrogen can be passed and which is connected with a "10-bulb tube" for absorbing the hydrogen sulfide. Flush out the apparatus with hydrogen and run into the flask 100 cc. of hydrochloric acid (sp. gr. 1.1). After the reaction has moderated heat the solution just to boiling for 5 minutes after the steel

has dissolved, while passing hydrogen through the apparatus. The solution in the absorption tube should contain about 6 or 7 g. of sodium hydroxide in a volume of 50 to 60 cc. With as little water as possible wash the contents of the bulbs into a flask containing 10 cc. of 0.3 *N* hypobromite solution, let stand for 3 to 4 minutes, add 2 to 3 g. of potassium iodide in solution, dilute to 150 cc., add conc. hydrochloric acid till neutral, and then 5 cc. more. Titrate the iodine with 0.1 *N* thiosulfate solution. If hypochlorite is used more sodium hydroxide must be added.

Precautions.—If the solution is not sufficiently alkaline, oxidation will be incomplete.

The solution when neutralized must be kept cool enough to avoid volatilization of iodine.

Low results will be obtained unless the apparatus is flushed out with hydrogen.

Table V shows the results obtained by this procedure. 10 cc. of hypobromite solution was used in all determinations except those marked with an asterisk, in which hypochlorite was used.

TABLE V.

No. of Expt.	Description of steel.	Weight. G.	S found. %.	S present by certif.
1	0.1% C.	5.0018	0.080	0.080
2*	"	5.0000	0.080	
3*	"	5.0000	0.081	
4	1% C.	5.0001	0.026	0.028
5	"	5.0020	0.027	
6*	0.2% C.	5.0057	0.026	
7	30	5.0044	0.031	0.033
8	"	5.0000	0.032	
9	32	5.0040	0.025	0.024
10	33	5.0022	0.028	0.028
11*	"	5.0000	0.027	
12*	"	5.0000	0.028	

Procedure for Sulfides.

If the sulfide is soluble in hydrochloric acid, no preliminary treatment is required. Insoluble sulfides are first ignited with powdered iron (reduced by hydrogen) free from sulfur, in an atmosphere of hydrogen or carbon dioxide, the ferrous sulfide⁶ thus formed being soluble in acids. The sample is treated in the same way as described for steels, except that 0.6 *N* hypobromite and 0.2 *N* thiosulfate solutions are more convenient, and the volume of the former must be increased according to the amount of sulfide present. Table VI shows the results obtained with samples of zinc and cadmium sulfides and mixtures of the two. Hypochlorite was used in Expts. 3 and 4. In Expts. 11 and 12 the sulfide was first

⁶ Zehetmayer, *Z. angew. Chem.*, **23**, 1359 (1910).

ignited with powdered iron, and the slightly higher value obtained is due to reduction of a small amount of sulfate which was present.

TABLE VI.

Expt.	Description of sample.	Wt. of sample. G.	NaBrO added. Cc.	S found. %.	S found by iodine titration. %.
1	CdS	0.1328	20	21.17	21.00
2	CdS	0.1520	20	20.97	
3	CdS	0.1078	20	21.01	
4	CdS	0.1026	20	21.15	
5	ZnS	0.3714	60	32.02	32.00
6	ZnS	0.3024	50	32.05	
7	{ Mixture A }	0.0856	20	23.56	23.65
8	{ CdS+ZnS }	0.2692	50	23.67	
9	{ Mixture B }	0.1256	30	29.96	29.90
10	{ CdS+ZnS }	0.1830	30	29.92	
11	CdS	0.1456	40	21.43	21.45
12	CdS	0.1892	50	21.50	

The method may be applied to the direct oxidation of precipitated sulfides, but not natural sulfides. Zinc, mercuric and antimony sulfides were found to react readily with hypobromite and probably all others would do so. If free sulfur or polysulfide is also present, as is often the case, this too will be oxidized, although it has no effect in the iodine method.

It should be emphasized that all other reducing agents, ammonia for example, must be absent, since many substances not oxidized by iodine are oxidized by hypobromite.

Summary.

1. Sulfide is rapidly and completely oxidized to sulfate by excess of hypobromite in a solution 2.5 *N* with sodium hydroxide or by hypochlorite in a 4 *N* solution. The excess of oxidizing agent is determined iodometrically. Four times as much oxygen is required as in the usual titration with iodine.

2. The method gives accurate results in the determination of sulfur in steels and in sulfides, if care is taken to exclude all other reducing agents.

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