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## The Precipitation of Rhenium Sulfide from Ammoniacal Solution. A Separation of Rhenium and Molybdenum

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The action of hydrogen sulfide on alkaline rhenium solutions has received little systematic study, although the precipitation of rhenium sulfide from acid medium has been investigated in considerable detail.<sup>1</sup> According to Noddack, ammonium hydroxide–ammonium sulfide mixtures do not precipitate rhenium sulfide, but acidification of such a solution causes quantitative precipitation of the rhenium.<sup>2</sup> Briscoe, Robinson and Stoddart observed that hydrogen sulfide produced a pink color in ammoniacal perrhenate solutions, followed by partial separation of colloidal rhenium heptasulfide. The rhenium was not completely precipitated when the mixture was acidified. No quantitative data were given.<sup>1c</sup>

The present paper is a study of the precipitation of rhenium sulfide by hydrogen sulfide from alkaline, especially ammoniacal, solution. Since our experiments indicated that the precipitation from ammoniacal solution was practically quantitative, the obvious possibility of the separation of molybdenum and rhenium through this radical difference in properties was also investigated.

### Experimental

**Rhenium.**—Commercial "pure" rhenium (99.5%) containing sulfur and carbon was dissolved in nitric acid, and the filtered solution treated with hydrochloric acid on the water-bath to destroy the nitric acid. The rhenium was then precipitated several times with hydrogen sulfide from 5 *N* hydrochloric acid. The washed sulfide was dissolved in nitric acid–hydrochloric acid and the excess nitric acid removed by heating with concentrated hydrochloric acid. This solution was evaporated almost to dryness, the residue dissolved in water, and the solution made ammoniacal with 15 cc. of 28% ammonium hydroxide per 0.05 g. of metal. The rhenium was precipitated several times from this medium by hydrogen sulfide. The washed sulfide was dried and ignited in hydrogen (about 1000°) to constant weight. The purified rhenium gave no chemical test for molybdenum. This material was used for preparing the rhenium solutions used in the experiments. All the rhenium solutions were standardized by precipitating with hydrogen sulfide from hydrochloric acid solution and igniting the sulfide in hydrogen to constant weight.

**Molybdenum.**—A special grade of MoO<sub>3</sub> was sublimed once in a current of air. In preparing the molybdenum solutions a weighed quantity of the sublimate was dissolved in the minimum amount of ammonium hydroxide and diluted with water.

The precipitations with hydrogen sulfide were carried out under pressure. All precipitates were collected in 15-cc. König crucibles. The rhenium sulfide precipitated

(1) Geilmann and Weibke [(a) *Z. anorg. allgem. Chem.*, **195**, 289 (1931)] and Biltz and Weibke [(b) *ibid.*, **203**, 3 (1931)] found the precipitation from hydrochloric acid solution to be quantitative, but Briscoe, Robinson and Stoddart [(c) *J. Chem. Soc.*, 1431 (1931)] were able to precipitate the sulfide completely only by treating the hydrochloric acid solution of a perrhenate with sodium thiosulfate.

(2) Noddack, *Z. anorg. allgem. Chem.*, **181**, 1 (1931); **183**, 353 (1929); *Z. Elektrochem.*, **34**, 627 (1928).

from acid solution was washed with dilute hydrochloric acid saturated with hydrogen sulfide. The precipitate obtained from ammoniacal solution was washed with dilute ammonium hydrogen sulfide-ammonium chloride solution (see below). After washing, the drying and reduction were carried out in an apparatus made from a transparent quartz weighing bottle with a gas-tight lid. An entrance tube for hydrogen was sealed into the upper part of the vessel and the outlet was placed on the opposite side near the bottom. To facilitate efficient heating of the crucible it was convenient to have the quartz vessel only slightly larger than the crucible. For preliminary heating a Meeker burner was used. The final ignition was made with a gas-air blast.

**Precipitation of Rhenium from Hydrochloric Acid Solutions.**—For the experiments summarized in Table I solutions containing 0.0446 g. of rhenium in a total volume of 50 cc. were treated with hydrogen sulfide at room temperature.

TABLE I

Expt.	Medium	Approx. time for appearance of ppt.	Re found, g.	Remarks
1	9 <i>N</i> HCl	Immed.	0.0446	Fine ppt., settled v. slowly
2	4.4 <i>N</i> HCl	1 min.	.0445	Cryst. ppt. settled v. rapidly
3	2.3 <i>N</i> HCl	3 min.	.0445	Violet to brown color in soln. sev. hrs.
4	1.1 <i>N</i> HCl	30 min.	.0446	Faint violet then brown in 15 min.
5	0.001 <i>N</i> HCl	24 hrs.	...	Pptn. complete after several days
6	0.001 <i>N</i> NH <sub>4</sub> OH	72 hrs.	...	Faint violet color, large amt. of ppt.
7	"Neutral"	....	...	Slight pptn. after several days

When the concentration of the ammonium hydroxide was increased the precipitation of the rhenium from this medium became approximately quantitative, although the precipitation was very slow. The typical results in Table II were obtained by treating rhenium solutions containing 15 cc. of 28% ammonium hydroxide in a total volume of 50 cc. with hydrogen sulfide for forty-eight to seventy-two hours. It was necessary for the ammonium hydroxide to be completely saturated with the hydrogen sulfide before appreciable precipitation began. This behavior probably accounts for the statements of other workers on the action of ammonium sulfide on rhenium solutions.

TABLE II

Expt.	Medium	Re present, g.	Re found, g.
1	NH <sub>4</sub> OH	0.0446	0.0445
2	NH <sub>4</sub> OH	.0504	.0498
3	NH <sub>4</sub> OH	.1008	.1007
4	NH <sub>4</sub> OH	.1512	.1508

Solutions containing the same amounts of rhenium in the presence of 4.5 *N* hydrochloric acid were treated with hydrogen sulfide. In each case the precipitation was precisely quantitative. The violet coloration which was observed when the sulfide was precipitated from ammoniacal solution gradually disappeared, although a very characteristic yellowish-bronze color remained in the filtrate, which usually contained a few tenths of a milligram of rhenium. When the sulfide precipitated from ammoniacal solution was washed with water, hydrogen sulfide water, or dilute ammonium sulfide, a violet colored filtrate, due possibly to a colloidal dispersion of the sulfide, or to the slight solubility of a thio compound, was obtained. On acidification of 100 cc. of this liquid with hydrochloric acid and treatment with hydrogen sulfide, a black precipitate appeared and quickly coagulated. After ignition the precipitate weighed 1.2 mg. Washing with ammonium hydrogen sulfide-ammonium chloride solution prevented the appearance of the violet color in the filtrate. The sulfide from acid solution yielded a colorless filtrate regardless of the washing medium.

In rhenium solutions alkaline with sodium hydroxide or potassium hydroxide, hydrogen sulfide produced a deep brown color and some precipitate after several hours. The precipitate was practically unfilterable.

**Separation of Molybdenum and Rhenium.**—Ammoniacal mixtures of solutions of rhenium and molybdenum in various proportions were treated with hydrogen sulfide at room temperature for forty-eight to seventy-two hours. After the rhenium sulfide had been filtered off and washed, the filtrate containing the molybdenum was acidified with hydrochloric acid and the precipitate washed with dilute hydrochloric acid saturated with hydrogen sulfide, then with hydrogen sulfide water. The precipitate was then dried and ignited in hydrogen at 450–550° and weighed as  $\text{MoS}_2$ .<sup>3</sup>

TABLE III

Expt.	Total vol., cc.	$\text{NH}_4\text{OH}$ , cc.	Re present, g.	Re found, g.		Mo, g.	
				1st pptn.	2d pptn.	Present	Found
1	50	10	0.0045	0.0046	...	0.0500	0.0502
2	130	20	.0045	.0113	0.0046	0.5000	...
3	150	30	.0088	.0130	.0082	1.0000	...
4	50	10	.0446	.0441	...	0.0052	.0054
5	50	10	.0446	.0446	...	.0500	.0502
6	50	10	.0504	.0507	...	.0500	...
7	100	15	.0504	.0509	.0507	.0500	...
8	100	15	.0504	.0517	.0509	.1000	...
9	50	15	.0504	.0513	.0505	.1250	.1246
10	100	15	.0504	.0523	.0511	.1500	...
11	100	15	.0504	.0525	.0509	.1500	.1495
12	100	15	.0504	.0522	.0507	.1500	.1496
13	50	15	.1113	.1113	...	.0010	.0012
14	50	15	.1262	.1268	.1261	.0500	.0499

As the results in Table III show, when the proportion of molybdenum was large a single precipitation with hydrogen sulfide failed to yield a precipitate of rhenium sulfide free of molybdenum. In these cases the precipitates, or the metals obtained by the reduction thereof, were redissolved and the rhenium again thrown down from ammoniacal solution. The second or third precipitation always gave the expected value for the rhenium. It was very difficult to wash the precipitate of rhenium sulfide free of molybdenum after the mixture had been transferred to the filter. This difficulty was minimized, however, when the precipitate of rhenium sulfide was either relatively very large or very small. It was found necessary to work with a volume of at least 50 cc. for each 0.05 g. of molybdenum present, otherwise ammonium thiomolybdate crystallized out while the rhenium sulfide was precipitating. In some instances this would have given an embarrassingly large volume; in such cases the mixture was warmed until the thio salt redissolved.

### Summary

The precipitation of rhenium sulfide from ammoniacal solution by hydrogen sulfide is approximately quantitative.

The separation of rhenium and molybdenum by treatment of the ammoniacal mixture with hydrogen sulfide has been studied.

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