CXCV.—*The Sulphides and Selenides of Rhenium.*

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The selenides of rhenium have not yet been described, and considerable uncertainty exists regarding sulphides higher than the disulphide. By treating the higher oxide (Re_2O_7) with hydrogen sulphide, W. and J. Noddack obtained material considered first to be ReS_2 (*Z. anorg. Chem.*, 1929, **181**, 1) but subsequently described as ReS_3 (*Ber.*, 1930, **63**, 16), which at 800° in a stream of carbon dioxide yielded ReS_2. The reduction of this disulphide by hydrogen at 1000° (Noddack, *loc. cit.*) gave the earliest ratio used in calculating the atomic weight of the metal. Hönigschmid and Sachtleben (*Z. anorg. Chem.*, 1930, **191**, 309) did not describe the primary product which they converted into disulphide by heating in nitrogen. Geilmann and Weibke (*ibid.*, 1931, **195**, 289) separated rhenium with hydrogen sulphide under special conditions and estimated the metal subsequently as nitron per-rhenate (Geilmann and Voigt, *ibid.*, 1930, **193**, 311) after oxidising the precipitate. Beyond mention of a difficulty in precipitation and a tendency to colloidal suspension, the nature of this sulphide was not discussed.

The present communication describes further work on the sulphides, whereby it appears that the *heptasulphide* (Re_2S_7) is precipitated by hydrogen sulphide, but never in our experience, and contrary to that of Geilmann and Weibke (*loc. cit.*), in quantitative yield. The same sulphide is, however, quantitatively precipitated by sodium thiosulphate. There is evidence that the alkali thioper-rhenate corresponding to this sulphide exists in solution, although it has not been separated therefrom. The disulphide is the only compound resulting from the thermal dissociation of the heptasulphide, and is also produced if the metal be heated in sulphur vapour. The existence of these sulphides only would be anticipated from the relationship of rhenium to tungsten and osmium, thus :

Group VI.	Group VII.	Group VIII.
WS_2	ReS_2	OsS_2
WS_3	Re_2S_7	OsS_4

Experimental.

Rhenium Heptasulphide.—Preparation. (i) When hydrogen sulphide is passed into ammoniacal aqueous potassium per-rhenate, the solution turns pink and slowly deposits this sulphide from a semicolloidal suspension. On subsequent acidification with hydrochloric acid, the sulphide is converted into a form fairly easy to separate by filtration, but precipitation is never quantitative. About 0·25 g. of potassium per-rhenate, dissolved in 15 c.c. of water containing 3 c.c. of ammonia (*d* 0·880), was saturated with hydrogen sulphide and the solution was just acidified with hydrochloric acid and filtered through a Gooch crucible. The precipitate obtained was well washed and dried in a vacuum desiccator over phosphoric oxide.

For analysis, a known weight of sulphide in a boat was reduced by hydrogen. An electrically heated silica tube furnace attaining a temperature of approximately 900° was used, and the hydrogen sulphide led therefrom into standard iodine solution. The back titre of the residual iodine with sodium thiosulphate, together with the weight of the metallic residue, gave the data in Table I, which indicate that the sulphide initially formed is neither the ReS_2 nor the ReS_3 mentioned above, but the *heptasulphide.*

TABLE I.

Sulphide used, g.	Rhenium after reduction.	Sulphur found, g.	Re, %.	S, %.	Total.
0·1647	0·1026	0·0619	62·30	37·58	99·88
0·1258	0·0784	0·0472	62·32	37·52	99·84
0·1197	0·0742	0·0451	61·98	37·68	99·66
0·1347	0·0839	0·0502	62·29	37·27	99·56
		Mean	62·22	37·51	99·74
		Re_2S_7 requires	62·40	37·60	—

(ii) There is no visible reaction when a solution of potassium per-rhenate is warmed with sodium thiosulphate, but if the mixture be acidified, not only is sulphur deposited, but on boiling, rhenium separates in a more or less colloidal form unless the thiosulphate is in excess, whereupon quantitative precipitation as heptasulphide results. About 0·25 g. of potassium per-rhenate was dissolved in water containing 10 c.c. of 5*N*-hydrochloric acid. To this solution heated to boiling, hot sodium thiosulphate was added until the heavy flocculent rhenium sulphide separated. After a further 2 mins.' boiling, the colourless supernatant liquor was obviously free from colloidal sulphide, and the precipitate, which settled readily, could then be filtered off together with the precipitated sulphur upon a tared Gooch crucible. After the precipitate had been well washed with water and dried over phosphoric oxide in a vacuum, the sulphur was completely removed from it by extraction with boiling toluene. This required about 12—14 hours and gave a powder containing much adsorbed solvent held so tenaciously that it was only completely removed by heating at 275° in a vacuum for 4 hours. The final product was weighed in the Gooch crucible in which the operations had been conducted and was analysed by reduction in hydrogen (*vide supra*) and proved to be heptasulphide. From Table II, which gives the data for four experiments, it is clear that the process affords a method for the estimation of rhenium, which under suitable conditions and with the quantity here used has an error not exceeding about ± 0·02%.

TABLE II.

Potassium per-rhenate, g.	Sulphide, g.	Calc. for Re_2S_7, g.	Sulphide. Re, %.	S, %.	Total.
0·3083	0·3176	0·3181	62·27	37·51	99·78
0·3424	0·3519	0·3533	62·35	37·49	99·84
0·2778	0·2860	0·2865	62·42	37·57	99·99
0·4130	0·4251	0·4260	62·37	37·62	99·99
		Mean	62·37	37·55	99·90

Properties. The heptasulphide is a black amorphous powder which dissociates below its melting point. It is an active adsorbent, taking up toluene and other organic solvents in considerable quantities and with considerable swelling. The adsorption is reversible, but as the process is repeated the material becomes less active and finally ceases to adsorb. This change is probably attributable to surface poisoning by oxygen, of the type recently reported by Allmand and Chaplin (*Proc. Roy. Soc.*, 1930, **129**, 235) for charcoal. When brought into hydrogen at the atmospheric temperature, dried material frequently underwent spontaneous reduction, without apparent rise in temperature, indefinite quantities of sulphur being removed before the reaction ceased. These phenomena were not further investigated and are quoted simply as further evidence of surface activity.

The red solutions formed by treating alkaline per-rhenate with hydrogen sulphide probably contain thioper-rhenate ($KReO_4 + 4H_2S \longrightarrow KReS_4 + 4H_2O$), since this may be supposed readily to yield Re_2S_7 on acidification ($2KReS_4 + 2HCl \longrightarrow 2KCl + H_2S + Re_2S_7$), but attempts to isolate such a solid failed. Concentrated solutions yielded only impure potassium per-rhenate, whilst those more dilute gave only rhenium sulphide when concentrated by freezing or slow evaporation, or on addition of alcohol.

Rhenium Disulphide.—The disulphide is prepared as a black powder by heating rhenium to redness with excess of sulphur in a Rose crucible under hydrogen sulphide (Table III). It is also obtained by heating the heptasulphide in a vacuum to red heat (compare Noddack, *loc. cit.*; Hönigschmid and Sachtleben, *loc. cit.*).

No evidence was obtained of any sulphide lying between Re_2S_7 and ReS_2 when the heptasulphide was heated to 250° in an atmosphere of nitrogen, the course of the thermal dissociation

TABLE III.

Metallic Re, g.	Product, g.	Calc. for ReS_2, g.	Product. Re, %.	S, %.	Total.
0·1915	0·2586	0·2573	74·51	25·42	99·93
0·1026	0·1383	0·1379	74·39	25·67	100·06
0·1759	0·2371	0·2364	74·46	25·52	99·98
0·1876	0·2522	0·2522	74·49	25·65	100·05
		Mean	74·46	25·54	100·00
		Calc. for ReS_2	74·40	25·60	—

being followed by means of a spring balance sensitive to ± 0·0004 g. and special precautions being taken to minimise the effects of convection currents. Under these conditions the loss of weight was strictly proportional to time until the composition of the disulphide was approached; the rate of loss then became negligible.

Rhenium Heptaselenide.—This was obtained in the same manner as the heptasulphide by substituting hydrogen selenide for the sulphide. Hydrogen selenide was passed over-night into a solution of 0·25 g. of potassium per-rhenate in 30 c.c. of water containing 0·25 g. of potassium hydroxide to dissolve any liberated selenium. The *heptaselenide*, which was precipitated without the evident formation of intermediate compounds, was collected on a Gooch crucible, well washed with water, and dried over phosphoric oxide in a vacuum. Alcohol was avoided in the washing, since the selenide, like the sulphide, adsorbs it in quantity.

Analysis was effected by reduction in the Rose crucible with hydrogen, the crucible being unglazed, since glaze is attacked. The results (Table IV) establish the formation of the heptaselenide.

TABLE IV.

Selenide, g.	Metal, g.	Re, %.	Calc. for Re_2Se_7, g.
0·1246	0·0503	40·37	0·0501
0·1759	0·0702	39·91	0·0707
0·1162	0·0471	40·52	0·0467
	Mean	40·27	
	Re_2Se_7 requires	40·19	

This compound is similar to the corresponding sulphide, being black and adsorbing organic solvents in quantity with swelling. It is also reduced by hydrogen at ordinary temperatures but does not show this phenomenon so markedly as the sulphide.

Rhenium Diselenide.—If the higher selenide be heated in a vacuum at 325—330° for 9 hours, selenium is lost and the *diselenide* remains (Table V). The compound appears to be very stable in air, and not attacked except by strong oxidising acids.

TABLE V.

Rhenium heptaselenide, g.	Residue, g.	Calc. for $ReSe_2$, g.
0·1672	0·1257	0·1244
0·1527	0·1147	0·1136
0·1276	0·0942	0·0949

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