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## A CONTRIBUTION TO THE CHEMISTRY OF RHENIUM

By G. E. F. Lundell and H. B. Knowles

## ABSTRACT

A study of the behavior of rhenium when dilute solutions of potassium perhenate are acidified with sulphuric acid, cooled, and passed through the Jones reductor, indicates that rhenium forms a compound in which it has a valency of minus one, and that the rhenium in this compound is oxidized to a valency of plus one if the diluted sulphuric acid solution is protected from oxygen and warmed to approximately 50° C.

In the course of the investigation, it was also found (1) that rhenium can be electrodeposited from diluted (5+95) sulphuric acid solution; (2) that deposits are slightly contaminated; and (3) that the deposited metal can be oxidized directly to perrhenic acid by exposure to moist air, oxygen, or by making the deposit the anode in a water solution.

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## I. INTRODUCTION

In the periodic classification of the elements, rhenium is grouped with manganese and eka-manganese<sup>1</sup> in arrangements based on the atomic numbers of the elements, the number of shells in the atoms, and the type and number of electrons in the incompleated shells. In the ordinary periodic arrangements these elements are arranged in subgroup A of the seventh group, while fluorine, chlorine, bromine, iodine, and eka-iodine are placed in subgroup B.

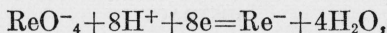
The valencies of manganese range from two to seven in its ordinary compounds. The valencies of the members of the halogen subgroup range from minus one, which is common to all, to plus seven, which is exhibited by chlorine and iodine. If rhenium follows manganese in its valencies, one might expect the lowest valency to be two and the highest valency to be seven. If rhenium follows the halogen subgroup, the lowest valency should be minus one and the highest plus seven.

<sup>1</sup> Element of atomic number 43, named masurium by W. Noddack, I. Tacke, and O. Berg, (*Die Naturwissenschaften* 13, 567, 1925), who claim to have discovered evidence of its existence in certain platinum and columbium ores.

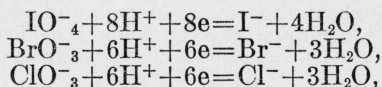
There is no question that rhenium exhibits a valency of seven in its oxidized compounds. On the other hand, its lower valencies have not been fixed, and, so far as we have been able to ascertain, no evidence as to a valency lower than plus one has been noted in any of its compounds.

The chief purpose of this article is to point out that rhenium apparently follows the halogens in their lower as well as in their higher valencies, and that a compound having a valency of minus one is formed when a *cold, dilute* solution of potassium perrhenate in diluted sulphuric acid (5+95)<sup>2</sup> is passed through a column of amalgamated zinc (Jones reductor).

Possibly, the reaction takes place as expressed by the equation,



which is strictly analogous to the reactions,



which take place when solutions of periodates, iodates, bromates, chlorates (and even perchlorates to a slight extent) are similarly treated.

If the reaction proceeds as indicated, the product should, of course, be called hydrorhenic acid, corresponding to the halogen acids. As will be seen, we have not been able to isolate the compound, but we believe that the evidence shows quite conclusively that rhenium forms a compound in which it has a valency of minus one.

The sections that follow deal with the reactions that indicate the existence of this compound. In addition, there are included certain observations on the properties of rhenium and its compounds that were made in the course of the work.

## II. EXPERIMENTAL

### 1. REAGENTS, REDUCTOR, AND TECHNIQUE

The source of the rhenium used in this investigation was a potassium perrhenate which had been examined by both chemical and spectrochemical methods. In the latter, only a trace of magnesium and faint traces of silicon, calcium, and iron were indicated as impurities, and their total amount was estimated to be of no significance in the present investigation. In the chemical tests, the percentage of  $\text{Re}_2\text{O}_7$  in the salt was determined electrolytically by deposition from diluted sulphuric acid solution (5+95), followed by corrections for undeposited rhenium and for impurities in the deposit as described in section 6. The percentage of  $\text{K}_2\text{O}$  was determined by dissolving the salt in diluted sulphuric acid, filtering in turn after precipitations with hydrogen sulphide and ammonium hydroxide, evaporating, treating with sulphuric and hydrofluoric acids, igniting, and finally treating with water and igniting until constant weight was obtained. The percentage of  $\text{Re}_2\text{O}_7$ , 83.66, and of  $\text{K}_2\text{O}$ , 16.43, found, agreed with the calculated values 83.73 and 16.27 within the experimental errors of the

<sup>2</sup> Prepared by diluting 5 volumes of sulphuric acid (sp gr 1.84) with 95 volumes of water. When no dilution is specified the use of the concentrated reagent is intended.

methods of determination. No silicon, calcium, magnesium, or iron was found in 0.07-g samples.

The solution of the perrhenate used in the tests to be described was prepared by dissolving 16.6774 g of the salt and diluting to exactly 4 liters with diluted sulphuric acid (2.5+97.5). Its calculated rhenium content was 0.002684 g per ml as compared with 0.002681 found by actual test.

Reduction with zinc and sulphuric acid was done in every case in a Jones reductor 18 inches in length, 1 inch in diameter, and filled with 20-mesh granulated zinc which had been amalgamated with approximately 5 percent of mercury.

The diluted sulphuric acid (5+95), the water, and the sulphuric acid solution of the perrhenate used in the reduction were all thoroughly boiled to expel oxygen, allowed to cool under oxygen-free carbon dioxide, and chilled to approximately 5° C before passing them through the reductor.

Immediately before use, the reductor was washed with warm diluted sulphuric acid followed by cold water, and then freed from entrapped air by placing water in the receiver, tightly stoppering the top of the completely filled reductor, and then alternately applying and releasing suction until no more gas was set free. The receiver was then emptied and again attached. In most reductions all air was first washed out of the receiver, and the solution afterward caught in it was protected from air by the use of carbon dioxide, drawn from a cylinder of the liquefied gas and freed from any small oxygen content by passage over rolls of copper gauze heated at 500° C.

The procedure generally followed in reductions was first to draw through 50 ml of the cold diluted acid, next 500 ml of the cold diluted acid solution containing from 0.0134 to 0.0268 g of the perrhenate, then approximately 50 ml of the cold acid to wash out the rhenium, and finally approximately 100 ml of the cold water to wash out the acid. In some experiments the reduced rhenium solution was caught in the carbon-dioxide filled receiver, in others it was caught under an excess of an oxidant protected by carbon dioxide.

## 2. OXIDATION OF THE REDUCED COMPOUND

The reduced rhenium compound is a very powerful reducing agent, reacting with salts of copper and silver to yield the elements, with compounds such as titanous sulphate to form compounds of lower valency, and even with sulphuric acid if the concentration of the compound is appreciable or the solution is warm. The reaction of the reduced compound with sulphuric acid determines the conditions that must obtain in successful reductions in the Jones reductor, and necessitates the use of solutions that are rather dilute (<0.03 mg of Re per milliliter) and ice-cold. Under such conditions the reduced compound showed no detectable change in valency in 1½ hours when protected from the air by bubbling a brisk stream of carbon dioxide through the solution. The reduced compound can be quantitatively oxidized to the heptavalent state by passing a stream of air or oxygen through the solution.

In table 1 are shown the results obtained in experiments in which the reduced solution was caught (1) in a CO<sub>2</sub>-filled receiver; (2) in an excess of acidified ferric sulphate solution; (3) in an excess of a solu-

tion of molybdic acid; and (4) in an excess of a standard solution of potassium permanganate. In (1), (2), and (3) the final solution was titrated immediately with a standard solution of potassium permanganate. In (4) the excess of permanganate was determined by adding 1 to 3 ml excess of an equivalent solution of ferrous sulphate and then titrating with permanganate. In all titrations care was taken to maintain an oxygen-free atmosphere.

The rhenium-oxygen ratios are based on the amounts of rhenium that were taken and the amounts of permanganate that were consumed. The average calculated valency,  $-1.04$ , is considered to be in substantial agreement with  $-1$  in view of the difficulties of the determination.

TABLE 1.—*Valency of rhenium after reduction in a Jones reductor*

Re taken	0.1 N $\text{KMnO}_4$ required	Atomic ratio Re/O	Calculated valence change of Re	Calculated valence of Re
1. SOLUTION CAUGHT UNDER $\text{CO}_2$				
g	ml			
0.002683	1.18	1:4.10	8.2	-1.2
.002683	1.21	1:4.20	8.4	-1.4
.005366	2.27	1:3.94	7.9	-0.9
.005366	2.27	1:3.94	7.9	-0.9
.008049	3.48	1:4.03	8.1	-1.1
.010732	4.69	1:4.07	8.1	-1.1
.013415	5.86	1:4.07	8.1	-1.1
.02683	11.45	1:3.98	8.0	-1.0
2. SOLUTION CAUGHT UNDER EXCESS OF $\text{Fe}_2(\text{SO}_4)_3$				
0.002683	1.18	1:4.10	8.2	-1.2
.005366	2.26	1:3.92	7.8	-0.8
.008049	3.52	1:4.07	8.1	-1.1
.010732	4.68	1:4.06	8.1	-1.1
.0128	5.40	1:3.93	7.9	-0.9
.0129	5.55	1:4.01	8.0	-1.0
.013415	5.94	1:4.12	8.2	-1.2
.013415	5.75	1:3.99	8.0	-1.0
.013415	5.95	1:4.13	8.3	-1.3
3. SOLUTION CAUGHT UNDER EXCESS OF $\text{H}_2\text{MoO}_4$				
0.013415	5.72	1:3.97	7.9	-0.9
4. SOLUTION CAUGHT UNDER EXCESS OF $\text{KMnO}_4$				
0.0130	5.52	1:3.96	7.9	-0.9
.013415	5.70	1:3.96	7.9	-0.9
.013415	5.72	1:3.97	7.9	-0.9
.02683	11.51	1:4.00	8.0	-1.0
.040245 <sup>a</sup>	16.90	1:3.91	7.8	-0.8
.067075 <sup>a</sup>	27.66	1:3.84	7.7	-0.7
Average calculated valency				-1.04

<sup>a</sup> Not included in average because numerous experiments demonstrated that these concentrations are too great for complete reduction.

It might be argued that some of the permanganate was used up in reactions other than in the oxidation of rhenium. This seems unlikely, because results agreed within experimental error regardless of whether the reduced compound was titrated directly with dichromate, ceric sulphate, or permanganate, caught in an excess of permanganate, or titrated with permanganate after it had been caught under solu-

tions of ammonium vanadate, ammonium molybdate, potassium dichromate, ceric sulphate, titanic sulphate, or even potassium perchlorate—all of which are reduced to lower valencies by the rhenium compound. It seems hardly possible that substances of such differing oxidation-reduction potentials would enter into reactions (other than with rhenium) that all caused essentially the same consumption of oxidant.

It should be noted that a dilute solution of rhenium remains *colorless* during its passage through the Jones reductor, and that the cold solution of the reduced compound takes on a *yellow to amber yellow color* in the early stages of a titration in which permanganate is added very slowly. It is significant that the same *yellow color* slowly develops if the reduced solution is protected from oxygen and is allowed to become warm (approximately 50° C) as a current of oxygen-free carbon dioxide is passed through it. In either case, the solution again becomes colorless long before oxidation of the rhenium is complete.

As shown in table 2, the rhenium-oxygen ratio is 1:3, if the dilute sulphuric acid solution of the reduced rhenium compound is protected from oxygen, warmed moderately, and allowed to stand for 30 to 60 minutes. The rhenium-oxygen ratio indicates that the reduced compound has been oxidized to a valency of plus one in a solution containing no free oxygen and no compounds other than dilute sulphuric acid, zinc sulphate, and (at first) molecular hydrogen. It was suspected that under the changed conditions (digestion in warm solution) the reduced compound might have reduced sulphuric acid, possibly to form hypophenous acid



corresponding to the "hypo" acids of the halogens. No attempt was made to identify sulphur dioxide, but it was found that a volatile compound of sulphur is formed, because definite tests for the  $\text{SO}_4$  ion were obtained when the stream of carbon dioxide was passed through an alkaline solution of hydrogen peroxide, which was afterwards acidified, boiled, and treated with barium chloride. The reduction of sulphuric acid is not surprising, since this also takes place with hydriodic acid but at somewhat higher concentrations and temperature.

TABLE 2.—Valency of rhenium after reduction in a Jones reductor, followed by digestion in warm dilute sulphuric acid solution protected from oxygen

Re taken	0.1 N KMnO <sub>4</sub> required	Atomic ratio Re/O	Calculated valence change of Re	Calculated valence of Re	Period of digestion	Final temper- ature
g	ml				min	°C
0.013415	4.31	1:2.99	5.98	+1.0	30	45
.013415	4.32	1:3.00	6.00	1.0	45	45
.013415	4.29	1:2.98	5.96	1.0	45	45
.013415	4.30	1:2.99	5.98	1.0	45	45
.02683	8.60	1:2.99	5.98	1.0	45	45
.013415 <sup>a</sup>	4.30	1:2.99	5.98	1.0	60	45
.013415 <sup>a</sup>	4.27	1:2.97	5.94	1.1	60	45
.013415 <sup>b</sup>	4.27	1:2.97	5.94	1.1	60	45
.013415 <sup>b</sup>	4.30	1:2.99	5.98	1.0	60	45
Average calculated valency.....				1.02	-----	-----

<sup>a</sup> Titrated with  $\text{KReO}_4$  at the start, and finished with  $\text{KMnO}_4$ .

<sup>b</sup>  $\text{H}_2$  used instead of  $\text{CO}_2$ .

The compound corresponding to the 1:3 ratio is not stable enough to withstand prolonged digestion in the warm sulphuric acid solution. It was noted that no detectable decomposition occurred when the compound was heated at 72° C and titrated in the course of 30 minutes. In other tests it was noted that there was a slight falling off in permanganate consumption in warm solutions that had been allowed to stand for some time, for example, 4.14 and 4.04 ml of 0.1 *N* at the end of 2 and 3 hours, as against 4.34 ml and 4.31 ml at the

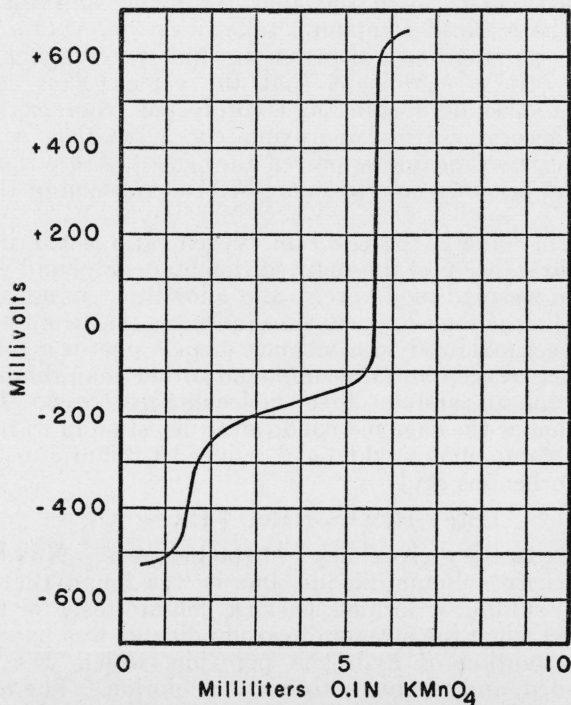


FIGURE 1.—*Typical curve obtained in potentiometric titrations of the reduced rhenium compound.*

end of 30 minutes and 1 hour, respectively. Incidentally, no evidence of the formation of a volatile compound of rhenium was discovered in this or any other stage of the work.

### 3. POTENTIOMETRIC TITRATION

In a number of experiments, attempts were made to titrate the solution of the reduced rhenium compound potentiometrically with 0.1 *N* KMnO<sub>4</sub> in the hope that potential changes might yield additional information on the course of the oxidation. In this work a 0.1 *N* calomel half-cell, a platinum indicator electrode, a Leeds & Northrup student type potentiometer, and the usual accessories were used. In a few tests a gold electrode was substituted for the platinum electrode, with no improvement in the results. When titrated immediately, solutions containing 0.0134 g of the reduced rhenium compound showed a marked increase in potential after the addition of from 1.40 to 1.50 ml of 0.1 *N* KMnO<sub>4</sub>. During this titration the

solution gradually acquired the same yellowish color that had already been noted, and this color likewise disappeared on further addition of permanganate. A typical curve is shown in figure 1. It is interesting to note that the amount of rhenium taken should require 1.44 ml of 0.1 *N*  $\text{KMnO}_4$  for oxidation from a minus one to a plus one valency. In a few cases a slight tendency for a break in potential at approximately 0.7 ml of 0.1 *N*  $\text{KMnO}_4$  was noted, a point which would coincide with oxidation to a zero valency. No other sharp break occurred until the amount of permanganate required for complete oxidation had been added.

#### 4. ELECTRODEPOSITION OF RHENIUM

In tests of methods which could be used to determine how much rhenium was present in the rhenium salt and in the portions of rhenium solution that were taken for test, it was found that rhenium could be deposited quite satisfactorily from solutions containing sulphuric acid, but not from solutions containing nitric acid.

The most satisfactory results were obtained by the use of (1) a stationary cathode of sand-blasted platinum gauze and a spiral platinum anode inclosed in an unglazed mullite thimble; (2) diluted sulphuric acid (5+95) as electrolyte; and (3) electrolysis overnight with a current density of 0.25 amp/dm<sup>2</sup> and 2.34 volts between electrodes. The deposits were quickly washed with water, alcohol, and ether, dried for 10 seconds at 105° C, cooled in a desiccator containing concentrated sulphuric acid, and weighed after 15 minutes.

TABLE 3.—*Electrodeposition of rhenium*

Weight of deposit	Weight of Re recovered in electrolyte	Total weight of Re indicated	Weight of Re calculated on assumption that $\text{KReO}_4$ was 100.0% pure	Weight of impurity indicated in deposit
g 0.0135	g 0.0001	g 0.0136	g 0.0134	g 0.0002
.0133	.0005	.0138	.0134	.0004
.0133	.0004	.0137	.0134	.0003
.0136	.0001	.0136	.0134	•.0002
.0136	.0001	.0136	.0134	•.0002
.0136	.0001	.0136	.0134	•.0002
.0268	.0011	.0279	.0268	.0011
.0269	.0011	.0280	.0268	.0012
.0275	.0007	.0282	.0268	.0014

\* Determinations of the rhenium contents of these deposits indicated the presence of 0.00027, 0.00027, and 0.00019 g of impurities (see table 5).

Results obtained under these conditions are shown in table 3. In all of the tests the electrolytes were tested for rhenium by colorimetric comparison with standard solutions after adding potassium thiocyanate and stannous chloride, and extracting with ether.<sup>3</sup> The amounts recovered ranged from less than 0.1 mg to 1.1 mg. It will be noted that the total amount of rhenium found exceeded that expected in every case. The high results are believed to have been caused by slight oxidation, since most of the deposits appeared to be slightly stained either over the whole plate, or at some point such as the junction of the liquid and stem.

<sup>3</sup> L. C. Hurd and B. J. Babler. *Ind. Eng. Chem. Anal. Ed.* 8, 112 (1936).

In connection with the specification of a sulphuric acid solution in the electrolytic method, it should be remembered that more or less rhenium is lost by volatilization if sulphuric acid solutions are fumed strongly. No losses occur when hydrochloric or nitric acid solutions are evaporated to syrupy consistency under conditions that do not permit the formation of dry crusts. If evaporation with sulphuric acid is effected at as low a temperature as possible and stopped when fumes of the acid first appear, no loss of rhenium is believed to occur.

#### 5. OXIDATION OF METALLIC RHENIUM

One of the most remarkable properties of rhenium that was observed in the course of the tests is the ease with which the metal can be oxidized to perrhenic acid. The phenomenon was first noticed with rhenium deposited on platinum gauze electrodes which had been left in a large covered glass vessel for 21 days. When the electrodes were removed, it was found that the rhenium deposits had almost entirely disappeared, and that the electrodes were covered with a liquid of marked acid character. Subsequent tests showed that no appreciable attack takes place if plated electrodes are stored in a *dry* atmosphere, but that attack is so rapid in moist oxygen that deposits weighing from 0.0134 to 0.0268 g were completely oxidized to perrhenic acid in 24 hours or less. In tests in which electrodes were weighed before and after oxidation of the deposits, it was found that the increase in weight was always in excess of that required by conversion of Re to  $\text{HReO}_4$ . Although no attempt was made to ascertain the nature of the contaminant, the excess in weight was undoubtedly caused by water of hydration.

In another series of tests a number of deposits were exposed in an atmosphere of moist oxygen, and the resulting oxidized deposits were combined, diluted to 500 ml with carbon-dioxide free water, and thoroughly mixed. One 50-ml portion was acidified with sulphuric acid and found to consume no permanganate, thus indicating complete oxidation of the rhenium. Another 50-ml portion, when carefully neutralized with potassium hydroxide, evaporated to dryness, and examined under the microscope, was found to yield crystals of exactly the same type as the potassium perrhenate used in the investigation. In table 4 are shown the results obtained in titrations of the remaining four 100-ml portions under the conditions set forth.

TABLE 4.—*Titration of perrhenic acid*

Indicator	Treatment of solution	Weight of 0.05 N NaOH solution	
		Required	Corrected to phenolphthalein end point
		g	g
Phenolphthalein.....	Not boiled.....	1.83	-----
Do.....	Boiled for 10 min and cooled.....	1.82	-----
Methyl red.....	Not boiled.....	1.78	1.83
Do.....	Boiled for 10 min and cooled.....	1.75	1.80



The results of the series of tests on the oxidized deposits indicate that (1) rhenium metal can be completely oxidized to perrhenic acid by exposing it to moist oxygen; (2) perrhenic acid is a reasonably strong acid; and (3) a dilute solution of perrhenic acid undergoes no change upon boiling for a short period.

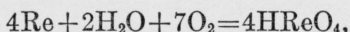
#### 6. STANDARDIZATION OF RHENIUM SOLUTIONS

The conditions that must be considered in establishing the rhenium content of a solution of a rhenium compound by electrodeposition are indicated in sections 4 and 5. These operations involve (1) electrodeposition of the rhenium; (2) determination of the amount of rhenium in the deposit by oxidizing the metal to perrhenic acid and then titrating with a standard alkaline solution; and (3) correction for any rhenium left in the electrolyte, as determined by colorimetric comparison with standard rhenium solutions.

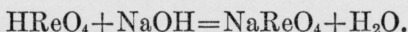
TABLE 5.—Standardization of a rhenium solution (5-ml portions of a solution containing 0.004169 (g) of  $\text{KReO}_4$  per milliliter)

Weight of deposit obtained by electrodeposition	Weight of rhenium			
	Calculated from titration of oxidized deposit	Left in electrolyte	Found in the 5-ml portion of solution	Calculated on assumption that $\text{KReO}_4$ was 100.0% pure
g	g	g	g	g
0.0136	0.01333	0.00007	0.01340	0.01342
.0136	.01333	.00005	.01338	.01342
.0136	.01341	.00002	.01343	.01342

The results that can be expected are illustrated in table 5. In these tests phenolphthalein was used as indicator, and titrations were made with a standard solution of sodium hydroxide under conditions that insured the absence of carbon dioxide. Calculations were made on the assumption that the oxidation of rhenium proceeds as indicated by the equation,



and that the neutralization takes place according to the reaction,



It will be noted that the rhenium content of a deposit thus determined is less in every case than the weight of the deposit, as has already been stated.

While the method of standardization is not as simple and direct as might be desired, it has no difficult features, and is apparently capable of yielding quite accurate results, provided the amount of undeposited rhenium can be kept so low that the shortcomings of the colorimetric method can be ignored.

WASHINGTON, March 30, 1937.