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To the Graduate Council:

I am submitting herewith a thesis written by David E. LaValle entitled "Some Quadrivalent Compounds of Rhenium and Technetium Containing Fluorine." I recommend that it be accepted for eighteen quarter hours credit in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemistry.

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Major Professor

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SOME QUADRIVALENT COMPOUNDS OF RHENIUM AND TECHNETIUM CONTAINING FLUORINE

A Thesis

Presented to

the Graduate Council of

The University of Tennessee

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

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by

David E. LaValle

December 1963

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PART A

POTASSIUM HEXAFLUORORHENATE(IV), POTASSIUM HEXAFLUORO-TECHNETATE(IV) AND RHENIUM NITROGEN FLUORIDE

CHAPTER I

INTRODUCTION

The compound potassium hexafluororhenate(IV) (K_2ReF_6) was first reported by Ruff and Kwasnik[1] in 1934. At this time, when much of the early work on the chemistry of rhenium was being done, the other analogous halogen complexes of rhenium were already known. The preparation of these complexes had generally been accomplished by the reduction with iodide ion of rhenium(VII) in the form of potassium perrhenate ($KReO_4$), to the quadrivalent complex, in a strong solution of the appropriate halogen acid.[2,3,4]

$$KReO_4 + 3KI + 8HCl \longrightarrow K_2ReCl_6 + 3/2\ I_2 + 2KCl + 4H_2O.$$

I. and W. Noddack[5] called attention to the dependence of the reaction velocity on the acid concentration: in 35 per cent hydrochloric acid it is fairly rapid; in 8 per cent it is slow. They also stated that the reduction occurs in 50 per cent sulfuric acid, in glacial acetic acid, and in 40 per cent hydrofluoric acid;* but they did not describe the product.

Ruff and Kwasnik, however, utilizing the reaction in 40 per cent hydrofluoric acid, reported the preparation of K_2ReF_6 as a bright green compound.

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*The strength of the concentrated acid as provided abroad seems to be 40 per cent. In the U. S. it is usually 48 per cent. The constant-boiling mixture is 35.5 per cent.

No further mention of the compound appeared until 1955. Late in that year Peacock,[6] after noting repeated failures to duplicate the method of Ruff and Kwasnik, reported the successful preparation of K_2ReF_6 by fusing the quadrivalent rhenium complex ammonium iodorhenate(IV) ($(NH_4)_2ReI_6$) in potassium bifluoride (KHF_2) at 250°. It was described as a white compound, remarkably stable, which could be recrystallized from water.

Early in 1956, Weise[7] published the results of his studies on the alkali fluororhenates and included a description of their magnetic properties. He described K_2ReF_6 as a white compound prepared by passing hydrogen fluoride over K_2ReBr_6 or K_2ReCl_6 at 400° for extended periods of time. He also prepared it by the method of Peacock, fusing the more conveniently available K_2ReBr_6 in KHF_2. The K_2ReF_6 obtained by this method was pink. He ascribed the pink color to the replacement of a small fraction of fluorine ligands by hydroxyl groups. He found no difference in the X-ray patterns of the pink and white compounds, which he attributed to the similarity in size of the two ligands.

Weise reported that pink K_2ReF_6 is converted to the white form by repeated recrystallizations from 40 per cent hydrofluoric acid or by passing hydrogen fluoride over the pink product. In this latter process the compound first became black, then green, and finally white. The green intermediate showed the X-ray pattern for K_2ReF_6 with a few extra lines.

The reported chemical analyses for fluorine were low: $\sim$3 per cent for the pink compound and $\sim$2 per cent for the white form.

(Peacock's white compound as reported was $\sim$ 3 per cent low in fluorine.) These discrepancies were not considered significant by Weise, however, because of the uncertainty in fluorine analyses.

The work in this laboratory was begun with the aim of producing pure K_2ReF_6, as a possible intermediate in the preparation of the lower fluorides of rhenium and as a "stand-in" for the preparation of K_2TcF_6. It meant, therefore, the preparation of the white form of K_2ReF_6 which both Weise and Peacock had described as the pure form of the compound.

CHAPTER II

RESULTS AND DISCUSSION

Numerous attempts were made to prepare K_2ReF_6 following the methods of Peacock,[8] Weise,[7] and the earlier method of Ruff and Kwasnik.[1] No white salt was ever obtained, although many preparations of pink K_2ReF_6 were isolated and identified.

The method of Peacock, fusion of $(NH_4)_2ReI_6$ in KHF_2, was tried with many variations. The products as identified by X-ray diffraction examination were predominantly $KReO_4$. When potassium hexaiodorhenate(IV) (K_2ReI_6) was fused in KHF_2, however, pink K_2ReF_6 was obtained.

In the analogous method of Weise, fusion of K_2ReBr_6 in KHF_2, the pink product always resulted. Weise's method of producing white K_2ReF_6 by passing hydrogen fluoride over K_2ReBr_6 at 450° for 10 hours could not be duplicated. An olive-drab product was obtained which resisted further change even after an additional 6 hours of treatment. The X-ray pattern showed the lines characteristic of K_2ReF_6 with some additional lines.

Many variations of the above methods were tried, including protection of the fusions by inert gas, addition of hydrogen fluoride during fusion, preliminary drying of the KHF_2 by electrolysis, extraction of the fusions with acid solutions, and extraction with methanol instead of water.

Having failed to produce the white salt by variations of the given methods, attention was turned to Weise's methods for conversion of the

pink salt to the white.

Attempts to recrystallize the pink salt from 40 per cent hydrofluoric acid were unsuccessful. The salt rapidly underwent transformation to green and black products when concentration was attempted by heating. Also the solubility of the pink salt and the transformation products in strong solutions of hydrofluoric acid was so great that crystallization did not occur short of evaporation to dryness, which yielded an olive-drab residue. The same result was obtained when hydrogen fluoride was passed over the salt.

These experiments terminated attempts to reproduce published methods, and attention was turned to some other aspects of the K_2ReF_6 problem.

The original method of Ruff and Kwasnik was re-examined in the hope of producing the green salt. In this aqueous method the initial reaction of $KReO_4$ and KI in 40 per cent hydrofluoric acid is followed by repeated evaporations to low volume in the same medium. A bright green salt was reported to be obtained finally by crystallization. Attempts to duplicate this procedure always resulted in an olive-drab product which was indicated by X-ray diffraction to consist of a single phase of large unit cell. A potassium determination indicated a content of 11.1 per cent compared with the calculated value of 20.7 per cent.

In another experiment K_2ReF_6 was produced directly from $KReO_4$ and KI in a combination of the aqueous method of Ruff and Kwasnik and

the fusion method. The mixture of $KReO_4$ and KI was added to molten KHF_2. No reaction occurred even when the mixture was heated to 800°. When the melt was cooled, however, and 5 ml. of water added followed by reheating, evolution of iodine occurred and after extraction of the cooled flux with water and the usual purification procedure, pink K_2ReF_6 was obtained. But when the experiment was repeated with the exception of adding 5 ml. of 48 per cent hydrofluoric acid instead of water, a slight initial reaction was observed which soon ceased and the product ultimately extracted from the flux was predominantly $KReO_4$.

The behavior of K_2ReF_6 in solutions of hydrofluoric acid was investigated because of the reported recrystallization from this medium. The pink salt was found to increase in solubility with increasing concentration of hydrofluoric acid. In all concentrations of acid a pink solution was obtained. Solutions in dilute hydrofluoric acid (2 to 5 per cent) were concentrated by heating, and the pink salt crystallized unchanged. In solutions of 20 per cent hydrofluoric acid and stronger, heating produced rapid changes of color; from pink to yellow to green and finally to black. The nature of the substances represented by these colors was investigated.

A light tan solid was precipitated from the yellow solution when an ether-alcohol mixture was added. An X-ray pattern indicated 90 to 95 per cent K_2ReF_6 and an additional unknown phase. The solid precipitated from the green solution was estimated to be about 90 per cent K_2ReF_6 with an additional unknown phase and some $KReO_4$. The black

solution yielded a black product consisting of about equal parts of K_2ReF_6 and $KReO_4$, and a smaller amount of an unknown phase.

Repeated evaporations to dryness of K_2ReF_6 in strong hydrofluoric acid produced an olive-drab substance in which K_2ReF_6 could not be detected. Predominant were $KReO_4$ and an unknown phase which compared in many respects with the olive-drab end-product obtained above by the method of Ruff and Kwasnik.

However, when a solution of K_2ReF_6 in strong hydrofluoric acid was evaporated to dryness in an inert atmosphere, the black residue produced the X-ray pattern for K_2ReF_6 with some additional lines.

The preparation of K_2ReF_6 was also attempted from rhenium tetrafluoride (ReF_4) and potassium fluoride (KF). Solutions of these substances in methanol were mixed, resulting in the immediate formation of a green precipitate. The X-ray photographs showed only halos. A potassium analysis by flame photometry indicated 19.8 per cent compared with the theoretical value of 20.7 per cent for K_2ReF_6.

Alternatively, an intimate mixture of the two substances, compressed in a steel cylinder which was then sealed in a quartz tube, was heated for 60 hours at 250° and finally for 4 hours at 300°. The dark grayish-green product was indicated by X-ray analysis to consist of K_2ReF_6 and an unknown phase. Leaching the dark material with methanol left a violet residue which was soluble in water and formed a stable violet solution. A potassium analysis of the violet substance indicated 16.0 per cent compared to 20.7 per cent calculated for K_2ReF_6.

These efforts terminated the preparative study of K_2ReF_6. The final analysis of the pink compound indicated: potassium 20.7 per cent (calc. 20.7), rhenium 49.5 per cent (calc. 49.2), fluorine 30.1 per cent (calc. 30.1). An infrared analysis was performed on the solid material but no evidence of the hydroxyl group was found.

As measured on a Cary spectrophotometer by following the increase of perrhenate ion in solution, the rate of hydrolysis of K_2ReF_6 is 0.17 per cent per day at 25° and 6.2 per cent per day at 60°. The solubility in cold water (25°) is about 2 g. per 100 ml.

From the pink K_2ReF_6 a quantity of ammonium hexafluororhenate (IV) ($(NH_4)_2ReF_6$) was prepared by an ion-exchange procedure. The thermal decomposition of this compound was studied in the hope of producing a lower fluoride of rhenium.

More desirable would have been an ammonium complex of rhenium(III). But numerous attempts to prepare the compound failed. Fusions of $ReBr_3$ with ammonium bifluoride (NH_4HF_2) always led to substances in which the replacement of the bromine was incomplete. When KHF_2 was used to conduct fusions at higher temperatures, K_2ReF_6 was obtained.

A thermogravimetric analysis indicated that $(NH_4)_2ReF_6$ decomposes in argon at 300°. Accordingly, decompositions were performed at this temperature in argon, in hydrogen fluoride, and in vacuo. Decomposition in hydrogen fluoride, as indicated by X-ray analysis, produced a mixture of unidentified phases.

Decomposition in argon and in vacuo, however, yielded a black substance which X-ray analysis indicated to consist of 97 per cent of

a single phase. From the powder diffraction data a tetragonal unit cell was postulated with a = 5.88 Å and c = 13.00 Å. Elemental analysis indicated a rhenium content of 83.5 per cent, nitrogen 6.3 per cent, and fluorine 8.3 per cent. Calculated for the hypothetical compound rhenium nitrogen fluoride (ReNF): rhenium 85.0 per cent, nitrogen 6.4 per cent, and fluorine 8.7 per cent. The residues in several trials were weighed, yielding values in per cent of original weight of 65.9, 65.2, and 64.4 compared with a calculated value for ReNF of 65.2 per cent.

The range of stability of ReNF is not great. The thermogravimetric analysis indicated complete decomposition at 500°. At 900° a slight inflection in the curve suggested the decomposition of a small amount of material, possibly rhenium nitride (Re_3N).[9]

Similar experiments were performed on ammonium hexafluorotechnetate(IV) ($(NH_4)_2TcF_6$), obtained analogously to the rhenium compound, but the amounts of material were too limited to permit adequate chemical analyses. The residue after decomposition of the $(NH_4)_2TcF_6$ in argon at 300° amounted to 53.5 per cent of the original weight. The calculated value for a residue of technetium nitrogen fluoride (TcNF) is 53.0 per cent; for technetium difluoride (TcF_2), 55.0 per cent. The residue was reduced to technetium metal in hydrogen at 500°. The loss in weight was 25.5 per cent. The calculated loss for TcNF is 25.0 per cent, for TcF_2 27.7 per cent. The unit cell derived from the powder diffraction data was hexagonal with a = 5.98 Å and c = 4.80 Å.

The hydrolysis of K_2TcF_6 in water as measured by the appearance of pertechnetate ion proceeds at the rate of only 0.015 per cent per day at 25° and 1.6 per cent per day at 60°--rates that are only about one-tenth those for the rhenium compound. It is a pale pinkish-lavender substance, soluble to the extent of about 1.5 g. per 100 ml. of water at 25°.

Since the inception of this work, K_2TcF_6 has been prepared by Schwochau and Herr.[10] Their description of the compound is in accord with the information that was obtained here except for a slight difference in the lattice parameters. They found for the tetragonal structure a = 5.807 Å, c = 4.645 Å compared to values here of a = 5.810 Å and c = 4.637 Å.

CHAPTER III

APPARATUS AND PROCEDURES

1. Materials

The ordinary chemicals used were reagent grade materials. $KReO_4$ and NH_4ReO_4 in better than 99 per cent purity were obtained from the University of Tennessee, and ammonium pertechnetate (NH_4TcO_4) was recrystallized from a slightly impure product obtained from the Isotopes Division of Oak Ridge National Laboratory. The hydrogen fluoride was a product of The Matheson Company, and was supplied in small cylinders. K_2ReBr_6 was prepared as described by Weise; potassium hexachlorotechnetate(IV) (K_2TcCl_6) as described by Nelson, Boyd, and Smith;[11] and $(NH_4)_2ReI_6$ as described by Peacock.[8] The preparation of ReF_4 is described in Part B.

2. Apparatus

Fusions were done in a 100-ml. platinum crucible provided with a cover. The heating was accomplished in a small electric crucible furnace just large enough to accommodate the crucible, which was supported so that 1/8 inch projected above the furnace and allowed fumes to escape into the atmosphere. A thermocouple led from the furnace to an indicating and controlling capacitrol.

Gaseous hydrogen fluoride when employed during fusions was conducted from the supply cylinder through 1/4-in. copper tubing connected

to, and terminating in, 6 inches of 1/4-in. platinum tubing. A side line with a valve was joined to the copper tubing to admit argon so that either or both gases could be directed down upon or below the surface of the melt.

For fusions or evaporations in a completely inert atmosphere a nickel tube about 40 inches long and 2 inches in diameter with flanged ends was used. The closures were made with flat nickel plates fitted with open 1/4-in. sections of copper tubing for the entrance and exit of gas, and with bolts which held them firmly against the flanges with Teflon "O" rings as seals.

The fusion mixtures were contained in platinum boats fashioned from platinum sheet, and solutions to be evaporated were contained in a platinum crucible resting in a nickel boat to facilitate insertion and removal. The tube was heated by an ordinary large-bore hinged-type tube furnace.

Filtrations were accomplished with a polyethylene Büchner-type funnel, holding ordinary filter paper inserted in a bell-jar arrangement so that suction could be applied. Strong solutions of hydrofluoric acid were centrifuged using plastic tubes.

The thermal decomposition of $(NH_4)_2ReF_6$ and $(NH_4)_2TcF_6$ in argon was done in a smaller version of the nickel tube previously described. When $(NH_4)_2ReF_6$ was decomposed <u>in vacuo</u> it was contained in a platinum boat situated at the closed end of a copper tube, the other open end of which extended beyond the hot zone of the furnace. The copper tube

rested horizontally in a quartz tube fitted with a water-cooled standard-taper ground joint and stopcock so that it could be detached from the vacuum system and transferred to a glove box without exposing the contents to the atmosphere.

3. Procedures

The fusions were made by grinding the halogen complexes to pass a 200-mesh screen in the inert-atmosphere glove box. A weight of KHF_2 was taken equal to 10 times the weight of the complex and melted in the 100-ml. platinum crucible in the furnace. The halogen complex was added a little at a time and allowed to dissolve. The crucible was covered and the temperature raised slowly to 700° over a period of about an hour. The trial was terminated by placing the crucible in an aluminum desiccator containing sodium hydroxide pellets and allowing it to cool. Sometimes it was cooled rapidly by removing it from the furnace with long forceps and suspending it in a Dewar of liquid nitrogen until it had solidified, then transferring it to the entrance chamber of the glove box.

The contents of the crucible were removed and examined in the glove box and usually ground to pass a 100-mesh screen to facilitate extraction with water. Extraction was accomplished using a minimum of cold water in a 300-ml. platinum evaporating dish while the 100-mesh material was stirred magnetically with a Teflon-covered bar.

After filtration the residue, which consisted principally of K_2ReF_6 (or K_2TcF_6), a small amount of KF, and some dark hydrolytic

products, was treated with hot water and heated gently for a few minutes to coagulate the black material. After the residue was removed by filtration, the pink solution was concentrated to crystallization while being magnetically stirred under an infrared lamp and then allowed to cool. Very fine semi-transparent pink leaflets of tetragonal symmetry resulted, usually in a yield of about 80 per cent.

The rapid recovery of products from solutions was accomplished by precipitation in ether-alcohol solutions. The water solution was poured into 10 times its volume of a 1:1 mixture of ethyl ether and methyl or ethyl alcohol. Immediate precipitation occured, but some digestion was permitted to induce crystallinity and to aid in filtration.

For the reaction of solid KF with solid ReF_4, crystals of completely anhydrous KF, which had been purified by zone-refining, were ground to pass a 325-mesh screen in an inert dry atmosphere and mixed with ReF_4. The mixture was placed in a small stainless steel cylinder between two close-fitting, movable plungers and compressed in a vise. The entire capsule was sealed in a nickel tube in an atmosphere of argon and heated for 60 hours at 250° terminating with 4 hours at 300°.

The conversion of K_2ReF_6 to $(NH_4)_2ReF_6$ was done by passing the solution of the potassium salt through a column containing Dowex 50W-X8 ion-exchange resin in the acid form and neutralizing the resulting fluororhenic acid(IV) (H_2ReF_6) with ammonium hydroxide. The $(NH_4)_2ReF_6$ was precipitated in an ether-alcohol mixture.

To convert K_2TcF_6 to the ammonium salt, 2.5 g. of the potassium compound was dissolved in a slurry of 6 g. of the resin in 20 ml. of

water in a beaker. After stirring the slurry for an hour, the solution was passed through a small column containing 5 g. of the resin. The resins in the beaker and in the column were rinsed until the total volume of solution was 100 ml. Only a small portion of the resulting H_2TcF_6 solution was neutralized to provide the $(NH_4)_2TcF_6$ used in the decomposition experiments.

4. Analyses

Samples containing the fluoride complex ion, $ReF_6^=$, were decomposed by fusion in sodium carbonate containing a small amount of sodium peroxide. For other substances alkaline hydrogen peroxide was usually sufficient.

Control determinations for rhenium and fluorine were done colorimetrically, rhenium with α-furildioxime and fluorine with Thoron.* Control potassium analyses were done by flame photometry.

Characterization and final analyses were done gravimetrically: potassium by precipitation as the tetraphenylborate, rhenium as tetraphenylarsonium perrhenate, and fluorine as lead chlorofluoride. Rhenium in ReNF was determined by reduction in hydrogen at 600°. The residue as indicated by X-ray analysis was rhenium metal.

The sample of K_2ReF_6 for the detection of hydroxyl groups by infrared analysis was prepared by mixing 3 mg. of the solid with 500 mg. of solid potassium bromide of spectroscopic grade and forming a pellet of the mixture.

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*Eastman chemical No. 6748: $HOC_{10}H_4(CO_3Na)_2N{:}NC_6H_4AsO_3H_2$.

CHAPTER IV

SUMMARY AND CONCLUSIONS

Attempts to duplicate reported methods of preparing white K_2ReF_6 were unsuccessful as were also suggested means of converting the pink salt to the white form.

Treatment in hydrogen fluoride yielded an olive-drab product producing the X-ray pattern of K_2ReF_6 and some additional lines. In strong solutions of hydrofluoric acid, decomposition of the compound occurred when heat was applied. When an inert atmosphere was provided a black form of K_2ReF_6 was obtained, also showing extra lines in the X-ray pattern.

Attempts to prepare the green K_2ReF_6 of Ruff and Kwasnik were also unsuccessful. The product obtained was an olive-drab substance similar to the one of the same color above in its X-ray pattern. The existence of the bright green compound cannot be entirely discounted, however. Green fluxes, solutions, and solids were observed many times during the course of experiment, and more refined methods may isolate such a compound. The reaction of ReF_4 and KF in methanol yielded an initial green compound with a potassium content approaching that of K_2ReF_6.

The pink material was finally accepted as satisfying sufficient criteria for a pure compound. The infrared analysis did not indicate a hydroxyl content beyond that already present in the matrix of KBr and

the low values for fluorine found by Weise for the pink salt were not confirmed. The pink compound can be recrystallized repeatedly from water.

The technetium compound analogous to K_2ReF_6 was prepared by the same method. It was found to be similar in color, solubility and structure to the rhenium compound, but somewhat more stable in solution.

From the two potassium compounds the corresponding ammonium salts were prepared by ion-exchange methods. Thermolysis of these ammonium analogues resulted in black substances which were indicated by X-ray analysis to be single phases of definite structure. The rhenium containing residue was identified by elemental analysis as having the composition indicated by the formula ReNF, and the technetium residue, from a consideration of a material balance, is probably of analogous composition. The interpretation of the powder diffraction patterns, however, suggested differing structures.

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PART B

RHENIUM TETRAFLUORIDE

CHAPTER I

INTRODUCTION

An obvious method of preparing lower fluorides of rhenium is the reduction of rhenium hexafluoride (ReF_6).* Ruff and Kwasnik[1] passed a mixture of ReF_6 with hydrogen or sulfur dioxide through a heated platinum tube and recovered a green solid now believed to have been a mixture of rhenium pentafluoride (ReF_5) and rhenium tetrafluoride (ReF_4).[2]

Hargreaves and Peacock obtained ReF_5 by the reduction of ReF_6 with tungsten carbonyl in tungsten hexafluoride as a solvent. It was described as a yellow oil solidifying at 25°. Pyrolysis of the pentafluoride at 240° left a pale-blue residue of ReF_4.

Malm and Selig[3] in their attempts to convert rhenium heptafluoride (ReF_7) to ReF_6 heated mixtures of the two compounds with excess rhenium metal at 300° in closed nickel cans in which pressures of 30 atmospheres developed. They obtained, in some cases, small amounts of a pale-blue non-volatile substance of the approximate composition of ReF_4.

From these experiments it might be assumed that ReF_6 is not easily reduced. However, it is known that most rhenium compounds are

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*This compound as ordinarily prepared has been shown by Malm and Selig[3] to contain small amounts of rhenium heptafluoride (ReF_7).

readily reduced to the metal in hydrogen. The complicating factor is the tendency of rhenium compounds of intermediate oxidation states to disproportionate when heated.

CHAPTER II

RESULTS AND DISCUSSION

In accord with the observations of Malm and Selig,[3] and from previous experience,[4] a method of reduction employing more than normal pressures to prevent disproportionation seemed desirable. These conditions were met by heating rhenium metal and ReF_6 in sealed nickel tubes to temperatures as high as 500°.

In typical runs, 2.5 g. of rhenium metal was contained in the tubes with about 8 g. of ReF_6, providing 100 per cent excess of the latter for the reaction yielding ReF_4. The tubes were seldom able to sustain pressures developed at temperatures greater than 400°. Bulging of the flattened ends was always evident, but rupture at higher temperatures occurred only through minute holes developing at imperfections in the welds. After reaction the tubes were opened at one end in an inert-atmosphere glove box, where they were transferred to glass sublimation tubes for subsequent removal of the volatile products by heating *in vacuo* at 100-200°.

In these sublimations a considerable amount of ReF_6 was always recovered in the liquid nitrogen trap. The products of the reaction were a small amount of pale-blue rhenium oxytetrafluoride ($ReOF_4$)[5] also found in the nitrogen trap, and a yellow oil mixed with a green solid which deposited in the cool parts of the sublimation tube. By heating the yellow oil and green solid gently with a burner, ReF_6 was

evolved, leaving behind ReF_5 which was sublimed into a small side-bulb having a constriction in the neck. After admitting nitrogen to the system, the greenish-yellow solid, ReF_5, in the side-bulb was heated gently resulting in disproportionation to ReF_6 and a residue of medium-blue ReF_4. The bulb was sealed off at the constriction and transferred to the glove box. An additional small amount of ReF_4 was usually recovered from the sublimation tube just outside the open end of the nickel reaction tube.

No trace of a fluoride lower than ReF_4 was ever discovered. The residue after sublimation was always rhenium metal--by its color and grain size obviously unreacted material, unlike the black powder resulting from disproportionation.

Variations in the above procedures, such as quenching the nickel tubes in liquid nitrogen, or allowing them to cool slowly, did not lead to results differing in a significant way. When the reactants were heated in a thick-walled (0.06 in.) nickel tube to 600°, only 15 per cent of the rhenium metal reacted. An attempt using 100 per cent excess of metal heated overnight at 400° led to the usual products, but the ratio of ReF_4 to ReF_5 was greater than previously.

The most successful trial by the sealed-tube method was performed in the usual manner (100 per cent excess of ReF_6), but the tube was heated for 4 days at 400°, followed by 20 hours at 500°. Approximately 60 per cent of the metal had reacted to produce mainly ReF_5, from which 3 g. of ReF_4 was obtained by disproportionation after

admitting nitrogen to the system (ReF_5 sublimes *in vacuo*).

The above experiments suggested that long periods of heating favored greater reaction of the substances, and excess of metal favored the production of the lower fluoride ReF_4.

A few experiments were performed in glass. ReF_6 was admitted to an evacuated bulb containing a small amount of rhenium metal heated to 200°. Reaction occurred in a short time but proceeded slowly. After 4 hours a number of well-formed, semi-transparent, pale-blue crystals of $ReOF_4$ had formed in the upper part of the bulb. A black film, presumably of rhenium oxytrifluoride ($ReOF_3$),[2] had formed on the other surfaces of the flask.

A final preparation of ReF_4 was made at atmospheric pressure. A chamber containing ReF_6 was opened to a nickel tube containing finely divided rhenium metal at 550°. Outside this hot zone the system was kept at $\sim$40° with heating tape to maintain a vapor pressure of ReF_6 just above one atmosphere. After 10 days the nickel tube was removed to the glove box and opened. Practically the sole reduction product was ReF_4 which had deposited in the nickel tube just beyond the hot zone. Only a trace of ReF_5 was found, farther along in the system. Approximately 4 g. of ReF_4 was obtained representing a conversion of 70 per cent of the ReF_6.

The ReF_4 was purified by sublimation *in vacuo* from a nickel boat contained in the sublimation tube. Sublimation began at 150° and was fairly rapid at 200°, producing a small amount of ReF_6 and leaving behind

in the boat a black residue, stable to at least 300°, which by X-ray crystallographic analysis was estimated to be 50 per cent rhenium metal and the remainder an unknown phase.

An elemental analysis of the purified ReF_4 indicated: rhenium 70.4 per cent, calc. 71.0; fluorine 28.6 per cent, calc. 29.0. The X-ray diffraction powder pattern could be indexed on the basis of a unit cell of tetragonal symmetry. (See Appendix.)

The solubility characteristics of ReF_4 were found to be rather unusual. In water it hydrolyzed immediately and deposited an insoluble black material. But in water containing a few drops of 30 per cent hydrogen peroxide no precipitate formed; a deep blue solution resulted which retained its color for half an hour. In methanol or absolute ethanol ReF_4 formed a solution which remained blue about half an hour, and when hydrogen peroxide was present in the alcohol, the blue color persisted for several hours.

When a methanol solution of ReF_4 was evaporated to dryness under reduced pressure, the resulting black residue produced an X-ray pattern similar to that for ReF_4, but with significant differences. The same treatment given to a methanol solution of ReF_4 containing hydrogen peroxide produced an X-ray pattern that was not identified.

CHAPTER III

EXPERIMENTAL

Rhenium hexafluoride was prepared from the elements, the metal obtained as described previously and the fluorine made available with its accessory apparatus in the Fluorine Laboratory of the Chemical Technology Division of Oak Ridge National Laboratory.

About 8 g. of the metal was contained in a nickel boat resting in a nickel tube, the entrance of which was closed by a cap held against a Teflon gasket with a threaded ferrule. A small side-arm tube was connected by ¼-in. copper tubing to sources of helium and fluorine. The rate of flow of these gases was indicated by flowmeters, and they could be mixed in any proportions.

The exit of the nickel tube led through 3/8-in. copper tubing to a flanged nickel can, 2 in. in diameter by 5 in. deep. A cover fitted with two Veeco-type valves with Teflon seats, was held against the flange of the can through a Teflon "O" ring (part A in Figure 1). The entrance to the can terminated at the cover, the exit tube extended nearly to the bottom, and the bottom half of the can was cooled in acetone-dry-ice mixture during operation, while the cover was heated with heating tape to ~100°.

The nickel tube, about 15 in. long and 1 in. in diameter, was heated by an ordinary, hinged-type tube furnace. A thermocouple was wired to the bottom of the tube so that the incidence of rapid reaction could be noted.

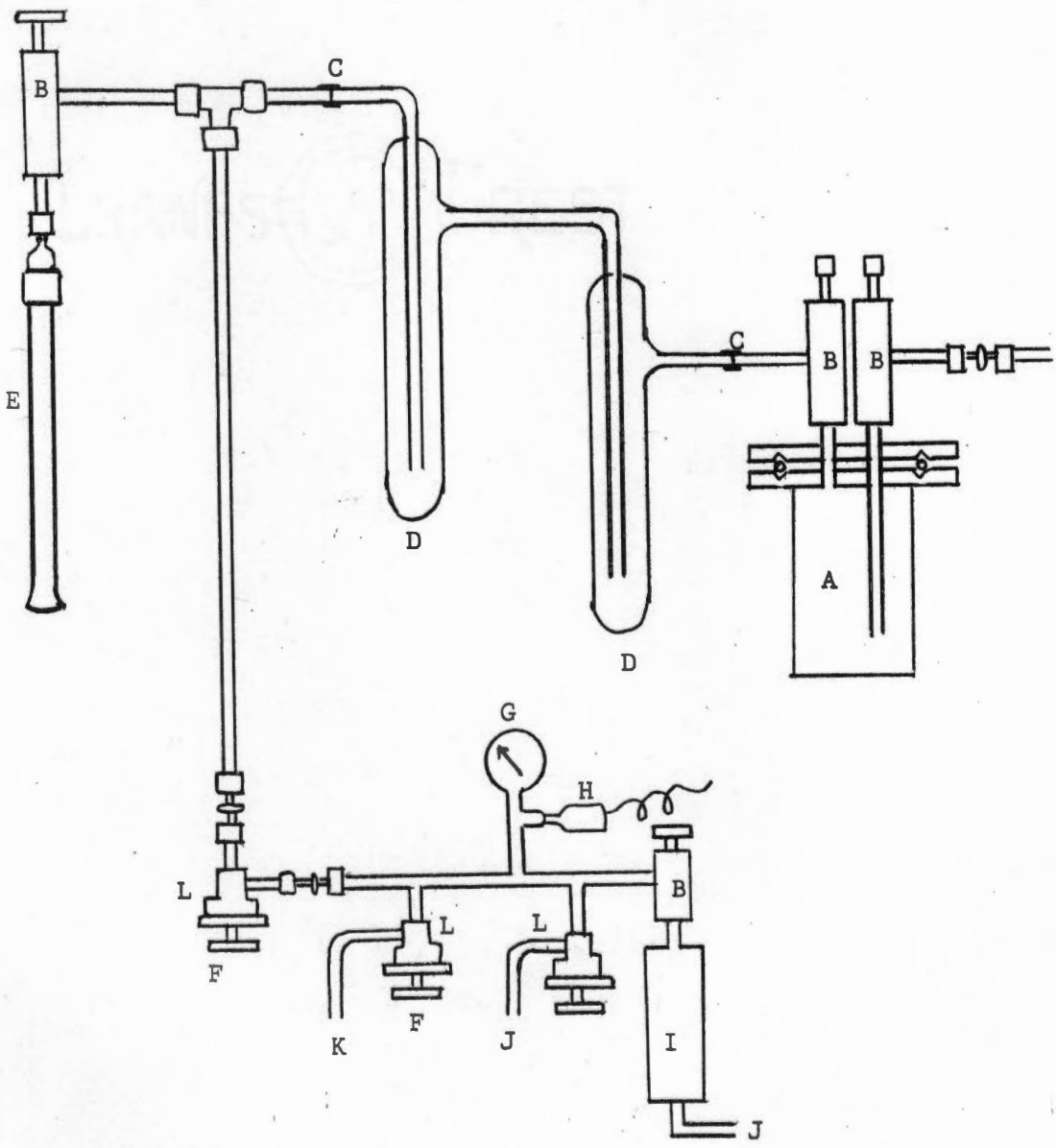


Figure 1. Vacuum system for transferring rhenium hexafluoride to nickel tubes.

After flushing the system with helium, fluorine was admitted to make up 50 per cent of the gas flow. The reaction began at room temperature, or higher, depending upon the state of subdivision and temperature of preparation of the rhenium metal. The rate of reaction was controlled by varying the helium flow. The tube was heated to a final temperature of 300°, the system cooled and flushed with helium, and finally the valves on the can closed and the can separated from the rest of the apparatus and attached to the vacuum system described below.

A schematic outline of this system is illustrated in Figure 1. A is the nickel can, B the Veeco-type valves, C Kovar glass-to-metal seals, D glass traps, E the nickel reaction tube, F a Kerotest valve with Teflon seat, G a vacuum-pressure gauge, H a thermocouple gauge, I a soda-lime trap, J outlets to a vacuum pump, K an entrance for nitrogen, and L Kerotest valves. Connections were made with Swagelok fittings and 3/8-in. copper tubing was used throughout.

After assembling the system, it was tested for leaks by disengaging it from its supports, replacing the air in it with helium at 15 p.s.i. above ambient pressure, and immersing the whole apparatus in water.

The nickel reaction tube was 12 in. long by ½ in. in diameter, flattened and welded at one end. After charging with 2.5 g. of rhenium metal (200-400 mesh), it was attached to the system, evacuated by a mechanical pump, and flushed several times with nitrogen.

After a final evacuation the previously attached can containing the ReF_6 was opened to the system and the ReF_6 allowed to sublime

into the first glass trap cooled with acetone-dry ice mixture. A small quantity of highly volatile material usually passed through the trap and out of the system. The ReF_6 was resublimed into the second glass trap cooled with liquid nitrogen. The valve to the pump was then closed and the ReF_6 sublimed into the nickel reaction tube.

Removal of the nickel reaction tube, flattening, cutting, and welding were done while liquid nitrogen remained around the tube. After the tube was sealed and had been allowed to come to room temperature, a spontaneous reaction usually occurred heating the tube to $\sim$100°. The reaction was continued by heating the tube in a furnace to $\sim$400° from 6 to 24 hours.

At the end of the heating period the tube was quenched in liquid nitrogen and rapidly transferred to the glove box. It was opened at one end and placed in a sublimation tube (part A in Figure 2) which was temporarily stoppered. It was attached to the vacuum system at the joint E, the trap F having previously been attached at G and the whole system flushed out with nitrogen which continued to emerge at E. As soon as the sublimation tube was attached at E the flow of nitrogen was stopped and the system immediately evacuated. All of these operations had to be done while the nickel tube still remained cold from the quenching in liquid nitrogen.

In Figure 2, B is the nickel tube, C a furnace, D a side-bulb to receive ReF_5, E the assembled "O" ring joint held together by a ball-and-socket joint clamp (not shown), I is a break-seal, and J a Kovar

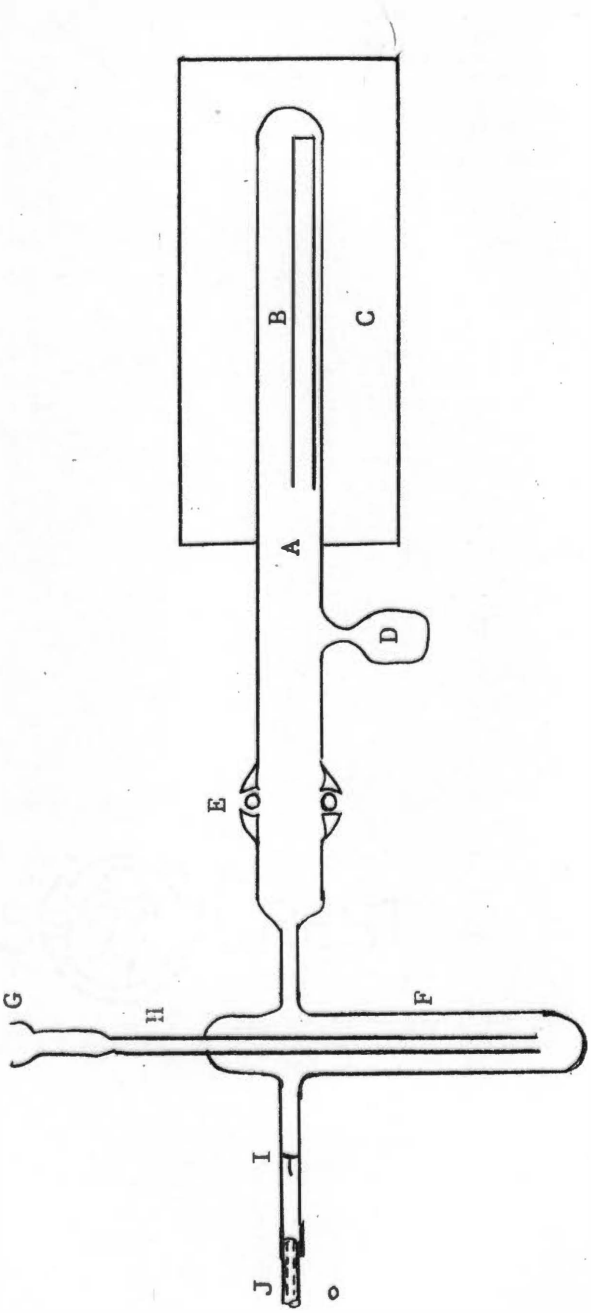


Figure 2. Sublimation tube.

glass-to-metal joint. The rubber "O" ring in the joint E was coated with a fluorinated lubricant.

The sublimation and disproportionation of the ReF_5 were performed as previously described, and the residue of ReF_4 in the bulb removed to the glove box where it was transferred to Teflon capsules having screw caps.

The ReF_6 in the liquid nitrogen trap was salvaged by sealing off the trap at H, reattaching it to the vacuum system through the break-seal I at J and subliming the ReF_6 into an evacuated nickel storage can fitted with a valve (part H in Figure 3).

Figure 3 shows the arrangement used for the preparation of ReF_4 at atmospheric pressure. B is the nickel reaction tube enclosed in furnace A. At C is a silver-soldered connection to copper tubing D provided with coils for air-cooling at E and F. Kerotest valves are at G, and I leads to the vacuum system. The ReF_6 is contained in H. Heating tape surrounded the system from H to F.

After the heating period the excess ReF_6 was condensed in H and isolated with the nearest valve G. The system was evacuated and filled with nitrogen to 3 p.s.i. above atmospheric pressure and the tube flattened and severed between F and E. After removal to the glove box the tube was opened at D with a tube-cutter.

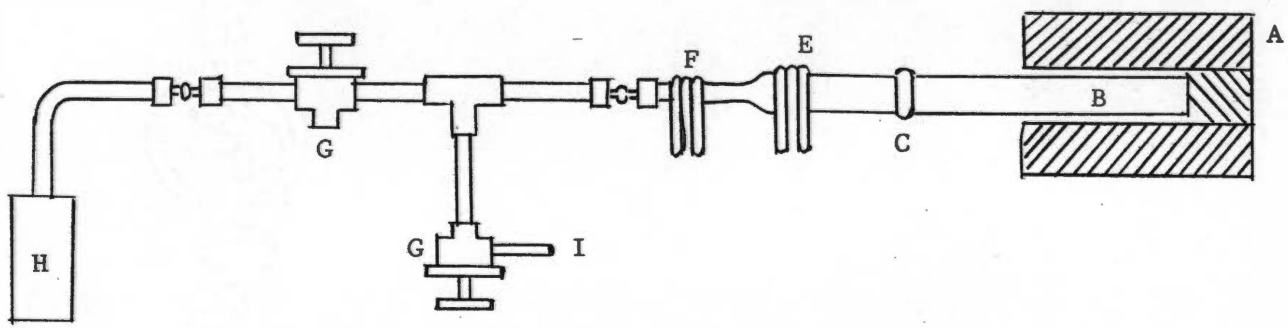


Figure 3. Arrangement for the preparation of rhenium tetrafluoride.

CHAPTER IV

SUMMARY AND CONCLUSIONS

The reduction of ReF_6 was attempted with rhenium metal under conditions of elevated pressure ($>$ 30 atmospheres) and temperature (400-500°). In these experiments, the substances generally recovered were (1) substantial amounts of unreacted ReF_6, (2) a predominant reduction product of ReF_5, and (3) small amounts of ReF_4. No trace of lower fluorides was found.

A method of obtaining ReF_4 from ReF_6 directly without the intermediate ReF_5 is described. Some of the properties of ReF_4 were determined.

There is some evidence that ReF_4 also disproportionates to some extent, when heated, into ReF_6 and a residue containing rhenium metal and an unidentified substance. If this latter substance is a lower fluoride, its identification might depend upon finding a method for separating it from rhenium.

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PART C

RHENIUM TETRABROMIDE

CHAPTER I

INTRODUCTION

The compound rhenium tetrabromide ($ReBr_4$) drew attention primarily as a possible intermediate for the preparation of lower fluorides of rhenium. The tetraiodide recently reported by Peacock, Welch, and Wilson[1] was neglected in favor of the tetrabromide because of the difficulties inherent in the use of iodides; the general tendency toward decomposition, the possibilities of polyiodide formation, and the presence of free iodine in the hydriodic acid used.

Not long after the report of the preparation of the tetraiodide Colton and Wilkinson[2] mentioned the preparation of the tetrabromide, which was assumed to be analogous to that of the iodide. Rhenium metal is dissolved in hydrogen peroxide to form perrhenic acid ($HReO_4$) which is reduced in the same manner as $KReO_4$ in the preparation of the potassium halogen complexes of quadrivalent rhenium. Here hexaiodorhenic acid(IV) (H_2ReI_6) is formed; which, after evaporation of the solution to dryness at room temperature and further desiccation, leaves a residue of rhenium tetraiodide.

CHAPTER II

RESULTS AND DISCUSSION

It was found that the analogous procedure did not lead to the preparation of a pure compound represented by the formula $ReBr_4$. The apparently dry black residue after evaporation of the solution of hexabromorhenic acid(IV), (H_2ReBr_6), continued to lose weight.

At the end of four days the composition was roughly equivalent to that of the hydrate, $H_2ReBr_6 \cdot 3H_2O$ (rhenium 28.2 per cent, calc. 25.8; bromine 64.1 per cent, calc. 66.4; water 7.0 per cent, calc. 7.5; sum of determined constituents: 99.3 per cent). At the end of 9 days a sudden break in the continuity appeared in the form of a reddish fluid which condensed on the walls of the desiccator. Weight loss, however, remained fairly constant at about 4 per cent per 3-day interval.

At the end of a month when the rate of loss had diminished by 50 per cent, an analysis was obtained to compare the black product with $ReBr_4$ (rhenium 34.6 per cent, calc. 36.8; bromine 62.5 per cent, calc. 63.2; sum of determined constituents: 97.1 per cent).

In an attempt to reach a stable phase the material was subjected to heating <u>in vacuo</u>. Beginning at 45° the temperature was gradually raised until, beyond 300°, volatilization was no longer evident.

The material had now separated into four fractions, three of which were characterized by elemental and X-ray diffraction analyses.

A black residue was found to correspond to rhenium oxytribromide ($ReOBr_3$). Just outside the hot zone was a dense layer of rhenium tribromide ($ReBr_3$) and farther on, attached to the walls in the cool parts of the tube, were numerous dark-blue, isolated, well-formed crystals of hexagonal symmetry. Analysis indicated the crystals to be rhenium oxytetrabromide ($ReOBr_4$).

The fourth fraction consisted of several substances condensed in the liquid nitrogen trap. The trap had been designed with constrictions so that it could be sealed and removed from the vacuum system, and with several side-arms so that further distillations could be conducted from the isolated trap. Some degree of separation of the volatile substances was achieved. In the main tube some transparent crystals of perrhenyl bromide (ReO_3Br), described by Colton and Wilkinson[2] were recovered and analyzed. Two other fractions, which were blue, could not be separated sufficiently to yield analytically significant results.

The compositions of the separated fractions are listed in Table I and the X-ray data are in the Appendix.

Rhenium tetraiodide was obtained during the preparation of a considerable quantity of K_2ReI_6 (170 g.). It precipitated as a very insoluble black substance, in the concentrated solutions employed, to the extent of about 5 per cent of the total rhenium involved, and it was identified by elemental analysis. No X-ray diffraction pattern could be obtained using copper Kα radiation probably accounting for its description by Peacock, Welch, and Wilson[1] as amorphous. But since the

TABLE I

ANALYSES OF PRODUCTS VOLATILIZED FROM PREVIOUSLY PRESUMED RHENIUM TETRABROMIDE (IN PER CENT)

	Rhenium		Bromine	
	Found	Calc.	Found	Calc.
ReO_3Br	58.6	59.3	24.4	25.4
$ReOBr_3$	43.0	42.1	54.5	54.2
$ReOBr_4$	35.6	35.7	61.0	61.2
$ReBr_3$	26.8	26.8	72.6	73.2

substance was definitely crystalline, chromium Kα and molybdenum Kα radiations were tried and from the latter a pattern was obtained from which the element iodine was identified. ReI_4 is reported as decomposing into rhenium triiodide and iodine in vacuo. Evidently molybdenum radiation is sufficiently energetic to accelerate this decomposition.

The structural identification of K_2ReI_6 is not as complete as it is for the corresponding compounds with chlorine and bromine. This fact is partly due to its comparative instability and consequent hydrolysis which may occur to some extent in the procedures used for its isolation from solution. In more recent times it has been prepared by Morrow[3] who noted some peculiarities in its chemical behavior and who assigned a tentative structure to it. Somewhat later Dalziel, Gill, Nyholm, and Peacock[4] suggested a somewhat different structure.

It was prepared here by starting with the highly soluble $HReO_4$, rather than the relatively insoluble $KReO_4$, in order to avoid prolonged concentration procedures. Portions of the product were recrystallized from 50 per cent hydriodic acid without producing any change in the X-ray pattern. The structure was found to be more in accord with the more recent one suggested above.

CHAPTER III

EXPERIMENTAL

A. $ReBr_4$

About 10 g. of rhenium metal obtained by the reduction of ammonium perrhenate with hydrogen, beginning at 250° and ending at 800°, was dissolved by oxidizing it to perrhenic acid with 15 per cent hydrogen peroxide. A small amount of an insoluble residue which has been identified as rhenium nitride (Re_3N)[5*] was removed by filtration. The filtrate was successively evaporated to low volume and diluted with water several times. Finally the viscous $HReO_4$ was dissolved in 50 ml. of 48 per cent hydrobromic acid and the resulting solution was saturated with hydrogen bromide gas. After standing overnight, the solution was evaporated to low volume by heating and transferred to a desiccator containing phosphorus pentoxide and pellets of sodium hydroxide, where it was allowed to remain until it became an apparently dry solid.

The heating *in vacuo* was done in a tube fitted with a water-cooled joint and a stopcock so that this portion of the apparatus,

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*A deliberate preparation of Re_3N was made by heating NH_4ReO_4 in a static atmosphere of hydrogen for 2 days. The metal was dissolved in 10 per cent H_2O_2 and the insoluble nitride removed by filtration.

CHAPTER IV

SUMMARY AND CONCLUSIONS

The existence of the compound $ReBr_4$ still remains in doubt. Its preparation following the method for the tetraiodide does not terminate in a definite composition indicative of $ReBr_4$, although by careful analytical surveillance of the decomposing $H_2ReBr_6 \cdot xH_2O$ a product of composition close to that of $ReBr_4$ may be obtained.

The chief reason for the difference in results may lie in the insolubility of the tetraiodide. In the preparation of K_2ReI_6, ReI_4 was isolated early in the procedure as an insoluble, anhydrous substance. By contrast, the bromide products remained soluble and when finally isolated were bound to various amounts of water, the removal of which resulted in the formation of hydroxy- and oxybromides. Several of the latter were isolated in the experiments. One of these, rhenium oxytribromide ($ReOBr_3$), had not been definitely characterized previously.

The compound K_2ReI_6 was prepared in a variation of the older procedure in order to achieve greater purity and thus eliminate some of the uncertainty in the structure. During the preparation an insoluble residue appeared which was isolated and identified by elemental analysis as ReI_4, but no X-ray pattern of the compound could be obtained.

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APPENDIX

APPENDIX

COMPILATION OF X-RAY DIFFRACTION DATA

TABLE II

RHENIUM AND TECHNETIUM COMPOUNDS: DEBYE-SCHERRER X-RAY DIFFRACTION DATA (Cu Kα RADIATION)

Compound	Unit Cell	Parameters (Å)
ReF_4	Tetragonal	a=10.12, c=15.95
$ReBr_3$	Monoclinic[a]	a=15.75, b=10.59, c=9.50, β=117.4°
$ReOBr_4$	Hexagonal[b]	a=11.49, c=17.44
ReNF	Tetragonal	a=5.88, c=13.00
(TcNF)[c]	Hexagonal	a=5.98, c=4.79
K_2ReF_6	Tetragonal	a=5.86, c=4.60 a=5.86, c=4.60[d] a=5.85, c=4.60[e]
K_2TcF_6	Tetragonal	a=5.81, c=4.64 a=5.81, c=4.65[f]

[a]From single crystal determination.

[b]Cr Kα radiation.

[c]Not identified by chemical analysis.

[d]From Peacock.

[e]From Weise.

[f]From Schwochau and Herr.

TABLE III

INTENSITIES AND INTERPLANAR DISTANCES FOR SOME RHENIUM COMPOUNDS
(Cu Kα RADIATION)

ReNF		(TcNF)[a]		$ReOBr_3$[b]		$ReOBr_4$[b]	
I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)
S	5.340	S	5.209	W	7.564	M	6.057
W-	4.874	S	4.791	S	6.826	M-	5.820
S+	3.493	S	3.502	M-	6.723	W	5.578
W-	3.339	M+	2.985	M	6.310	M-	5.272
M	3.243	M+	2.533	M	6.110	M+	4.998
M+	2.940	S-	2.279	W	5.245	M+	4.916
W	2.667	W	2.230	W	4.665	M	4.590
M+	2.578	M+	2.173	W-	3.925	W	4.341
M-	2.371	M-	1.959	W-	3.784	W+	4.143
M	2.248	M	1.871	W-	3.615	S-	4.009
M+	2.178	M	1.815	W-	3.420	S-	3.863
M	2.080	M+	1.760	W-	3,283	W+	3.737
M-	1.933	W-	1.738	W-	3.164	M-	3,610
M	1.918	W+	1.630	M	3.084	M	3.466
M	1.845	M	1.519	W	3.009	W-	3.286
M+	1.787	M	1.497	M-	2.928	M	3.153
W+	1.765	M-	1.435	M-	2.870	M-	3.091
M	1.749	M	1.407	M	2.759	M	2,974
M	1.618	M-	1.377	M	2.697	W+	2.914
M-	1.563	W+	1.361	M	2.658	S	2.800

TABLE III (CONTINUED)

ReF_4		K_2ReI_6[b]		$ReCl_3$		$ReBr_3$	
I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)
W	7.08	S-	6.370	W-	8.207	M	8.425
M+	5.34	M-	5.643	W	7.949	S+	7.081
S	5.04	M	5.482	M	6.875	M-	6.237
M+	4.745	M-	3.806	S	6.568	M+	5.277
W	4.484	M	3.489	W	6.054	M+	4.671
M	4.291	M	3.379	W-	5.161	M-	4.439
W	4.191	M+	3.346	W	5.045	W	4.250
M	3.952	S	3.209	M+	4.366	M	3.917
M	3.278	W	3.193	M-	3.672	M	3.619
S	3.198	M+	2.972	W	3.365	M-	3.480
M	3.121	S-	2.819	W	3.280	M	3.414
W	2.876	S-	2.765	M	2.926	W-	3.255
W	2.755	W-	2.561	M+	2.742	W+	3.153
W	2.660	W-	2.543	M-	2.679	S-	3.048
M	2.607	W+	2.508	S-	2.417	S-	2.931
W	2.578	M+	2.483	M-	2.365	W-	2.805
M-	2.529	W-	2.268	M	2.243	M	2.706
W	2.491	W	2.197	W-	2.214	W+	2.644
W	2.455	M	2.166	M	2.183	W+	2.600
M-	2.386	M	2.133	W-	2.053	S	2.529

[a]Not identified by chemical analysis.

[b]Cr Kα radiation.

VITA

David E. LaValle was born in Hurley, Wisconsin on August 31, 1914, and graduated from the Hurley High School in 1932. He received a B. S. degree in Chemistry from Michigan State University in 1942. He has been employed by the Hercules Powder Company at Radford, Virginia and the Phillips Petroleum Company of Bartlesville, Oklahoma. Since 1947 he has been on the staff of Oak Ridge National Laboratory.