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FIRST TECHNICAL REPORT,
AND
FIRST QUARTERLY REPORT

on

INVESTIGATIONS OF RHENIUM
I. A SURVEY OF THE LITERATURE

to

FLIGHT RESEARCH LABORATORY
WRIGHT AIR DEVELOPMENT CENTER
WRIGHT-PATTERSON AIR FORCE BASE
OHIO

November 7, 1952

by

C. T. Sims and E. N. Wyler

Contract No. AF 33(616)-232
Expenditure Order No. R-463-7 BR-1
For the Period June 23 to September 22, 1952

BATTELLE MEMORIAL INSTITUTE
505 King Avenue
Columbus 1, Ohio

February 4, 1953

Flight Research Laboratory
Wright Air Development Center
Wright-Patterson Air Force Base
Ohio

Attention WCRRL

Dear Sir:

Enclosed are 11 copies, including one reproducible copy, of a technical report covering the first quarter of work done during the period June 23 to September 22, 1952, under Contract No. AF 33(616)-232 on "Investigations of Rhenium". Copies have also been sent directly to those on the attached distribution list.

This report covers an extensive survey of the literature on rhenium. So far as we are aware, it contains or summarizes all of the known technological information on rhenium. Also of considerable interest to the reader will be the section on the projected as well as the known uses of rhenium.

It is the conviction of the research groups at Battelle concerned with rhenium that this metal is close to the stage where its great potentialities may be realized. We are now in the process of conducting experimental work toward this objective.

Yours very truly,

R. I. Jaffee

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FIRST TECHNICAL REPORT,
AND FIRST QUARTERLY REPORT

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INVESTIGATIONS OF RHENIUM
I. A SURVEY OF THE LITERATURE

CONTRACT NO. AF 33(616) 232

to

FLIGHT RESEARCH LABORATORY
WRIGHT AIR DEVELOPMENT CENTER

from

BATTELLE MEMORIAL INSTITUTE

by

C. T. Sims and E. N. Wyler

November 7, 1952

INTRODUCTION AND SCOPE

The first phase of the research program being conducted under Contract No. AF 33(616)-232, designed to investigate the physical and metallurgical properties of rhenium, is presented as this literature survey. To provide a sound basis for future experimental work, the survey includes all available data on rhenium, compiled and edited so as to present a complete but compact picture of the metal as it is now known.

This information, accumulating in the literature for the past twenty-seven years, has been classified into such major fields of interest as the history of rhenium, its occurrence, recovery and production, and its physical, chemical, electronic, and metallurgical properties. In addition, since a basic aim of this project is to evaluate, and arouse interest in, the prospective applications of rhenium, a quite complete section on the past, present, and future uses of the metal has been included. All of the references on rhenium, even those of only very remote value, have been listed in two distinct classifications: those which apply directly to the text, and those which have not been utilized in the text.

In general, it was found that information on the chemical properties of rhenium was abundant. Extensive work has been done on compound formation and analysis. However, physical-constant data were extremely scarce and usually only one source of information was available for those properties that were found. The physical metallurgy of rhenium is virtually an unexplored field and offers ample experimental opportunities.

DISCOVERY AND HISTORY

In the year 1869, the Russian chemist Mendeléef published his now famous periodic table. Numerous blanks appeared in the original chart, and Mendeléef predicted that these blanks would be filled with then unknown elements; he also predicted the properties these elements would have, and assigned atomic numbers and provisional names. In Group VIIb, headed by manganese, there were two unfilled spaces belonging to Element 43 and Element 75. To these, he assigned the provisional names of eka-manganese and dvi-manganese, respectively.

Despite near completion of the table by the 1920's, these two elements were still undiscovered. In 1925, the situation changed markedly, with almost simultaneous claims of discovery of Element 75 by three separate groups of workers.

W. Noddack, I. Tacke, and O. Berg[1, 2], German chemists, were the first claimants. From the predicted properties of Mendeléef, the natural occurrence of elements, and studies of the properties of manganese, they reasoned that the missing elements would be associated with platinum and would also occur in certain other ores, principally columbite. By chemical concentration of columbite, sperrylite, gadolinite, and fergusonite, they produced a product, which on X-ray analysis yielded spectral lines indicating the presence of eka- and dvi-manganese. They named the elements masurium (At. No. 43) and rhenium (At. No. 75), and also predicted their abundance in the earth's crust to be 10^{-13} and 10^{-12} parts, respectively. The name "rhenium" was in honor of the German Rhineland.

Meanwhile, F. Loring and J. Druce in England, while examining pyrolusite and crude manganese compounds, concentrated a new substance. A few months after the German claim, Druce[3] reported this substance as dvi-manganese, and presented chemical and X-ray evidence as proof. Loring[4] predicted it would form a series of oxides, of which the highest would be of the type M_2O_7.

Also in 1925, V. Dolejšek and J. Heyrovský[5] detected an impurity in the electrolysis of manganous sulfate solutions with the then unique dropping mercury cathode and automatically registering polarograph.

Concentration of the impurity gave the characteristic lines of Element 75. Years later, however, Heyrovský[6] admitted that the polarographic steps at -1.0 and -1.2 volts found in polarograms of commercial manganese solutions, which were the basis for his rhenium claim, must have been due to other elements.

Shortly after Dolejšek and Heyrovský's "discovery", they commenced criticizing the work of Noddack, Tacke, and Berg, claiming the Germans' X-ray lines were due only to thallium and zinc. The Noddacks* and Berg defended themselves[7, 8] and presented more evidence. Druce[9, 10, 11] and Dolejšek and Heyrovský[12, 13, 14] also presented chemical and X-ray evidence to add to the polemic situation. Russian investigators[15, 16] studied numerous platinum ores and vigorously denied the presence of rhenium therein. To further complicate the situation, Prandtl[17] and Herszfinkel[18] in 1927 denied that any of the foregoing scientists had found Element 75. Their main reasons were that other elements, principally zinc and thallium, were being mistaken for dvi-manganese in X-ray photographs.

Whether the Noddacks had actually found Element 75 in 1925 may still be problematical, but it is certain that by 1926 and 1927 it had been separated and concentrated by them, for work on its properties had commenced.[19] The name they had given it, rhenium (Rhinemetal), soon came into general use, and today Noddack, Tacke, and Berg are recognized as the discoverers of rhenium.[20] Element 43, now called technicium, was never produced by the Noddacks in any quantity and they are not credited with its discovery. Their early work was well summed up by Von Hevesy[21] who presented the following table of Roentgen spectra as their proof:

	Element 75				
	L_{α_1}	L_{α_2}	L_{β_1}	L_{β_2}	L_{β_3}
Observed	1429.9	1440.7	1235.0	1204.8	1216.0
Calculated	1430.6	1440.6	1235.5	1204.1	1216.9

Von Hevesy explained that even though the L_{α_1} line coincided with the Zn K_{α_3} line, it appeared too strongly to belong to zinc. The L_{β_1} line coincided with that of W L_{β_8}, but it was far too intense to be the tungsten line. L_{β_2} and L_{β_3} match up with Tl L_{α_1} and Tl L_{α_2}, but are of the expected rhenium, not thallium, intensity. The line L_{α_2} is characteristic of rhenium alone.

On the other hand, the work of Dolejšek and Heyrovský, as well as that of Druce, was severely taken to task by Hurd[22] some years later. Hurd and co-workers at the University of Wisconsin experimented extensively with manganese and pyrolusite ores, using procedures developed by the Europeans. Hurd emphatically denied the presence of rhenium in detectable amounts, and after testing ore to which rhenium standards were

*Walter Noddack married Ida Tacke in 1926, thus the disappearance of the name Tacke from the scene.

purposely added, he stated that the claimants could have found rhenium only by "an amazing sequence of incomplete precipitations, complete reductions, and tremendous absorptions". It was about this time that Heyrovský published his afore-mentioned refutation of a rhenium discovery claim, and Hurd's findings prompted Druce to publish a statement to the effect that he really hadn't been trying to claim discovery all along. Druce has continued very active in the rhenium field. He has written many reviews in the past twenty years, and has culminated this work with his book, Rhenium,[23] in 1948. This is the only modern authoritative text on rhenium, and covers the chemistry field exceedingly well. It is noteworthy, however, that Druce appears to be prejudiced against the Noddacks, and seems to continuously attempt to cloud their now substantiated claim for discovery, both in his papers and in the book. This prejudice must be borne in mind when reading Druce.

OCCURRENCE, ABUNDANCE, AND PRODUCTION

Originally, the Noddacks[1] estimated the rhenium content of the earth's crust at 10^{-12} parts. This value was later revised upward to about 4×10^{-9} parts after analysis of numerous minerals. Thus, rhenium is about 1000 times more rare than molybdenum, and 10 times more rare than iridium.[24] Analysis of meteorites, to find the "natural" abundance of rhenium at first gave theoretically low results.[25, 26] Further analysis of meteorites showed the early results to be faulty; Goldberg and Brown[27, 28] found from 0.28×10^{-6} to 1.45×10^{-6} part of rhenium present, values with good theoretical agreement. A possibility exists that rhenium is also present in the sun[29], but if so, its concentration is minute.[30] Fraunhofer lines show the strong Re 4889.38 A line missing.[31]

Numerous practical sources of rhenium have been uncovered. The basis for this information was also laid by I. and W. Noddack[32] who analyzed over 1800 minerals. Figure 1 shows the locations from which samples were procured and analyzed in the Scandinavian Peninsula. Others[33] have also searched for rhenium. The richest known sources are presented in Table 1, in a roughly chronological order of their study. It is immediately evident that early production of rhenium was from sparse sources of the metal indeed. Recent findings have uncovered relatively rich sources of rhenium; some concentrates, particularly molybdenite, contain nearly 25 per cent. Kronman[34] has suggested that rhenium probably accumulates in carbon-rich rocks also containing sulfur.

Despite no widespread production of rhenium in the United States, these new sources account partially for the reduction in price of rhenium since the early days of German production. In 1930 the price was about $1700 per pound[35], although Kroll[36] listed the "prewar price" as $4725

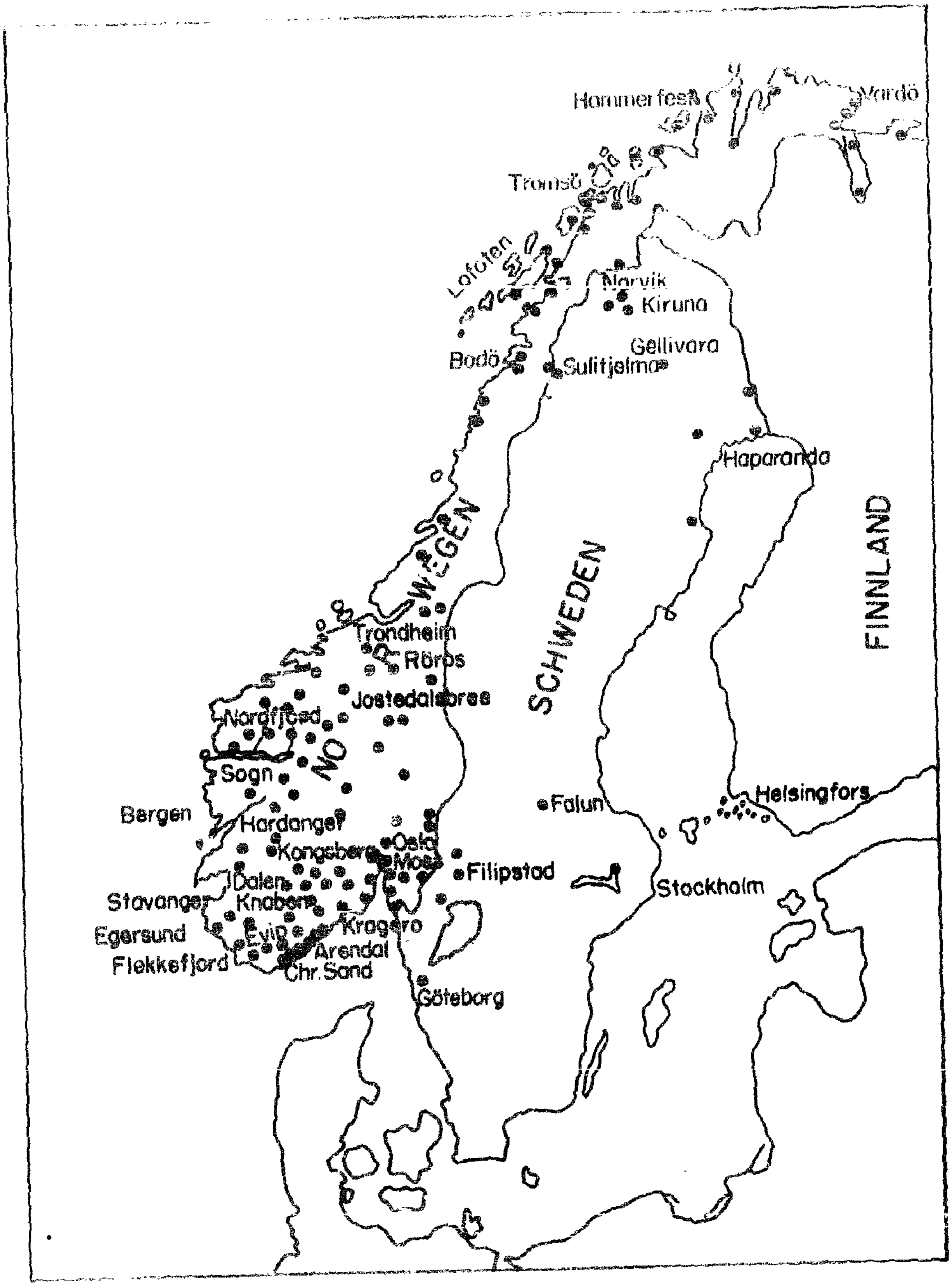


FIGURE I. SCANDINAVIAN MINERAL SOURCES INVESTIGATED FOR RHENIUM CONTENT
Noddack and Noddack [37]

C-4001

TABLE 1. IMPORTANT WORLD SOURCES OF RHENIUM

Source	Geographical Location	Composition of Basic Mineral	Rhenium Content, ppm*	Analysts and/or Reference
Alvite	Norway	$(Zr, Hf)SiO_2$	0.6	I. and W. Noddack[32]
Thortveitite	Norway	$Y_2Si_2O_7$	0.6	I. and W. Noddack[32]
Columbite	Norway	$(Fe, Mn)Nb_2O_6$	0.2	I. and W. Noddack[32]
Molybdenite	Norway	MoS_2	21.0	I. and W. Noddack[32]
Molybdenite	Japan	MoS_2	10.0	I. and W. Noddack[32]
Molybdenite	Siberia	MoS_2	0.6	I. and W. Noddack[32]
Molybdenite	Colorado	MoS_2	1.8	I. and W. Noddack[32]
Platinum Ores	Urals	-	0.8	I. and W. Noddack[32]
Gadolinite	-	-	1.1	I. and W. Noddack[32]
Gadolinite	Finland	-	>21.0	Aartovaara[38]
Potash Waste	Germany	-	-	Anon.[39]
Copper Slate	Mansfeld, Germany	CuS, MoS_2	5.0	Anon.[40]
Manganese Ore	Arkansas	-	10.0	Tyler[41]
Copper Ore	Arizona	CuS(?)	-	Tyler[42]
Molybdenite	Domestic U. S.	MoS_2	50,000	Tyler[43]
Molybdenite	Lainejau, Sweden	MoS_2	250,000	Aminoff[43,44]
Anode Sludge	Norway	-	-	Druce[45]
Gold Extraction Slag	Zmeinogorsk, Siberia	MoS_2	-	Druce[45]
Molybdenite	Northern Wisconsin	MoS_2	-	Works[46]**
Molybdenite	Unknown	MoS_2	320,000	Geilmann[47]
Molybdenite	Stavenger, Norway	MoS_2	310,000	Geilmann[47]
Molybdenite	Africa	MoS_2	280,000	Geilmann[47]
Molybdenite	Arendel, Norway	MoS_2	140,000	Geilmann[47]
Wulfenite	Unknown	$PbMoO_4$	Low	Geilmann[47]
Molybdenite	Kounrad, Kazakh	MoS_2	15,000	Stepanov[48,49,50]
Molybdenite	Tyznyauz, Kazakh	MoS_2	120+	Stepanov[48,49,50]
Molybdenite	Chikoy, Kazakh	MoS_2	120+	Stepanov[48,49,50]
Molybdenite	Australia	MoS_2	110	Morgan and Davies[51]
Glimmerscheifen	Norway	-	Poor	FIAT #697[52]
Flue Dust	Miami, Arizona	MoS_2	10-15,000	Melaven[33]
Flue Dust	Miami, Arizona	MoS_2	3-5,000	Melaven[33]
-	Kennecott Copper Company	-	220	Melaven[33]
-	Bingham, Utah (Kennecott)	-	-	N. Y. Times[53]

*It must be noted that the values presented are analyses of both natural ores and of concentrates.

**Shown by Melaven[33] to be worthless.

per pound. This latter price is false, a result of war economy. The present-day price of rhenium in the United States is around $800 per pound.[35] In Germany it is 11-14 DM per gram[24], one-third the price of iridium.

Melaven[33] has investigated over 100 domestic sources of rhenium. He has indicated that flue dust from copper ores containing molybdenite, collected by the Miami Copper Company of Miami, Arizona, is one of the few sources of rhenium containing a sufficiently high valuables content to be economically extractable.

The world production of rhenium has been very erratic. Figure 2 gives a rough approximation of production, and shows how discovery and utilization of the Mansfeld deposits spurred early high production.[24, 30, 39, 40, 54, 55] German production in the period 1939-1945 is unknown. A reasonable assumption is that it was level or rose slowly from the late thirties' output until the closing days of World War II, when all Germans turned to work more directly concerned with the hostilities.[24] German patents indicate rhenium was still available in the early 1940's. Now, France and England are producing rhenium[55A], but their source of concentrate is the United States.

Mansfeld, Germany, is in the Russian Zone. The Russians have been interested in rhenium for years as witnessed by their extensive work on catalytic properties. It must, therefore, be assumed that production of rhenium at Mansfeld continues under Soviet domination. The Noddacks[24] estimated present world production of rhenium as 2 to 3 tons per year. Since Britain and France, as well as the United States, are all producing rhenium at a low rate, their total production (estimated by the writer as about 500 pounds per year) subtracted from the Noddacks' 2 to 3 tons indicates the Russians have a healthy production indeed.

All rhenium used in the United States came from German sources until comparatively recently. When it was shut off by the war, Professor Melaven commenced production at the University of Tennessee in small quantities,[41] and when his process was patented in 1947, production increased.[43] Melaven has produced a total of 300 pounds of metal since 1947,[33] so his present production is assumed to be about 60 to 80 pounds per year. He estimates that expansion of his facilities would permit production of approximately 50 pounds of metal per week if a good concentrate were continuously available for processing. The concentrate should be available, for some figures[55B] indicate that U. S. production potential is of the order of 20,000 to 30,000 pounds per year.

Present world production centers may thus be considered to be:

1. Mansfeld, Germany (Russian dominated)
2. Balkhash, Kazakh (Russia)
3. France

4. Great Britain
5. University of Tennessee
6. Kennecott Copper Company

It is extremely important to compare the above list with the table previously presented listing world sources of rhenium (page 6). The comparison shows a striking fact. As far as can be ascertained from available information, although Swedish, Norwegian, and [illegible]can ores or concentrates contain the highest percentages of rhenium, none of these sources are presently being worked. From present estimates of potential production, the United States probably has the best resources and best potential production.

EXTRACTION

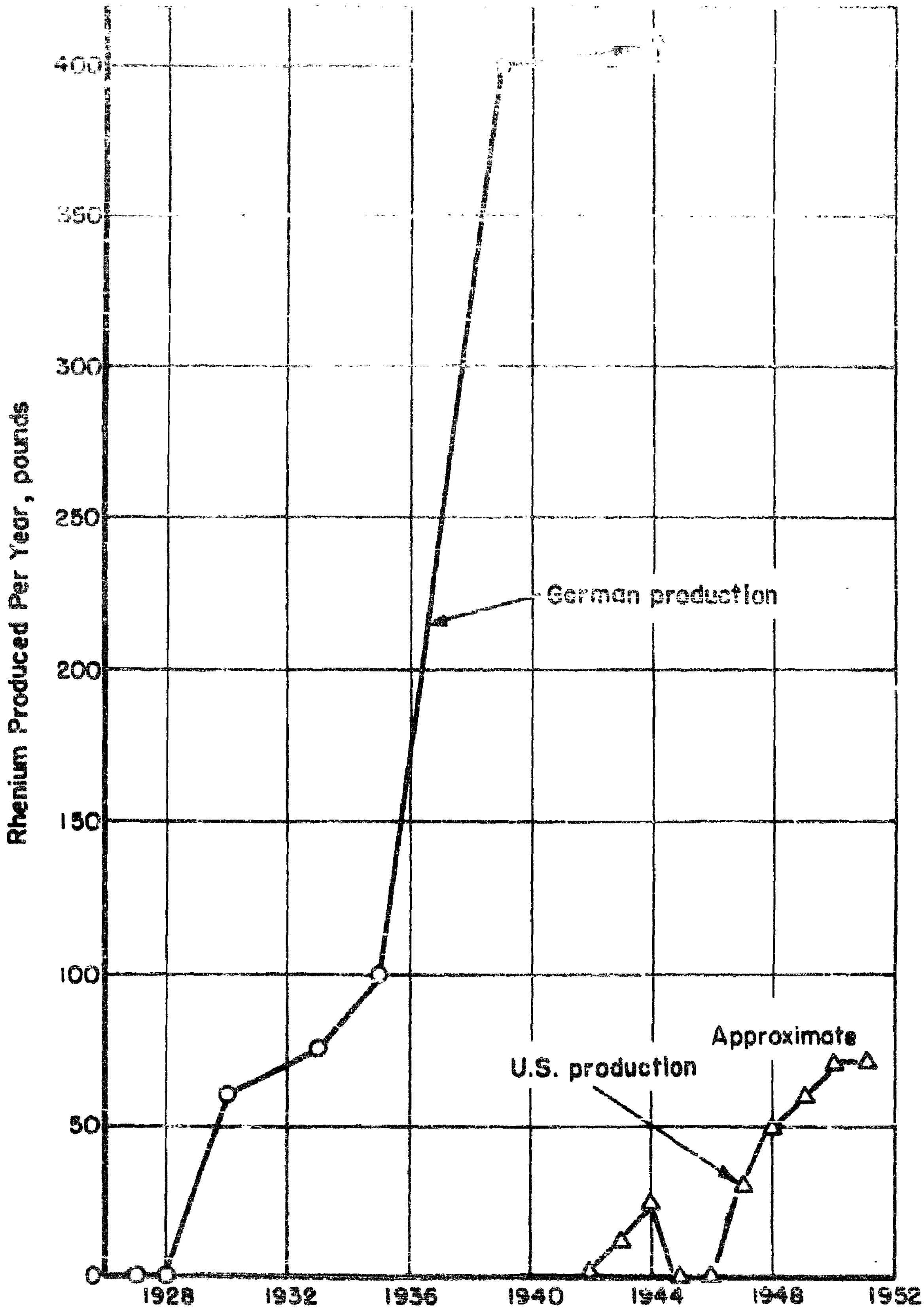
Numerous methods have been published and/or patented for the separation, concentration, and ultimate recovery of rhenium salts or metal from the ores in which it occurs. Some of these processes seem to be too complicated for other than macrolaboratory production, while others, such as that of Feit(56), are aimed directly at full-scale industrial recovery. All of these methods depend upon certain of the characteristic properties of rhenium and its compounds. Some of these properties are listed below.

A. Insolubility of rhenium disulfide.
B. High volatility of rhenium heptoxide.
C. High solubility of rhenium heptoxide.
D. Temperature dependence of the solubility of potassium perrhenate.

Whatever the initial steps in the recovery process, the last step involves conversion of some rhenium compound into metallic rhenium either as a powder or in a consolidated form. These reduction processes are discussed at the end of this section, following presentation of the methods for separation of rhenium salts.

The Noddack Processes

The first process developed by the Noddacks(57) was that used in their original detection of rhenium. Starting with platinum ores, they dissolved the ore in aqua regia, evaporated the solution, and then ignited the residue. The aqua regia insolubles were chlorinated and reduced. This product was mixed with the solution residue, and both were heated in oxygen and hydrogen to sublime the resultant rhenium heptoxide. A solution of the heptoxide was purified and then precipitated with hydrogen sulfide. Purification and X-ray examination for characteristic rhenium lines followed.



Note: Soviet production is not known and not indicated above. It may be on the order of tons per year (see text).

FIGURE 2. KNOWN PRODUCTION OF RHENIUM

A-4002

The Noddacks effectively strengthened their claim as discoverers of rhenium by isolating rhenium from molybdenite. The general method depended on the solubility of high oxides in mineral acids, and also on water-soluble salts of the type X_2ReO_4. In their process[58, 59, 60, 61], molybdenite was dissolved in nitric acid and the molybdenum separated by precipitation as ammonium phosphomolybdate. This process was repeated many times until the bulk of the molybdenum was removed. The rhenium was then coprecipitated with nickel, copper, cobalt, iron, platinum, vanadium, and usually residual molybdenum, all as sulfides. Nickel, cobalt, copper, and iron were next separated by a hydrogen reduction. Re-solution, reprecipitation, and reduction occurred. Rhenium was converted to the oxide and sublimed. Water solution of the oxide and purification followed. The final reduction produced the metal. The process was long and complicated, as many of the steps had to be done over and over. This process is probably not suitable to large-scale commercial production.

One patent[62] suggested a practical selective crystallization method, whereby acid solutions of rhenium salts were evaporated with other metal salts. If the first settling salts were removed, the liquid was then found to be enriched in rhenium. Another method[63] was suggested for separation of rhenium from residues (probably from the Mansfeld copper schist). Solution in nitric acid was followed by chlorination and then acid precipitation of the sulfide. The precipitate was cleaned extensively and finally converted to a solution of perrhenate ion. Potassium perrhenate is insoluble in potassium hydroxide solution, so by this action crystalline potassium perrhenate was separated.

The Feit Process

The Feit process[56, 64, 65] was probably the most important development in rhenium recovery until very recent years. It was used for German production of rhenium from a complex sulfide slime, the by-product from refinement of Mansfeld copper schist. The method was cheap and relatively simple. Slime was extracted with water, to which was added ammonium sulfate. Copper, nickel, and zinc were precipitated as double ammonium sulfates. These were removed and more ammonium sulfate precipitated complex compounds of molybdenum, vanadium, and phosphorous. The addition of potassium chloride to the filtrate formed crystals of crude potassium perrhenate. Several recrystallizations produced a pure product. Reduction of the perrhenate at red heat produced impure rhenium metal, which was purified by leachings with water.

Feit also extracted rhenium from molybdenum pigs.[24] In one method, the pulverized pigs were treated with cold sulfuric acid in a manner which produced an enriched precipitate of potassium perrhenate. In a second method, the oven pigs were melted with sodium sulfate so that rhenium and [illegible] were brought into solution. Separation and concentration of rhenium metal was then completed.

In the reduction processes, Feit[66, 67] found that if rhenium compounds, ready to be reduced at high temperatures with hydrogen, were mixed with a substance that did not allow fusion of the compound at the reduction temperature, reduction would be considerably facilitated. Iron or hematite, mixed with the reducible rhenium compound, will prevent agglomeration in this manner.

Feit's processes have probably been considerably modified[68], but their use continued in Germany at least until 1946.[52]

The Driggs Process

The first American patent on commercial production was obtained by F. Driggs.[69] His procedure was based on the theory that if reducing agents such as sulfur and phosphorus were removed from a rhenium source, oxidation of the rhenium to higher oxides would be simplified. The higher oxide, Re_2O_7, was then volatilized, recovered, purified, and reduced to the metal. Most of the action occurred in a roasting step, where niter cake ($NaHSO_4$) was a[illegible]d to insure formation of Re_2O_7. The process is shown in a flow she[illegible]igure 3.

Russian Processes

The first Russian work on recovery was a laboratory method developed by Kronman, Bibikova, and Aksenova[70] in 1933. Molybdenite was dissolved in nitric acid, the solution diluted, and molybdenum trioxide filtered out. The filtrate was distilled with carbon dioxide and then hydrochloric acid to remove interfering elements. Sulfides of rhenium and molybdenum were precipitated with hydrogen sulfide from acid solution. The rhenium sulfide was freed from molybdenum with hydroxyquinoline. Rhenium was again precipitated, but by nitron as nitron perrhenate. Nitron is a common reagent for this task.

Industrial production evidently began when the Balkhash works in Kazakh, refining molybdenum ores, were investigated for the presence of rhenium. Rhenium was being lost through the stack during roasting of molybdenite.[71] In 1936, wool bags placed in the stack to trap the flue dust were found to retain some rhenium. Finally, in 1946, it was realised that rhenium was present in considerably higher quantities than previously estimated, and Stepanov[49] recommended commencement of a rhenium-extraction plant. Experiments must have been conducted, for shortly it was reported[50] that flue gases containing rhenium, passed through an

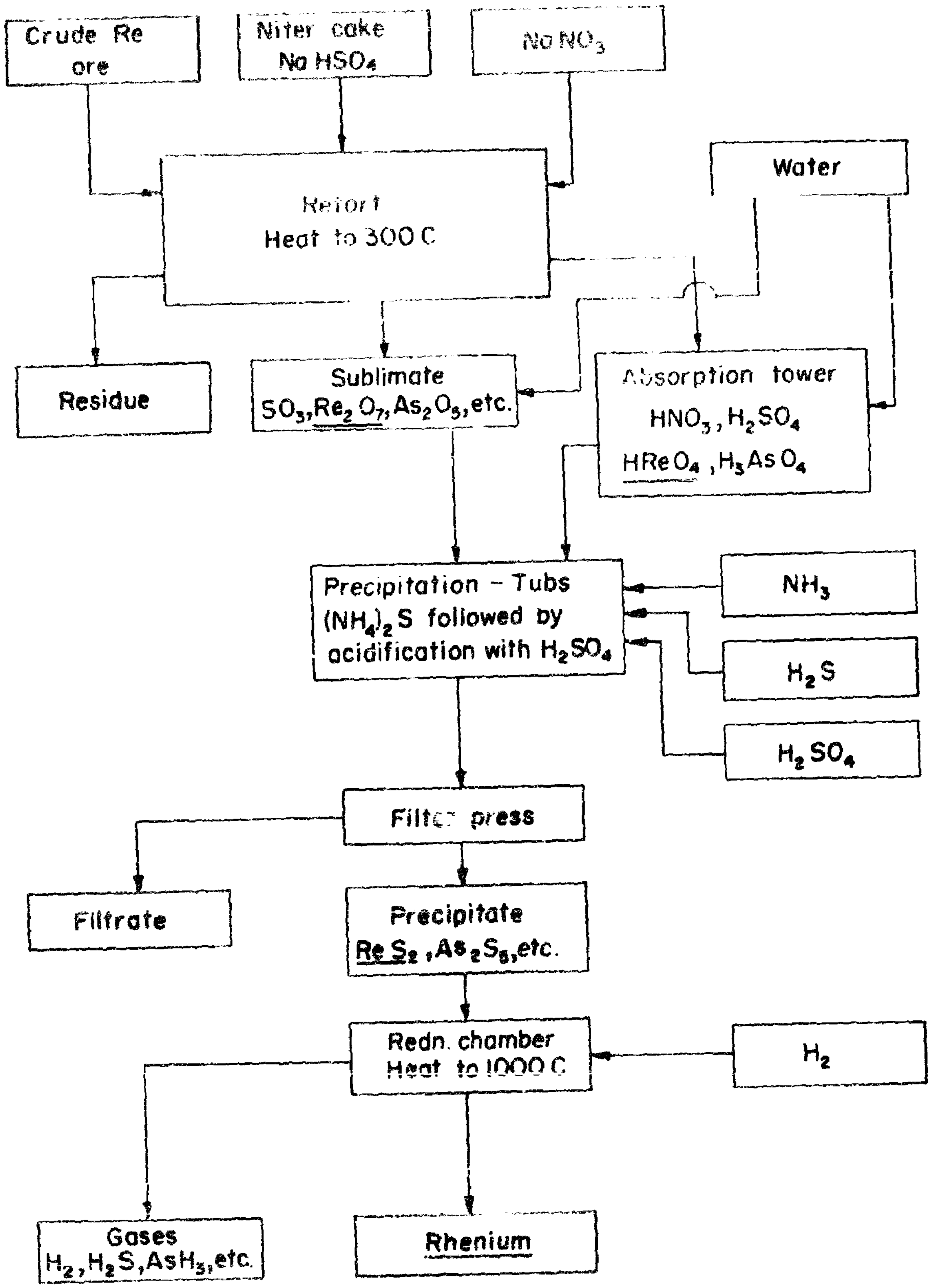


FIGURE 3. DRIGGS PROCESS FOR THE RECOVERY OF RHENIUM

A-4003

asbestos filter, retained over 50 per cent of the metal. If the flue gases were washed in a scrubber, 6 to 10 per cent of the rhenium was saved. A combination scrubber and electrofilter retained 86 to 90 per cent. It is probable that the Russians are now producing rhenium at this plant.

The Tennessee Process

Rhenium was supplied to the United States by the A. D. McKay Company of New York, prior to World War II. This was a German product, and when war intervened, further procurement was blocked. The University of Tennessee had been conducting research on rhenium and, with their supply cut off, began experimentation to produce rhenium from domestic sources. Melaven and Bacon(72) then patented a process for rhenium recovery from flue dust. The process is currently being used there(33), and the rhenium is sold commercially.

A flow sheet (Figure 4) illustrates this process. Rhenium-bearing flue dust, product of a roasting operation, is received at the University. It contains molybdenum and rhenium oxides and molybdenum sulfide. The concentrate is mixed with water and filtered. The soluble rhenium heptoxide is thus removed from the other more insoluble factions. The filtrate is pumped to a mixing vat and solid potassium chloride added. This precipitates crude perrhenate which is subsequently purified. The process is straightforward and simple.

French Processes

Several patents appeared in 1950-51 on French work with rhenium. All deal with the separation of rhenium from molybdenite and involve interesting processes. The first of these(73) required dissolution of the molybdenite in acid or alkaline aqueous solution and adjustment of the pH to 8 or 9. Then a solution of MR_4^+ was added, where:

M = N, P, As, or Sb
R = hydrocarbon radical, such as phenyl

A chloroform solution of tetraphenylarsonium chloride is an example. The chloroform solvated the perrhenate and the aqueous solution was removed. Then 12N hydrochloric acid was added (alone, or with reducing agents, or 0.1N perchlorate solution) to the chloroform solution. Rhenium passed into the aqueous layer, which was distilled until the rhenium started to come over. The residual solution was processed to yield rhenium metal.

Bertolus(74, 75) developed a process which separated rhenium from molybdenum by fractional volatilization of the oxides. Copper sulfide ore

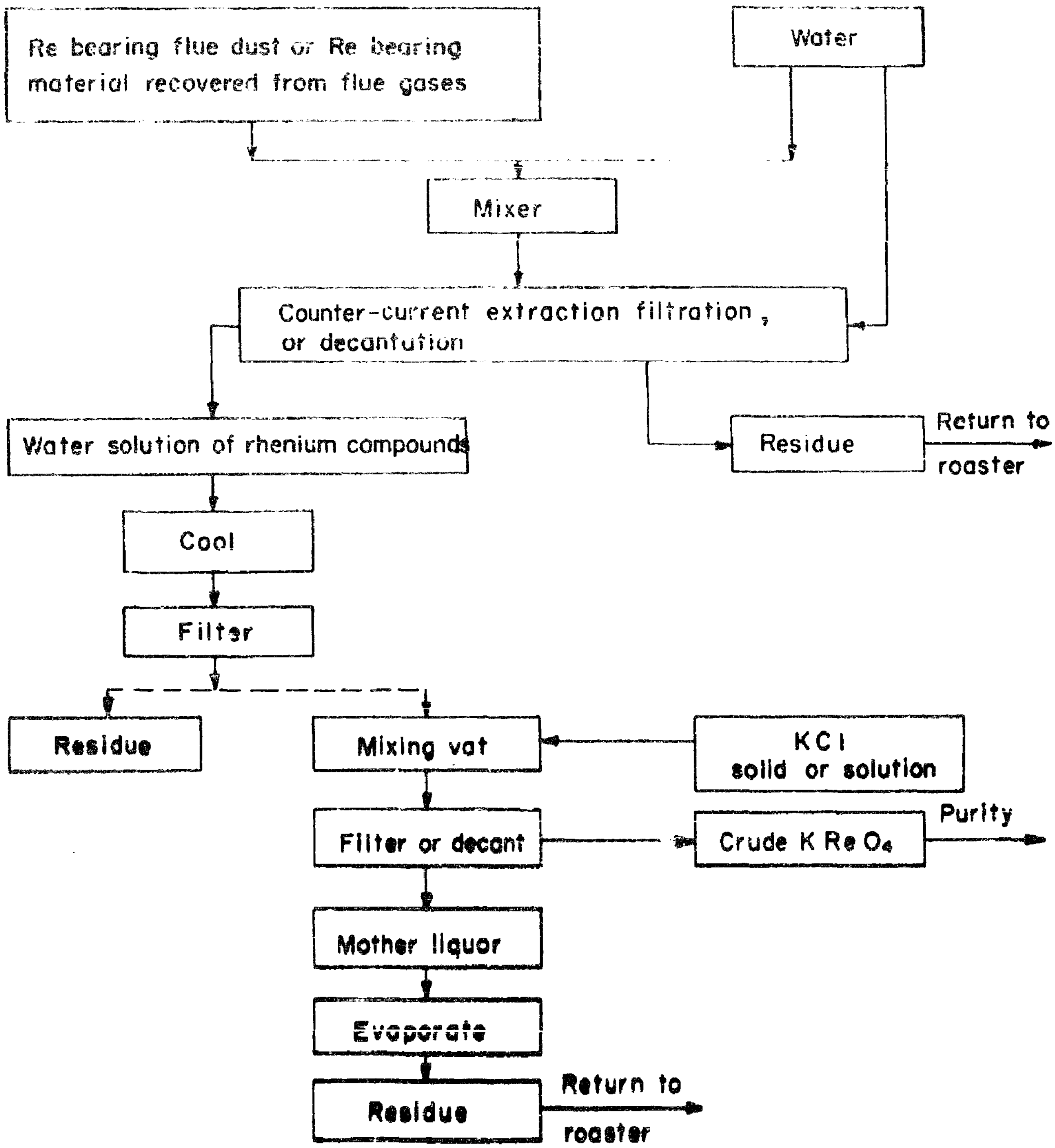


FIGURE 4. TENNESSEE PROCESS FOR THE RECOVERY OF RHENIUM

A-4004

was selectively flotated to give a product rich in molybdenite, containing 1:3000 to 1:5000 parts of rhenium. The molybdenite was then roasted in air at 500 to 600 C. When sulfur in the concentrate started to oxidize, the reaction became exothermic, but was held down to about 500 to 600 C by cooling the oxidizing gases. After sulfur removal was complete, Re_2O_7 formed. This was allowed to volatilize, but the temperature was kept below 700 C to prevent volatilization of the molybdenum oxide. The gases were mixed with cool air and sent to a multicyclone precipitator at 250 to 300 C. A counter-current water washer removed most of the rhenium. The balance, as entrained droplets of solution, was removed in another cyclone precipitator. This process is simple and continuous; it is probably responsible for present French production of rhenium.

Ion-Exchange Separation

Very recently, Fisher and Meloche[76] have reported on the ion-exchange technique as applied to the separation of rhenium from molybdenite. They stated that in 1947 Alexander, at the University of Wisconsin, separated rhenium and molybdenum as perrhenate and molybdate, using the anion-exchange resin Amberlite IR-4B at a pH of 4.8. The column was elutriated of the molybdate with buffered sodium hydroxide.

Fisher and Meloche continued this work, but decided to use Amberlite IRA-400, an exchange resin with greater basicity than the IR-4B. A solution of perrhenate and molybdate (ratio 1:3000) plus 10 per cent sodium hydroxide was passed through an exchange column containing the Amberlite IRA-400. One hundred ± 0.5 per cent of the molybdate was recovered in the effluent. The perrhenate remained in the resin. The column was washed with water, dilute hydrochloric acid, and finally 7-8 N acid. This removed 99 ± 3 per cent of the available perrhenate in a concentrated state which was easily converted to a useful crystalline compound.

The process is excellent, but obviously expensive and definitely time consuming. Thirty hours actual running time were required. Ion exchange, however, is a growing field, and this process achieves a truly complete separation of these difficult-to-separate components. Further development may make this process economically feasible.

Miscellaneous Methods

It was early suggested[77] that a low-temperature roast of copper schist residues containing molybdenite would allow leaching out of the rhenium as potassium perrhenate. This is somewhat analogous to the process disclosed in Melaven's patent.

Much of the Russian work has involved the use of special distillants such as carbon dioxide and hydrochloric acid.[70] Originally utilized to remove impurities, a hydrochloric acid distillation was later used[78] to distill off rhenium heptachloride from nitric or sulfuric acid baths.

As will be noted in the analytical chemistry section of this report, it has been known for some time that if precipitation of rhenium sulfide from an alkaline solution could be effected, separation from molybdenum would be relatively simple. Molybdenum sulfide is fully soluble in alkaline solution as is usually rhenium sulfide. However, Voigt[79] found that if an alkaline solution containing molybdenum and rhenium sulfides (saturated with hydrogen sulfide) were cooled below -5 C, rhenium sulfide would precipitate leaving the molybdenum in solution. This was applied to recovery of rhenium from a furnace pig.

Hixson and M[illegible]r[80] used organic solvents to recover metal values, such as rhenium, from their compounds by interrelated cycles. The rhenium-rich ore or tailings were dissolved in acid. The metal valence was adjusted to allow future solubility in some organic solvent, but the rhenium radical was kept in combination with the elements originally present; i.e., still in aqueous solution. The impure aqueous solution was extracted by a hydrophobic selective organic solvent, and the solvent solution was then re-extracted with water.

Rhenium present in smelting residues and zinc dust, in Japan,[81] can be leached out with water after a sulfuric acid treatment. Also, perrhenic acid in sulfuric acid solution[82] may be separated from molybdic acid by adsorption on Norit (vegetable char) which adsorbs molybdic acid more slowly than perrhenic acid. Evidently this method has not been attempted commercially.

REDUCTION TO METAL

Numerous methods have been reported for the reduction of rhenium compounds to metal. The methods nearly always yield the metal in a powdered form.

Reduction of Heated Oxides by Hydrogen

The most common oxide, rhenium heptoxide, can be reduced by hydrogen[83], but with some difficulty as the heptoxide is so highly volatile. The initial reduction temperature is slightly above 100 C, where the reduction occurs in several stages. The yellowish heptoxide changes to green, blue, then black oxides before the grayish metal powder appears. Druce[84] notes that when the black rhenium dioxide state is reached, reduction temperature should be raised to above 500 C to obtain the metal powder.

Reduction of Heated Sulfides by Hydrogen

Powell[85] recommends reduction of the heptasulfide as the best hydrogen reduction method. A hot acid solution of potassium perrhenate is saturated with hydrogen sulfide, producing the heptasulfide. This is introduced into the reduction tube wet to prevent oxidation. The heptasulfide is nonvolatile and reduces easily in hydrogen at a red heat, although some sulfur is retained in the metal. This is removed by continued high-temperature reduction.

Reduction of Heated Halides and Oxyhalides by Hydrogen

According to Druce[84], hot hydrogen will reduce rhenium halides at about 250 to 300 C according to the equation:

$$2ReCl_3 + 3H_2 = 2Re + 6HCl$$

The inference is that the oxyhalides may also be reduced in this manner, although no further details are presented.

Reduction of Heated Perrhenates by Hydrogen

The most common methods for preparation of rhenium powder are by the reduction of either potassium or ammonium perrhenate.

Potassium perrhenate is reduced with hydrogen[83] at a fairly low temperature. The potassium is converted to potassium hydroxide which is removed by leaching with water. Repeated reductions and leachings are usually carried out for two or three cycles. Melaven[33] reduces the potassium perrhenate at 300 C under 3000 psi in a silver-lined bomb. The reaction[84] is:

$$2KReO_4 + 7H_2 = 2KOH + 2Re + 6H_2O .$$

Unfortunately, complete leaching of the hydroxide is difficult if not impossible, and potassium perrhenate-prepared metal usually possesses some occluded K_2O (around 0.5 per cent).

Ammonium perrhenate can also be reduced to the metal in a similar manner, and is thought to produce a purer[illegible] and also more active[85] product. Melaven first produces the metal from potassium perrhenate (as above), then oxidizes it to rhenium heptoxide. The heptoxide is solvated in water and ammonium perrhenate prepared by passing gaseous ammonia through the solution. This is then reduced to the metal powder.

Another perrhenate commonly used because of its analytical value is nitron perrhenate.[86] This organic salt has the advantage that it can readily be reduced to recover the rhenium content. After an analysis, the precipitate is heated in a current of hydrogen where it melts and breaks down.[84] Alcohol extraction removes the organic components and the resultant mass is again hydrogen reduced to produce a pure product.

Electrolysis of Aqueous Solutions

Several authors, principally Hölemann[87], Fink and Deren[88], and Netherton and Holt[89] have electrolyzed acid, alkaline, and neutral baths to give precipitates or plates of rhenium metal. Their work is discussed below under Electrodeposition.

Thermal Dissociation

The first vapor deposition of rhenium was accomplished by the Noddacks[37, 90] who heated a 0.02-mm platinum wire electrically in an atmosphere of rhenium chloride (valence not mentioned) at 1200 to 1400 C. The chloride dissociated on the hot wire surface and deposited rhenium on the wire. Agte, Moers, et al.[91, 91A], used the same process, but deposited rhenium on a 0.03-mm tungsten wire at higher than 1800 C.

Chlorine freed by these reactions[92] will reassociate with a source of rhenium in the system and act as a carrier, continually depositing rhenium on the wire, until all the rhenium is exhausted. Eventually, a rhenium rod or wire with a tungsten (or platinum) core is prepared. This process is important in the manufacture of lamp filaments, for which several patents have been drawn.

The Thermite Reaction

The thermite reaction, so well known with iron oxide and aluminum powder, can also be performed with rhenium dioxide and aluminum.[93]

The reaction is:

$$3ReO_2 + 4Al = 2Al_2O_3 + 3Re \ .$$

This produces metallic rhenium, which, of course, must then be separated from the aluminum oxide, a step which probably precludes this reduction method from ever acquiring any commercial importance.

CONSOLIDATION AND FABRICATION

Except for the vapor-deposition processes, all of the above reduction methods result in a rhenium product in powder form. The powder must be consolidated into a useable massive state; even the vapor-deposited metal should be further consolidated before a sound structure is realized. The following procedures might be used for this purpose.

Electric-Arc Melting

It is believed that rhenium powder or sections cut from a crystal bar can be fused by arc melting with inert electrodes in a water-cooled copper crucible or hearth. This melting method is being used extensively for producing ingots of molybdenum, titanium, and zirconium. If it can be applied to the production of rhenium ingots suitable for fabrication, it would simplify the consolidation problem considerably.

Sintering

Rhenium powder has been pressed into bars and electrically sintered in hydrogen at 1000 C by the Noddacks.[37]

A more complete description of sintering processes is given in Agte's paper.[91, 94] Powder from the Siemens and Halske Company, possessing a high volume and deep-black color, was pressed at 2000 kg/cm^2 into a 3 x 3 x 40-mm rod. Presintering was carried out in dry hydrogen in a tube furnace where the rod was heated only to 500 C. It achieved sufficient strength so that a hole for melting point determination could be bored with a steel drill without crumbling of the bar. The rod was then sintered at 1000 C in hydrogen where it became very hard and dense, possessing a platinum-like glaze. No information on sintering time or current was reported.

Methods for sintering of rhenium alloys have been mentioned in patent literature by Kurtz and Williams[95, 96], who recommend a sintering range of 1500 to 1850 C under dry hydrogen.

Workability

Agte, et al.[91, 94], found that rhenium sintered at "moderate" temperatures is brittle at room temperatures. However, if sintering is carried out close to the melting point, a certain cold ductility is exhibited in a compression test (liberal translation of "Zerkleinerungsversuch" gives "crushing" test, which may mean size reduction in a device such as a machinist's vise). High-temperature-sintered rhenium can be worked at "high temperatures". Forging can be accomplished (in several stages) at about 800 C, and forging and rolling can be carried out at "high temperatures".

The sintered material behaves differently than vapor-deposited rods, which were described as very soft and pliable, akin to copper. These were coiled, bent, drawn, rolled, etc., but only in small steps. The strength increases during these manipulations.

Bridgman[97] reported that rhenium sheared quietly when subjected simultaneously to high shearing stress and high hydrostatic pressure. Many substances explode under this treatment.

PHYSICAL PROPERTIES

The physical properties of rhenium have been grouped under three major headings: Physical Constants, Spectra of Rhenium, and Nuclear Properties.

Physical Constants

Atomic Weight

Rhenium's position in the periodic table between the Elements tungsten (at. weight 183.92) and osmium (190.2), obviously places its weight between these two values. Loring[98] first suggested an approximation of 187 for the atomic weight, and then Washburn[99] calculated 187.4, a value later shown to be slightly high. From the specific heat[100], the atomic weight is calculated to be 187 by Dulong and Petit's law (see Specific Heat).

The first experimental determination was by the Noddacks[101], who reduced rhenium disulfide in hydrogen, to obtain a value of 188.71 ± 0.15. Schacherl[102] repeated this and obtained 188.7 ± 0.25, but these values were also high due to incomplete reduction of the rhenium disulfide. Hönigschmid and Sachtleben[103] converted silver perrhenate into silver bromide by a painstaking procedure. The perrhenate was prepared in a very pure state several times by three different procedures. The products were fused, and the reaction completed; weight calculations gave a result of 186.31 ± 0.02. This was accepted by the German Atomic Weight Commission in 1931[104], and has not been challenged since, although Aston[105] calculated 186.22 from the correct proportions of the two naturally occurring isotopes, Re^{185} and Re^{187}. The value 186.31 ± 0.02 is the accepted one.

Crystal Structure

Rhenium was found to possess a hexagonal close-packed structure by both Goldschmidt[106, 107] and Agte[91, 94]. They disagreed on lattice constants, so other investigators also made measurements. Results of these measurements and the calculations of atomic radius and volume are shown in Table 2. The values of atomic radii fall approximately between those of tungsten and osmium, as would be expected from the periodic position of rhenium. The lattice constants calculated by Moeller and by Stenzel and Weertz seem to be based on purer material than that of Agte or Goldschmidt, as molybdenum would interfere with this type of data more than potassium. Furthermore, the two values agree quite closely, so the results of Stenzel and Weertz are recommended as probably the more accurate.

TABLE 2. LATTICE CONSTANTS, ATOMIC RADIUS, AND ATOMIC VOLUME OF THE RHENIUM ATOM

Investigator	Year	Lattice Constants a, A	Lattice Constants c, A	c/a	Atomic Radius, A	Atomic Volume, A^3	Remarks
Goldschmidt	1929	2.752	4.448	1.616	1.371		0.3% Mo
Agte, et al.	1931	2.765	4.470	1.616	1.382		0.3% Mo
Moeller[108]	1931	2.755	4.450	1.615	1.378*		0.5% K_2O
Stenzel and Weertz[109]	1933	2.7553	4.4493	1.6148	1.3777*		
Biltz and Meisel[110]	1931					8.82**	-

The lattice constants (a) are accurate to ±0.001 A except those found by Stenzel and Weertz, which are claimed to be accurate to ±0.01%.

*Calculated by the writer
**At absolute zero

The crystal structures of a few rhenium compounds have been reported, the type and dimensions of which are recorded in Table 9 in the Chemical Properties section of this report.

Density

Using the atomic weight found by the Noddacks[101], Goldschmidt[106, 107] calculated the density of metallic rhenium as 21.33 (containing 0.3 per cent molybdenum). This was corrected to 21.40 ± 0.06 for pure rhenium. However, it is known[103] that Noddacks' atomic weight is a false basis for calculation; as a result, Agte[91, 94] calculated 20.53 from the presently accepted atomic weight of 186.31. Experimentally, he found a value of 20.9 for annealed rod. Agte's calculated value is accepted today.

The densities of numerous rhenium compounds are recorded in Table 9 of the Chemical Properties section.

Melting Point

The melting point of rhenium has, more than any other, stirred the imagination of scientists. Rhenium has a very high melting point, second only to tungsten. Agte and co-workers[91, 94] used the drilled-hole method (in an argon atmosphere) to find a value of 3440 ± 60 K. Their rhenium was procured from I. and W. Noddack, and contained only 0.01 per cent impurities. Shortly thereafter, Jaeger and Rosenbohm[100] reported 3160 C. Within the limits of accuracy at such high temperatures, the values are identical. 3440 K is the most commonly used value in the literature. Melting points for tungsten and rhenium on three temperature scales may be tabulated:

Metal	Melting Point C	Melting Point K	Melting Point F
Tungsten[111]	3380	3653	6110
Rhenium	3170 ± 60	3440 ± 65	5740 ± 110

Boiling Point

The boiling point of very high melting metals is difficult to determine, but Richardson[112] estimated by spectroscopic techniques that carbon-saturated rhenium (rhenium takes up little carbon) boils at approximately 5900 C. Tungsten boils somewhere in this neighborhood; one source[113] listed 5930 C. Thus, the boiling point of rhenium is one of the highest known.

Parachor

The parachor of rhenium was determined[illegible] from three different rhenium compounds:

ReO_2Cl_3 — 78.9

Re_2O_7 — 68.9

ReO_3Cl — 76.4

The most significant of these three values is 76.4 because the authors found that ReO_3Cl was colorless, mobile, and easily purified, and possessed a freely moving miniscus. The value for ReO_2Cl_3 is considered inaccurate, because it gave a poorly defined miniscus, even though 78.9 is close to that predicated on the basis of the parachors of tungsten and osmium.

Specific Heat

The specific heat was measured by Jaeger and Rosenbohm[100] in a metal calorimeter, from 0 to 1200 C. The value at t degrees may be calculated from the equation:

$C_p = 0.03256 + 0.$[illegible]$625 \times 10^{-5}t$ cal/g/C.

A mean value for 0 to 20 C is given as 0.03262 cal/g/C.

According to a basic relationship revealed by Dulong and Petit, the product of the saturation value of the specific heat and the atomic weight for a metal is 3R, where R is the gas constant (2 cal per deg). This value is not adhered to by all metals, particularly at elevated temperatures. For rhenium, 3R is surpassed at -66 C. A value of 0.0346[101, 115] cal/g/C has also been reported, but Jaeger and Rosenbohm's work appears to be the most complete and accurate.

Linear Thermal Expansion

The linear thermal expansion of close-packed hexagonal rhenium was determined by Agte, et al.[91, 94] Measurements were taken at room temperature and 1917 C by X-ray methods. There was no variation with temperature and the c-axis expansion was 2.6 times that of the a-axis. The results were:

$\beta\,[001] = 12.45 \times 10^{-6} \pm 8\%$

$\beta\,[100] = 4.67 \times 10^{-6} \pm 8\%$

Since the linear expansion of glass is about 9.0×10^{-6},[116] it should be possible to seal rhenium to it.

Specific Electrical Resistance

The basic room-temperature resistivity of rhenium has been measured by Agte, et al.[91,94], to be 21.1×10^{-6} ohm-cm (± 15 per cent), for both vapor-deposited and drawn wire. The wires were 100 per cent dense and contained impurities. This is the value accepted today. The temperature coefficient of resistance over the range 0 to 100 C is the constant value 3.11×10^{-3}. Other values of the resistivity, ρ, and the temperature coefficient of resistance determined by Agte and also by Meissner and Voigt[117] are found in Table 3. The temperature range covered is from -271.64 to 2710 C. The resistivity of rhenium is approximately four times that of tungsten at room temperature and 1.7 that of tungsten at 2500 C. This value falls between those for lead and strontium.

TABLE 3. THE SPECIFIC ELECTRICAL RESISTANCE OF RHENIUM AT VARIOUS TEMPERATURES*

Temperature, C	Resistivity, ρ, ohm-cm: After Meissner and Voigt	Resistivity, ρ, ohm-cm: After Agte, et al.	Temperature Coefficient of Resistivity From 20 C, C^{-1}: After Agte, et al.
-271.64	2.06×10^{-6}	--	
-268.78	2.08×10^{-6}	--	
-252.55	2.08×10^{-6}	--	
-194.71	4.68×10^{-6}	--	
-190	--	4.94×10^{-6}	3.65×10^{-3}
-184.77	5.39×10^{-6}	--	
-30	--	15.4×10^{-6}	3.35×10^{-3}
0	--	19.8×10^{-6}	3.11×10^{-3}
0.16	18.9×10^{-6}	--	
20	--	21.1×10^{-6}	3.11×10^{-3}
100	--	26.1×10^{-6}	3.11×10^{-3}
2130	--	125×10^{-6}	2.23×10^{-3}
2420	--	130×10^{-6}	2.14×10^{-3}
2710	--	134×10^{-6}	1.98×10^{-3}

*Compiled from data of Agte, et al.[91,94], and Meissner and Voigt[117]. Other compilations may be found in Mellor[120] and Noddack[37].

Vapor Pressure

No research appears to have been completed on this property, so it must be considered unknown.

Spectral Emissivity

The first data on spectral emissivity were calculated by Becker and Moers[118] using values of the black-body melting temperature found by Agte, et al.[91, 94], and themselves, from the following equation:

$$l_n A_\lambda = \frac{C_2}{\lambda} \quad \frac{1}{T_W} - \frac{1}{T_S} \quad ,$$

where

T_W = true temperature,

T_S = brightness temperature,

λ = 0.650 micron.

C_2 = 14,330, a universal constant for radiation processes.

The value of A_λ was found to be 0.42.

Levi and Esperson[119] reported a value of $A_\lambda = 0.366$. The black-body temperature versus brightness temperature of a rhenium surface (rhenium plated on tungsten) is shown in Figure 5, compared with tungsten and molybdenum.

Magnetic Constants

Rhenium was found to have a paramagnetism independent of temperature, in the early 1930's. Numerous papers were published, of which a brief summation of the reported values follows:

Date	Investigators	Coefficient of Magnetism, X, cgs units	Temperature Range, C
1931	Albrecht and Wedekind[121]	$+0.046 \times 10^{-6}$	--
1933	Perakis, Capatos and Kyriakedes[122, 123]	$+68.7 \times 10^{-6}$	20, -23, -79
1934	Perakis and Capatos[124]	$+0.046 \times 10^{-6}$	--
		$+0.037 \times 10^{-6}$	--
1934	Perakis and Capatos[125]	$+0.369 \times 10^{-6}$	20
1935	Perakis and Capatos[126]	$+0.368 \times 10^{-6}$	-190 to 25

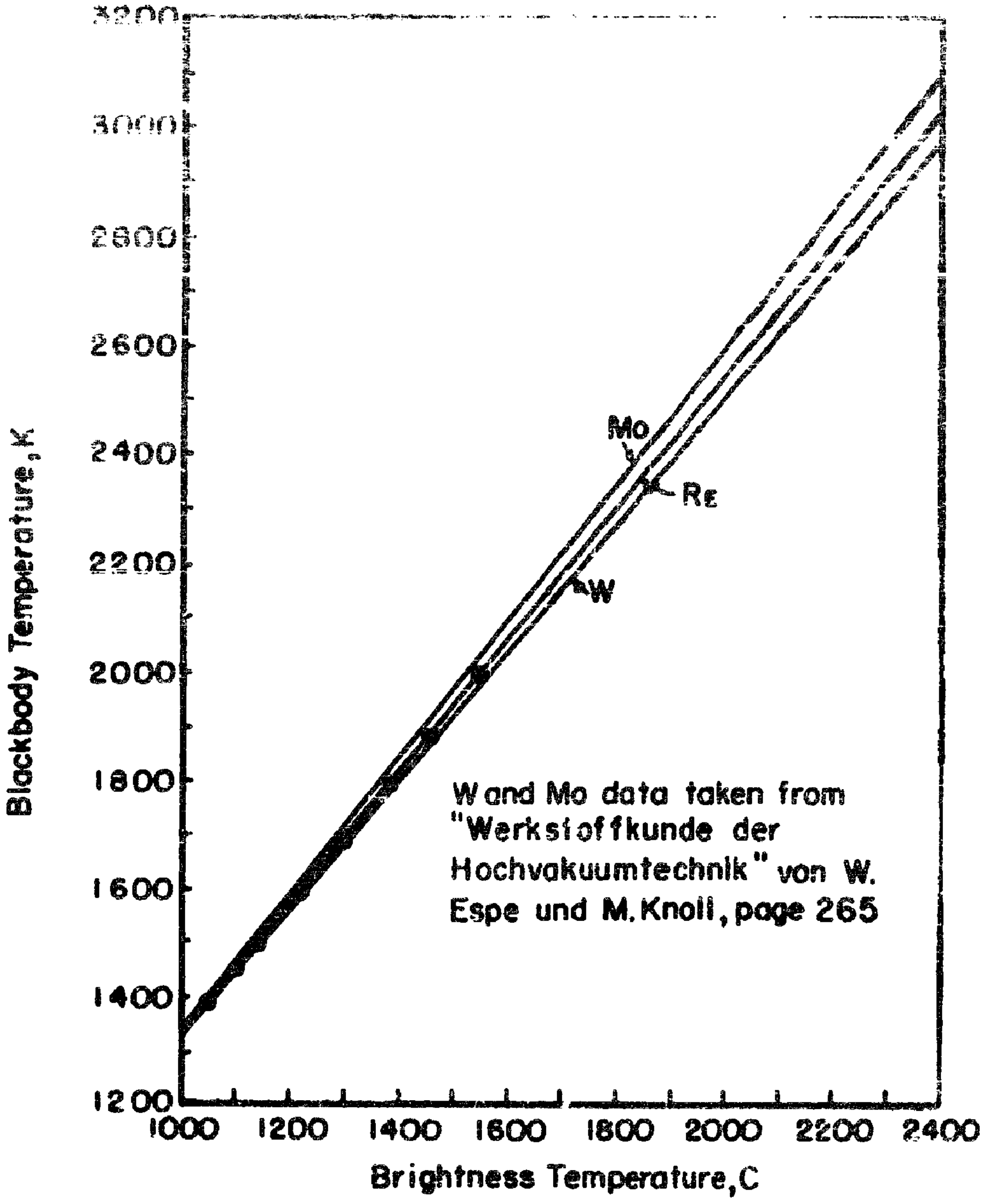


FIGURE 5. BLACKBODY TEMPERATURE PLOTTED AGAINST BRIGHTNESS TEMPERATURE FOR MOLYBDENUM, RHENIUM, AND TUNGSTEN
Levi and Esperson(119)

A-4008

Perakis and Capatos have done the only extensive work in this field, so it must be assumed that their latest values are the most correct. They also determined several values for the temperature-independent paramagnetism of Re^{+7}:

$$\chi = 0.04 \times 10^{-6}$$ (124)

$$\chi = 0.044 \times 10^{-6}$$ (125)

$$\chi = 0.049 \times 10^{-6}$$ (126)

Thus, it can be seen that the specific susceptibility for Re^{+7} is one-eighth that of the pure metal, assuming the last value is most correct. Re^{+4} has a variable paramagnetism.[127] Numerous values have been calculated for rhenium compounds[128, 129], the more important of which have been recorded in Table 9.

The magnetic moment of isotopes $_{75}Re^{185}$ and $_{75}Re^{187}$ was first calculated to be 3.3 nuclear magnetons for both, but more recent work by Alder and Yu[130] has produced these results:

Isotope	Magnetic Moment, nuclear magnetons
$_{75}Re^{185}$	3.1433 ± 0.006
$_{75}Re^{187}$	3.1755 ± 0.006

This all supports the thesis that, for atomic nuclei with an odd number of protons and an even number of neutrons, the moment is from 4.6 to 0.1.[131] Perakis, Karantassis, and Capatos[127] found the moment of Re^{+7} to be 3.83 Bohr magnetons, which agreed closely with 3.87 Bohr magnetons determined experimentally. From this was derived the above conclusion that Re^{+4} has a variable paramagnetism.

Position in the Electromotive Series

The electrode potential of rhenium[120] versus the normal calomel electrode in 2N sulfuric acid is 0.6 volt. This places rhenium between copper and thallium in the electromotive series, a mildly noble position.

Spectra of Rhenium

The Optical Spectrum

Measurements on the arc spectrum of rhenium commenced about 1931 when several investigators[132, 133, 134, 135] became interested in this phenomenon. Using rhenium nitrate, Schober[134] measured the arc

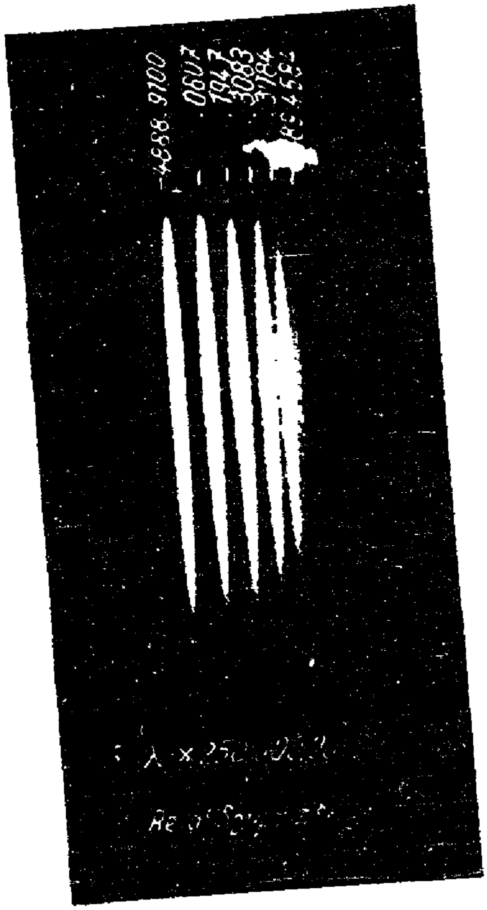


Abb. 6. Hyperfeinstruktur der Linie 4889 nach Meggers.

spectrum from 2200 to 6700 A with a large concave Rowland grating. He found about 410 lines. In the same year, Meggers(136, 137) at the U. S. Bureau of Standards recorded over 3000 lines from measurements taken between 2100 and 8300 A. Pure potassium perrhenate on silver electrodes was the medium. A few of the more important of these lines are recorded in Table 4. It is noteworthy that Meggers reported that at least 25 per cent of the lines showed hyperfine structure. For instance, the strongest line, 4889.15 A, has six components, and the reported wavelength of this line is an average of the wavelengths of these six components. This type of structure is shown in Figure 6, where the wavelengths of the six components are also recorded. 560 of the lines showed an intensity greater than 20 on a 1-to-2000 scale. These were classified as a combination of 115 levels, belonging to quartet, sextet, and octet systems. Meggers found the ionization potential to be 7.85 volts.

TABLE 4. MAJOR LINES IN THE OPTICAL SPECTRUM OF RHENIUM

Wavelength, Angstroms	Relative Intensity	Remarks
3460.47	600	Raie ultime
3464.46	400	
4513.31	300	
4889.15*	2000	Strongest, blue
5270.98*	400	Green
5275.57*	1000	Green
5834.31		

*Strongest in the visible spectrum

Meggers(138) later explored the infrared region to 11,000 A, and other investigators(139, 140, 141) supplemented his work. King(142) observed furnace spectra of tungsten and rhenium and concluded that all of the rhenium lines originated in the lowest energy levels of the atom. These arc spectra are useful for quantitative analysis. Although rhenium content must be less than 1 per cent, Piña de Rubies(143) determined the numbers of rays corresponding to rhenium contents of 5×10^{-5}, 10^{-6}, 10^{-7}, and 10^{-8}. Rhenium in materials such as calcite and molybdenite concentrates can be determined from 0.002 to 0.1 per cent by using the intensity of lines 3451.88, 3460.47, and 3464.72 A.(144) Manganese interferes, up to 16 to 20 per cent, but molybdenum does not.

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FIGURE 6. HYPERFINE STRUCTURE OF THE LINE 4889 A

Meggers From Noddack and Noddack(37)

Englemann(145) studied spectral distribution curves, and from these caluclated photoelectric thresholds.

Material	Wavelength	Remarks
Rhenium block	2677 A	Not in vacuum
Precipitated Re	2671	Not in vacuum
Rhenium wire	2830	Partial vacuum
Rhenium	2799	Calculated by Fowler theory
Rhenium	2480	Probably best value for completely outgassed condition
Rhenium	2487	Corresponds to exit energy

Thus, the optical spectrum of rhenium has been determined from about 2000 to 11,000 Angstroms.

The X-Ray Spectrum

X-rays were instrumental in the isolation of rhenium[1, 2, 3, 5, 14], and as a result information on the spectrum of rhenium was available at an early date. The principal X-ray lines are reported in Table 5. The work of early investigators was checked by Cauchois[149, 150, 151], who has done extensive work in this field determining some of the less common rhenium lines.[151, 152] Other studies on new or minor X-ray lines have been completed by Lindberg[153, 154] and Beuthe[148] (M-series), Inglestam[155] (K-series), and Klinkenberg[156]. Klinkenberg notes that the 6s electron is more tightly bound than the 5d electron.

TABLE 5. PRINCIPAL X-RAY SPECTRUM LINES OF RHENIUM

	X-Ray Lines in Angstroms				
Line	Dolejšek 1926(14)	Berg and Tacke 1926(101)	Wennerlöf 1928(146)	Beuthe 1928(147, 148)	Cauchois 1936-7(149, 150)
L_{α_1}	1430	1429.9	1429.97	1429.8	1429.97
L_{α_2}	-	1440.7	1441.0	1440.7	1440.96
L_{β_1}	1253.3	1236.2	1236.03	1235.9	1236.92
L_{β_2}	1204.3	1204.8	1204.08	1203.8	1204.15
L_{β_3}	-	(1216)	-	1217.6	1217.81
L_{β_4}	-	-	-	1256.3	1256.60
L_{β_5}	-	-	-	1174.7	1174.80
L_{β_6}	-	-	-	1248.1	1248.46
L_{β_7}	-	-	-	1183.3	1183.71
L_{β_8}	-	-	-	1190.0	-
L_{β_9}	-	-	-	1162.4	1162.48
$L_{\beta_{10}}$	-	-	-	1169.8	1169.74
$L_{\beta_{15}}$	-	-	-	1205.7	1205.71
L_{γ_1}	1059	-	-	1058.7	-
L_{γ_2}	-	-	-	1029.8	1030.25
L_{γ_3}	-	-	-	1023.5	1024.06
L_{γ_5}	-	-	-	1034.3	1034.92

Voth[157] determined the relationship between K_{α}, $K_{\alpha'}$, K_{β}, and K_{γ} to be as follows:

$$\frac{E_{\alpha\alpha'}}{E_{\beta\gamma}} = 1.859^{12.785} \approx 7^{-0.691}$$

Three methods were used: the transition method of Küstner, the double-filter method of Ross, and the triple-filter method of Wollam.

The K-absorption limit for rhenium was listed as 173.5 A by Polland(158) and Wennerlöf(37). This was recently revised to 172.66 A by Manescu.(159) Several physicists have found the L-absorption limits; their work is summarized:

	Beuthe(148)	Sandstrom(149,160)	Cauchois(149)	Manescu(161)
L_I	987.1	987.3	987.52	-
L_{II}	-	1035.4	1034.73	-
L_{II}-white ray	1034.0	-	1034.33	-
L_{III}	-	1175.5	1174.63	1174.63
L_{III}-white ray	1173.8	1172.7	1174.05	1174.05

Manescu(161) also studied and recorded the absorption edges for the double hydrate of rhenium dioxide and for potassium perrhenate. A high-transmission region, α, and a low-transmission region, β, were found.

Nuclear Properties

Nuclear Moment

The nuclear moment of both naturally occurring isotopes of rhenium, $_{75}Re^{185}$ and $_{75}Re^{187}$, is 5/2.(105, 162) It was noted in the Optical Spectrum section that many of the rhenium lines are hyperfine. The hyperfine lines, if resolved, show "Flag" patterns caused by a diminishing of intensities from one side to the other. Since this "Flag" effect is regular, both isotopes must have the same moment, 5/2.(163, 164, 165) This is characteristic of atoms with two isotopes, of odd atomic number, and odd atomic weight(166), and was verified by Schmidt, who also found that μ = 3.3 Kernmagnetons for $_{75}Re^{185,187}$. Schüler and Korshing(167) found that an addition of 2 neutrons to the nucleus ($Re^{185} \longrightarrow Re^{187}$) increased the ratio of the magnetic moment to the atomic number by 1.0108. This addition(168) produced only a small change in the magnetic moment (about 1 per cent), which is characteristic of other elements similar to rhenium, such as thallium and copper. Because of the production of a minimum change, the heavier isotope has the greater magnetic moment. These authors also found marked deviation from the interval rule in the term fine structure which allowed calculation of the quadrupole moment, $+2.6 \times 10^{-24}$ for the LS coupling (verified by Solomon(169)). This implies a lengthened nucleus. Introduction of the two neutrons also alters the quadrupole moment (a few per cent) but in the opposite direction from the magnetic moment. The isotope displacements were about 60×10^{-3} cm^{-1}, with $_{75}Re^{187}$, toward the red. Hill(170) has summarized the information as follows:

Nucleus	Q	I	Nucleon Configuration, Unfilled Shells
$_{75}Re^{185}$	+2.8	5/2	3d 5/2 protons, $m_j = \pm 1/2 (5\frac{1}{2})$ positive Q
$_{75}Re^{187}$	+2.6	5/2	3d 5/2 protons, $m_j = \pm 1/2 (5\frac{1}{2})$ positive Q

Isotopes of Rhenium

Naturally Occurring Isotopes. It has been noted above that rhenium has two naturally occurring isotopes, $_{75}Re^{185}$ and $_{75}Re^{187}$. These occur in the ratio of 1:1.62(105, 161) and the packing fraction is -1 ± 2, identical with osmium.

Of the two isotopes, $_{75}Re^{187}$ is the more interesting. It is radioactive and gives off a β-particle.(43, 171, 172) Its half-life was found to be $(4 \pm 1) \times 10^{12}$ years by Naldrett and Libby(171); this data was confirmed and broadened by Sugarmann and Richter(173) who stated that the half-lives of $_{75}Re^{187}$ cluster into two groups, 4×10^{12} and 6.5×10^{12} years. The β-range is 3.5 mg of aluminum/sq cm, giving an upper energy limit of about 43 ekv. $_{75}Re^{187}$ also possesses a short-lived isomer, a comparatively rare occurrence among atomic nuclei. The isomer, $_{75}Re^{187*}$, was found by DeBenedetti and McGowan(174, 175) who assigned it a half-life of 0.65×10^{-6} second with an energy of 0.62 mev. They later(176) estimated the half-life to be $(2.9 \pm 0.6) \times 10^{-7}$ second. Its existence was confirmed by Bunyan, et al.(177), who found a half-life of $(5.26 \pm 0.12) \times 10^{-7}$ second.

The isotopes of rhenium are also produced, of course, as decay products of $_{74}W^{185}$ and $_{74}W^{187}$. In fact, a study of the disintegration of 24-hour $_{74}W^{187}$ led to the discovery of $_{75}Re^{187*}$.(174) In general, $_{74}W^{185}$ yields a 0.55-mev β-particle when decaying to $_{75}Re^{185}$.(178) $_{74}W^{187}$ decays to $_{75}Re^{187}$ through emission of a 1.4-mev β-particle, or a complicated series of γ-ray emissions.(178, 179, 180)

Perlman and Friedlander(181) bombarded $_{75}Re^{187}$ with 100-mev and 50-mev X-rays. They found the (γ, η) yields, relative to $N^{14}(\gamma, \eta)N^{13}$ yield as unity, to be 82.5, 82.0.

Artificial Isotopes of Rhenium. Numerous radioactive isotopes of rhenium have been produced artificially. The first step in this direction was by Amaldi, D'Agostino, and Sigré(182), who claimed neutron bombardment produced a 37-hour period. This has not been found since, but Fermi(183) with the above authors, found a half-life of about 18 to 20 hours. This was confirmed(184), and one of 85 hours was also found. Other investigators soon were working in this field, their work being summarized in Table 6.

It can be seen from the table that about seven artificial isotopes of rhenium are now known, $_{75}Re^{182}$, $_{75}Re^{183}$, $_{75}Re^{184}$, $_{75}Re^{186}$, $_{75}Re^{188}$, and probably $_{75}Re^{189}$ and $_{75}Re^{191}$. Although not reported in the table, $_{75}Re^{194}$ also has evidently been prepared and studied to a limited degree.(211) Of all these, $_{75}Re^{186}$ and $_{75}Re^{188}$ are by far the most common, and when formed from rhenium occur in close proportion to the natural abundance of $_{75}Re^{185}$ and $_{75}Re^{187}$.(106)

In general, the preparation of the lower isotopes of rhenium ($_{75}Re^{182}$, $_{75}Re^{183}$, and $_{75}Re^{184}$) has been by bombardment of tantalum, tungsten, or rhenium with 20 to 40-mev particles(195, 204, 212), 20-mev deuterons(187, 195, 213), or 10-mev protons(188, 195, 204, 213). For example, Gile, Garrison, and Hamilton(179, 180) produced the following reactions from tungsten and tantalum:

$Ta^{181}\ (\alpha, n)Re^{184}$	$W^{182}\ (d, n)Re^{183}$
$Ta^{181}\ (\alpha, 2n)Re^{183}$	$W^{183}\ (d, 2n)Re^{183}$
$Ta^{181}\ (\alpha, 3n)Re^{182}$	$W^{183}\ (d, n)Re^{184}$
	$W^{184}\ (d, 2n)Re^{184}$
	$W^{182}\ (\alpha, pn)Re^{184}$

The common isotopes such as $_{75}Re^{186}$ and $_{75}Re^{188}$ are produced by irradiation of rhenium with X-rays(196), or slow and fast neutrons(185, 214), irradiation of compounds(194), or irradiation of some other metal(191). The higher isotopes, $_{75}Re^{189}$ or $_{75}Re^{191}$, are prepared by neutron or X-ray irradiation of rhenium or some other neighboring element.(201, 202)

Other Nuclear Properties

Rhenium was found by Goldsmith and Rasetti(215) to exhibit resonance capture for neutrons of high energies (30 to 85 v). The capture cross section for slow neutrons was calculated by Sinma and Yamasaki(216), who found a cross-section value of $\sigma = 85 \times 10^{24}$ cm^2 for $_{75}Re^{185}$ and $\sigma = 63 \times 10^{24}$ cm^2 for $_{75}Re^{187}$. The thermal-neutron cross section reported by the AEC is 84 barns per atom.(217) Seren, Friedlander, and Turkel(218) measured these properties of rhenium powder as listed on page 38. $_{75}Re^{185}$ possessed a large capture cross section according to Cork(193) and also according to Hibdon and Meuhlhause(219), who did further work on this subject. Harris, et al.(220), measured the neutron-absorption cross section for rhenium in the neutron flux of the Argonne heavy-water reactor, and found the σ_{pile} to equal 120 barns. Pomerance(220A) determined the thermal-neutron-capture cross section to be 84 barns. Meuhlhause(221) also measured the average number of γ-rays and ν_γ/neutron capture for rhenium. The value for (odd, even) ⟶ (odd, odd) is 3.2.

TABLE 6. INVESTIGATIONS ON THE

Source	Ref. No.	Year	Re^{182} Half Life	Re^{182} Energy, mev	Re^{182} Type of Radiation	Re^{183} Half Life	Re^{183} Energy, mev	Re^{183} Type of Radiation
Fermi, et al.	183	1935						
Kurchatov, et al.	184	1935						
Simma and Yamasaki	185, 186	1939						
Fajans and Sullivan	187	1940						
Creutz, et al.	188	1940						
Miller and Curtiss	189	1946						
Hess, et al.	190	1947						
Goodman and Pool	191	1947						
Wattenberg	192	1947						
Cork, et al.	193	1948						
Mandeville, et al.	194	1948						
Williamson and Hicks	195	1948	64 hr	0.11, 0.27 0.60 0.22, 1.5	Particles Particles γ	13 hr	1.6	γ
Perlman and Friedlander	196	1948	–	–	–	–	–	–
Cork	197	1949	–	–	–	–	–	–

RADIOACTIVE ISOTOPES OF RHENIUM

Isotopes										
Re^{184}			Re^{186}			Re^{188}			Re^{189}	Re^{191}
Half Life	Energy, mev	Type of Radiation	Half Life	Energy, mev	Type of Radiation	Half Life	Energy, mev	Type of Radiation	Half Life	Half Life
						18-20 hr	–	–		
			85 hr	–	–	18-20 hr	–	–		
			90 hr*	1.2	–	16 hr	2.5	–		
52 days	0.85	γ	90 hr	–	–	18 hr	–	–		
54 days	0.1, 0.22, 0.86 ~1.0	β β γ	–	–	–	–	–	–		
–	–	–	–	–	–	18 hr	0.16, 0.48, 0.64, 0.94, 1.43	γ γ γ		
–	–	–	90 hr	–	–	18 hr	–	–		
–	–	–	92.8 hr	1.07	β	18.9 hr	2.05	β		
–	–	–	–	–	–	–	<1.63	γ		
–	–	–	91 hr	0.70 0.64	β γ	~16 hr	–	–		
–	–	–	–	–	–	18 hr	0.23 1.91 0.16	β β γ		
~80 days	0.1 1.0	Particles γ	–	–	–	–	–	–		
–	–	–	92.0 hr	1.07	β	–	–	–		
–	–	–	91 hr	0.64	–	16 hr	–	–		

TABLE 6.

Source	Ref. No.	Year	Re^{182} Half Life	Re^{182} Energy, mev	Re^{182} Type of Radiation	Re^{183} Half Life	Re^{183} Energy, mev	Re^{183} Type of Radiation
Beach, et al.	198	1949	–	–	–	–	–	–
Langer and Price	199	1949	–	–	–	–	–	–
Grant and Richmond	200	1949	–	–	–	–	–	–
Butement	201	1950	–	–	–	–	–	–
Lindner and Coleman	202	1950	–	–	–	–	–	–
Chu	203	1950	–	–	–	–	–	–
Wilkinson and Hicks	204	1950	64 hr	0.11, 0.24 0.22, 1.5	Particles γ	~240 hr	0.16 0.4, 1.6	Particles γ
			12.3 hr	0.16, ~1 0.4, 1.6	Particles γ			
Metzger and Hill	205	1951	–	–	–	–	–	–
Lindner and Coleman	206	1951						
Steffen	207	1951						
Turner and Morgan	208	1951				120-140 days	0.1, 0.30 0.76 1.07	Particles Particles γ
Stover	209	1951	12.7 hr					

* Turner and Morgan also report that Re^{189} yields a 0.16 mev particle and a 1.0 mev gamma ray

(Continued)

Isotopes										
	Re^{184}			Re^{186}			Re^{188}		Re[illegible]	Re^{191}
Half Life	Energy, mev	Type of Radiation	Half Life	Energy, mev	Type of Radiation	Half Life	Energy, mev	Type of Radiation	Half Life	Half Life
–	–	–	90 hr	1.07 0.139 0.212	β γ γ	18 hr	2.10 [illegible]	β 5 γ's		
–	–	–	90 hr	1.063	β					
–	–	–	90 hr	1.095, 0.945, 0.64 0.132, 0.275	β β γ	–	–	–		
–	–	–	–	–	–	–	–	–	17 min(?)	17 min(?)
–	–	–	–	–	–	–	–	–	Months	–
–	–	–	90 hr	0.96	β	17 hr	2.2	β		
50 days	0.2, ~0.7 0.17, 1.0	Particles γ	–	–	–	–	–	–		
2.2 days	0.2, ~1	Particles								
–	–	–	90 hr	1.07 0.93 0.3	β β β	–	–	–	–	–
						16.9 hr				
			90 hr	1.070 0.942	β β					
50 ± 3 days	0.1, 0.2 0.7 1.00	Particles Particles γ							250-300 days*	
				See note below**						

** McGowan(210) states that the β-particles represent 90 per cent of Re^{186} decay.

	$_{75}Re^{185}$	$_{75}Re^{187}$
Natural abundance, per cent	38.2	61.8
Half-life A + 1 isotope, hours	90	18
Isotope cross section, barns	101	75.3
Natural atomic cross section, barns	35.5	46.5
Error, per cent	±20	±20
Mass absorption coefficient of β-particle, cm^2/g of aluminum	16.9	5.5

Dempster's packing-fraction curve indicated that no X-rays should result from K capture; this has been substantiated by experiment.(222) The low-energy-neutron resonance absorption, scattering intervals, and resonance scattering fractions Tn/T for $_{75}Re^{all}$ = 0.11.(223)

THE ELECTRONIC PROPERTIES OF RHENIUM

Since the discovery of rhenium in 1925, a comparatively small amount of work has been done on the investigation of the physical properties of the metal. This appears to be a result, at least in part, of the unavailability of sufficient quantities of the metal in a high state of purity. It is highly probable that if sufficient use is found for rhenium, a suitable means of producing metal with the required purity would be developed. For most electron-tube applications it is desirable to have the construction materials of very high purity, or at least of a controlled-impurity content.

Rhenium is believed to have physical and electrical properties which might make it a desirable material for certain electron-tube applications.

Emission Constants

Only two sets of emission constants for rhenium have been found in the literature. The first measurement of the emission constants of rhenium was made by Alterthum(120). These were determined for a surface of rhenium deposited on tungsten by vapor-phase decomposition of a rhenium halide. The values which were reported are a work function of 5.1 electron-volts when the Richardson constant is 200 amp cm^{-2} K^{-2}. The second set of constants, as determined at the Philips Laboratories by Levi and Espersen, (see Figure 7) gives a work function of 4.74 electron-volts with a Richardson constant of 720 amp cm^{-2} K^{-2}.(119) The surface used was

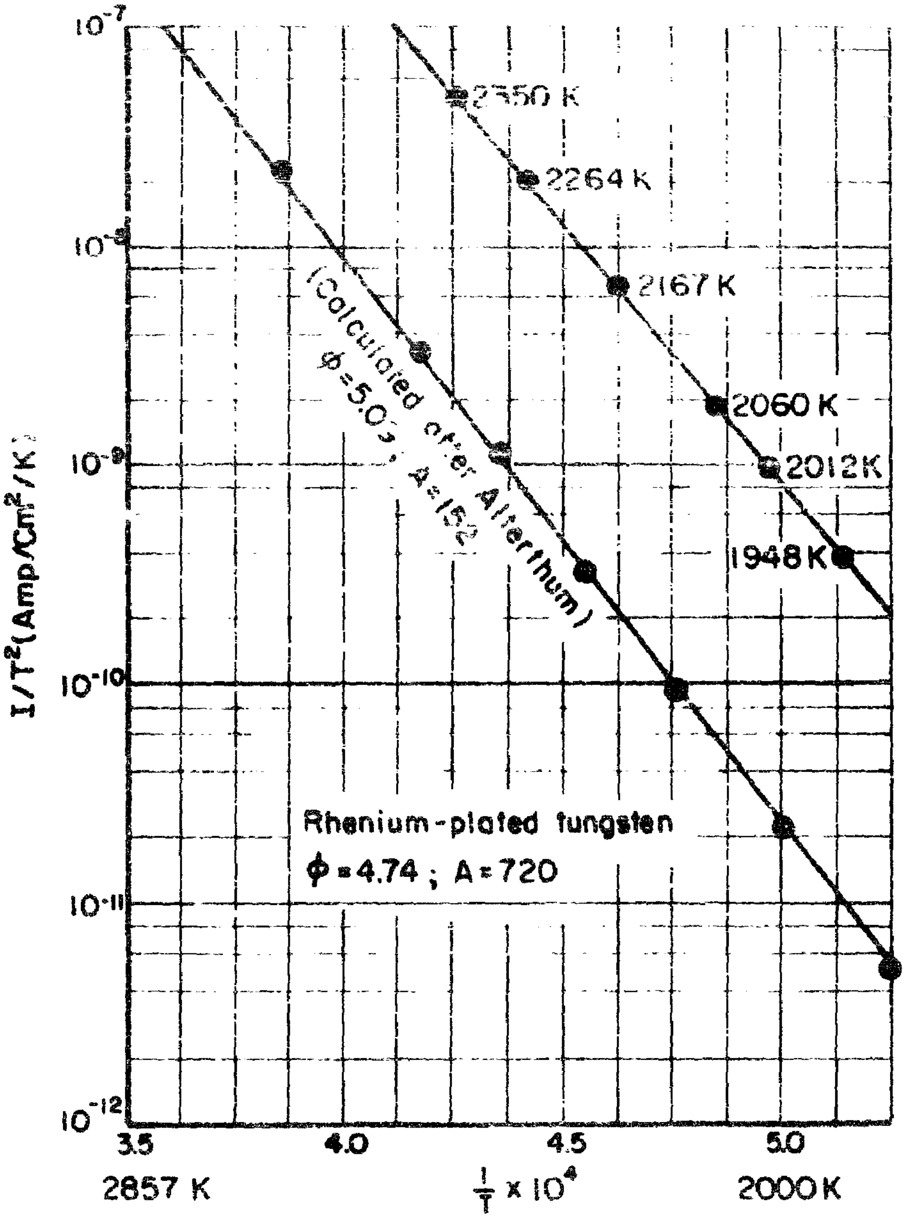

FIGURE 7. A RICHARDSON PLOT OF D-C EMISSION DATA TAKEN FROM AN AVERAGE OF ELEVEN DIODES HAVING RHENIUM-PLATED TUNGSTEN EMITTERS Levi and Esperson(119)

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formed by electroplating rhenium on a tungsten wire in the same manner as described by Fink and Deren.[88] The values were calculated from experimental measurements by employing the following equation:

$$J = AT^2 e^{-\frac{\phi}{KT}} ,$$

where

J is the measured emission current in amperes cm^{-2},

A is the Richardson constant,

T is the temperature, K,

ϕ is the work function,

K is the Boltzmann constant.

Theoretically, the Richardson constant should be 120 amp cm^{-2} K^{-2}. For most metals the experimental value for this constant is about 60 amp cm^{-2} K^{-2}. When the value of this constant significantly exceeds the theoretical value of 120 amp cm^{-2} K^{-2}, or, in the case of metals, 60 amp cm^{-2} K^{-2}, there are usually impurities present on the surface of the material.[224] For this reason it is believed that the emission constants which have been reported for rhenium are not those of the pure metal. The existing thermionic emission constants for rhenium indicate that additional measurements will be necessary in order to establish better values.

Secondary-Electron Emission

The secondary-electron emission of rhenium has been measured for bombarding energies of from 50 to 8000 electron-volts.[225] The maximum yield of 1.3 occurs at an energy of about 900 electron volts. For comparison, the maximum yield for tungsten is 1.38. The most probable energy of secondary electrons from rhenium was found to be approximately 5 electron-volts.

Photoelectric Threshold

The photoelectric threshold for rhenium was determined in 1933 by Engelmann.[144] Measurements were made on rhenium in both block and precipitated form in systems which were not evacuated. The photoelectric threshold reported for rhenium in block form was 2677 A. The photoelectric threshold for rhenium in the precipitated form was found to be 2671 A. The photoelectric threshold which was reported for a rhenium wire in a partial vacuum was found to be 2830 A. These three values were calculated from spectral-distribution curves.

When the Fowler theory was used to determine the photoelectric threshold of the rhenium wire in a vacuum, a value of 2799 ± 3 A was found. This threshold corresponds to a photoelectric work function of approximately 4.42 electron-volts. With the usual experimental procedures and techniques for evaluation of the data, photoelectric measurements of the work function, are not so sensitive to surface impurities and are more nearly correct than thermionic measurements. By comparison of the above photoelectric value with the thermionic emission work function, experienced technologists would accept the photoelectric value as being most nearly correct. If this value is correct, the work function for rhenium is slightly lower than the work function for tungsten.

Hall Effect

Ascherman and Justi have reported work on the electrical conductivity, magnetic increase of resistance, Hall effect, and superconductivity of rhenium.[226] The Hall constant for rhenium is reported to be anomalous, having a value of +3150 x 10^{-6} emu. The increase of resistance of rhenium in a magnetic field has the same characteristics as do other metals of uneven atomic number.

Rhenium becomes a superconductor at a temperature of 0.95 K.

Ionization of Sodium and Cesium Vapor on Glowing Rhenium Surfaces

The yields of ionized atoms in sodium and cesium vapor at a rhenium surface are 20 per cent and 50 per cent, respectively.[227] This compares with a value of 8.5 per cent for sodium vapor at a tungsten surface and 45 per cent for cesium vapor at a tungsten surface. The yield versus temperature relationship for cesium at the rhenium surface does not agree with Langmuir's theory since the absolute values of yields are below the theoretical amounts. For sodium vapor this relationship is that given by the Langmuir theory.

Detector Effect of Rhenium Sulfide

The detector effect of rhenium sulfide has been investigated by Tiede and Lemke.[228] The investigators prepared samples of molybdenum, tungsten, and rhenium sulfides for their tests. The detector effect was a measurable quantity for both molybdenum sulfide and tungsten sulfide, but for rhenium sulfide the effect was so small that it could not be measured with the equipment which was at hand.

The Electronic Properties of Rhenium as Compared With Other Refractory Metals

In order to facilitate evaluation of the possibility of using rhenium in electron tubes, Table 7 was assembled to compare the more pertinent properties which determine the performance of electron-tube components. As may be seen from the table, the spectral emissivity of rhenium is the lowest of those metals listed. This indicates that rhenium, without treatment, is the least applicable where heat dissipation by radiation is of prime importance. Rhenium has a higher electrical resistivity than any of the metals listed in the table. This would allow wire of larger cross section to be used for filament applications. The melting point of rhenium is second only to tungsten for the metals listed in the table. The secondary-emission yield is comparable to that of other metals listed. For most grid applications rhenium would have to be plated with gold or nickel because of its secondary-emission properties. Although the emission constants for rhenium have not been well established, it appears that rhenium might be a better emitter than tungsten. The information given in the table indicates that the boiling point of rhenium is comparable to that of tungsten. For most purposes it appears that rhenium might be superior to other refractory metals in electron-tube applications.

METALLURGICAL PROPERTIES

Information on the metallurgy of rhenium is extremely scarce. Only one measurement of the tensile strength and elongation has been carried out, and that on a very fine wire. A little more is known about rhenium alloys, but practically nothing about the alloy structures has been recorded.

Mechanical Properties

Tensile Strength and Elongation

Agte and co-workers[91, 94] found the tensile strength of 0.25-mm-diameter vapor-deposited rhenium wire (with 0.03 mm tungsten core) to be 50.6 kg/mm^2, or approximately 70,000 psi. The elongation of the wire in this determination was 24 per cent.

TABLE 7. COMPARISON OF PROPERTIES OF REFRACTORY METALS
(All references after Kohl[229] except those indicated)

Metal	Work Function, ϕ, electron-volts	Richardson Constant, A_1, $amp/cm^2/K^2$	Secondary Electron Emission Coefficient, δ_{max}	Electrical Resistivity, ohm-cm (20 C)	Melting Point, C	Boiling Point, C	Spectral Emissivity (0.665 μ)	Emission Current, amp/cm^2 (2600 K)
Molybdenum	4.37	115	1.25(a)	4.8×10^{-6}	2630 ± 50	4800	0.420(b)	2.74
Columbium	4.01	26	-	15.5×10^{-6}	2415 ± 15	>3300(b)	-	4.40
Tantalum	4.10	37	-	12.4×10^{-6}	2996 ± 50	-	0.493	4.43
Tungsten	4.56	45	1.4(a)	5.5×10^{-6}	3410 ± 20	5900	0.470(b)	1.41
Thorium	3.35(b)	60.2(b)	1.1(a)	18×10^{-6}(b)	1845(b)	~3000(b)	0.360(b)	0.376 (1873 K observed melting point)
Rhenium	5.1 4.47 4.42(c)	200 720	1.3	21.1×10^{-6}	3170 ± 50	5900	0.356(d)	0.30(e) 5.44

(a) After McKay[230].

(b) International Critical Tables[231].

(c) Calculated from photoelectric threshold determined by Fowler Plot (Englemann).

(d) $\lambda = 0.650\mu$ for rhenium.

(e) Emission current calculated for the two sets of constants.

Hardness

The Noddacks[37] first reported a hardness of 250 Brinell, but did not specify the state or purity of the rhenium metal. It was probably annealed. Fink and Deren[88] checked this with special measurements when they determined hardness values for electrodeposited rhenium. The hardness of the electrodeposited plate was also 250 Brinell, compared with 400 for chromium plate and 150 for rhodium plate.

In a study of the so-called "frictional strength" characteristics of rhenium-osmium alloys, Winkler[232] found Vickers values of 247 and 637 for pure rhenium in the annealed and cold-worked states, respectively. In these ranges of hardness readings, the Vickers value of 247 is practically identical to 250 Brinell. Winkler also reported readings of 463 Vickers for annealed tungsten and 483 for annealed osmium (see Table 8).

TABLE 8. CHARACTERISTICS OF SOME OSMIUM-RHENIUM ALLOYS (After Winkler)

Alloy	a	c/a	Abrasion Resistance	Scratch Hardness	Vickers Hardness (annealed)
100-Os	2.725	1.583	100	79	438
75-25	2.728	1.586	53	78	550
50-50	2.740	1.595	28	59	533
25-75	2.750	1.602	25	50	356
100-Re	2.754	1.613	21	32	247

Recently, hardness readings on cross sections of hot-wire-deposited rhenium were taken in this laboratory. The average hardness of pure hot-wire rhenium was about 170 Vickers.

Frictional Properties

These properties govern wear resistance, according to Winkler[232], who evaluated several metals from scratch-hardness measurements (Table 8). The scratch hardness was listed as 32 for "soft" and 36 for "hard" rhenium. The former value can be compared with 34 for tungsten and 79 for osmium. From these scratch hardnesses, Winkler showed that "frictional strength" increased from tantalum (atomic number 73) through tungsten (74) and rhenium (75) to osmium (76) and then dropped off rapidly for iridium, platinum, and gold (77, 78, and 79, respectively). Rhenium, then, was second in "frictional strength" only to osmium.

Abrasion Resistance

In the above study, the abrasion resistance was determined to be 11 for tungsten, 21 for rhenium, and 100 for osmium (see Table 7).

It is noteworthy that rhenium, although second best to osmium in the types of properties just discussed, betters tungsten on almost every count.

Alloys of Rhenium

Tungsten

Becker and Moers[118] determined the melting points in the system tungsten-rhenium. The alloys were prepared as small rods by sintering techniques and installed as anodes in an electric-arc system. After primary ignition of the anode, the current was raised until melting of alloy anode was observed, at which time a large melted bend was allowed to form in the head of the anode. True temperature was calculated and the results combined with the melting point determination of Agte, et al. [91, 94]. The resultant solidus curve is shown in Figure 8. It can be seen that the melting points of both pure metals were lowered by addition of the second component. However, a maximum occurred at about 60 per cent rhenium, which the authors assumed to be a new phase with a melting point of about 3010 C. The composition of this phase was equivalent to the formula W_2Re_3, and it formed a eutectic with tungsten and rhenium on both sides of the maximum. The melting points of these minima were 2890 C and 2820 C, respectively. Radiographic examination verified the presence of the new crystalline form, different from both tungsten and rhenium (Figure 9). It was also shown that W_2Re_3 was slightly miscible in tungsten as the saturated solid solution of the new phase in tungsten caused a lattice constant decrease of 1.4 per cent for the tungsten. Solution in rhenium was not proven. A limited solubility for both tungsten and rhenium in the W_2Re_3 phase seemed to exist.

Small amounts (0.5%) of rhenium added to pure tungsten markedly increased the electrical resistivity[91, 94] according to the following figures:

Wire Diameter	As Drawn	Recrystallized
0.15 mm	11.5%	12.3%
0.02 mm	13.5%	14.5%

Iron

This is the only binary system other than tungsten which has been reasonably well studied. Eggers[233] found five phases in establishing the

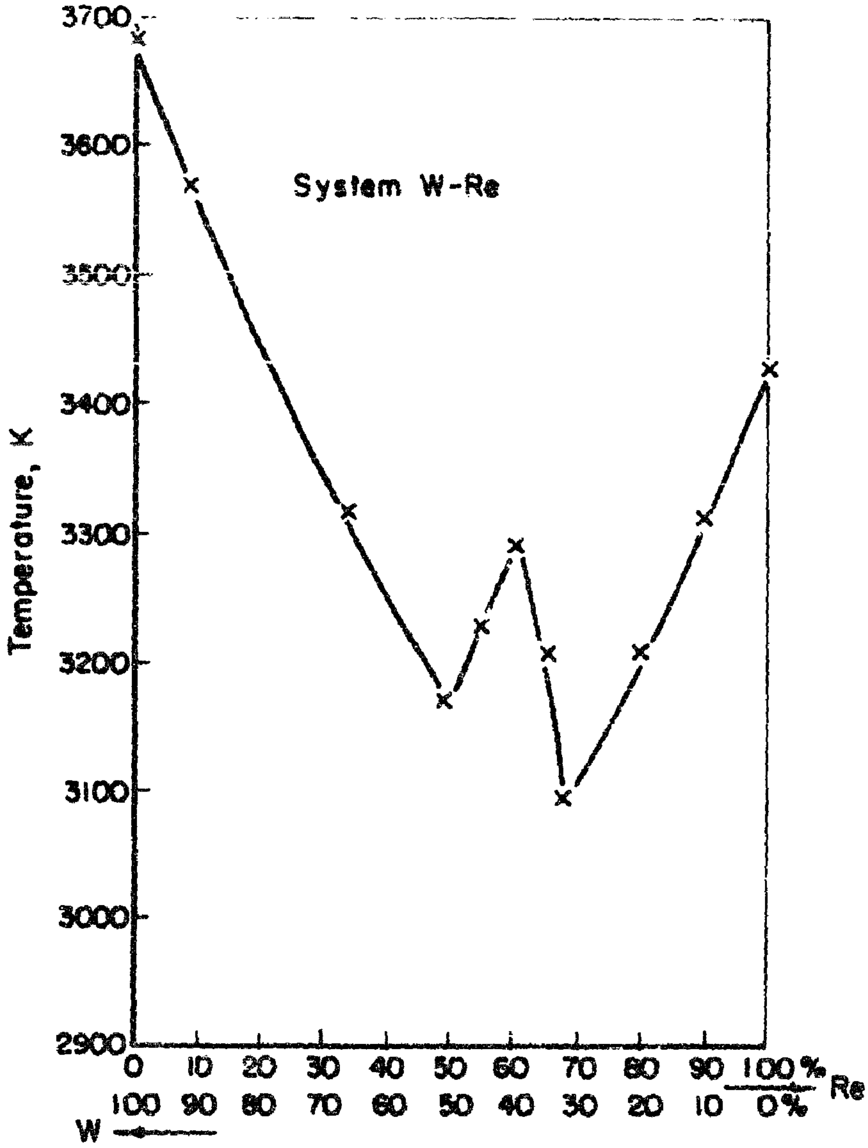

FIGURE 8. SOLIDUS CURVE OF THE TUNGSTEN-RHENIUM SYSTEM
Becker and Moers(118)

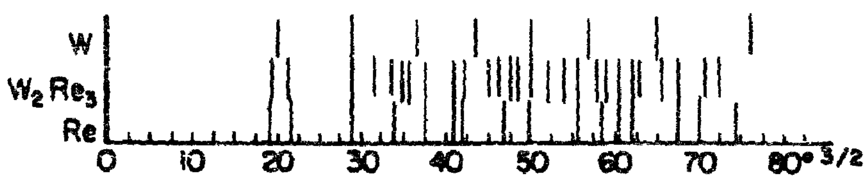

FIGURE 9. SCHEMATIC DIAGRAM OF THE DEBYE-SCHERRER-ROENTGEN PHOTOGRAPH OF W, W_2Re_3 AND Re
Becker and Moers(118)

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equilibrium diagram up to 50 per cent rhenium (Figure 10). The phases are:

1. ϵ-phase — This is probably Fe_3Re_2 and showed a low solubility for iron down to room temperature. It was very hard.

2. η-phase — A phase of wide solubility, apparently based on Fe_3Re, formed at 1205 C.

3. δ-iron — Decomposes eutectoidally to γ- and η-phases at 1540 C.

4. γ-iron — Face-centered gamma iron which dissolves up to 40 per cent rhenium at 1205 C.

5. α-iron — Body-centered alpha which dissolves up to 29 per cent rhenium.

Carbon

In general, rhenium does not react readily with carbon, and one writer(234) reported that rhenium-methane reactions were too slight for observation. Another(235) stated that no carbides were formed with rhenium. However, Trzebiatowski(85) heated rhenium in methane and reported an increase in the carbon content in the temperature range 800 to 2200 C. One per cent carbon was taken interstitially into the rhenium lattice, causing an expansion to take place.

When rhenium powder was treated with carbon monoxide, a more noticeable reaction occurred. The carburization effect depended greatly on the activity of the rhenium powder, the most active being a fine-grained product prepared by reduction of ammonium perrhenate.

Large-grained rhenium powder took carbon into its lattice from carbon monoxide at 410 to 1100 C, which resulted in a greater lattice expansion than when rhenium was treated with methane. This expansion then receded to smaller values (e.g., the solubility decreased) than those resulting from methane treatment if the temperature was raised above 1100 C.

The active, small-grained rhenium formed a new phase when treated with monoxide at 470 C or at 600 C. One analysis reported by Trzebiatowski for a 600 C test showed 4.9 per cent carbon content, but the other part from the same specimen showed only 1.0 per cent carbon, normally the highest carbon content found. The new phase probably is rhenium carbide or a mixture of carbides. This carbide was unstable at high temperatures, and decomposed above 1600 C to form rhenium metal as one of its decomposition

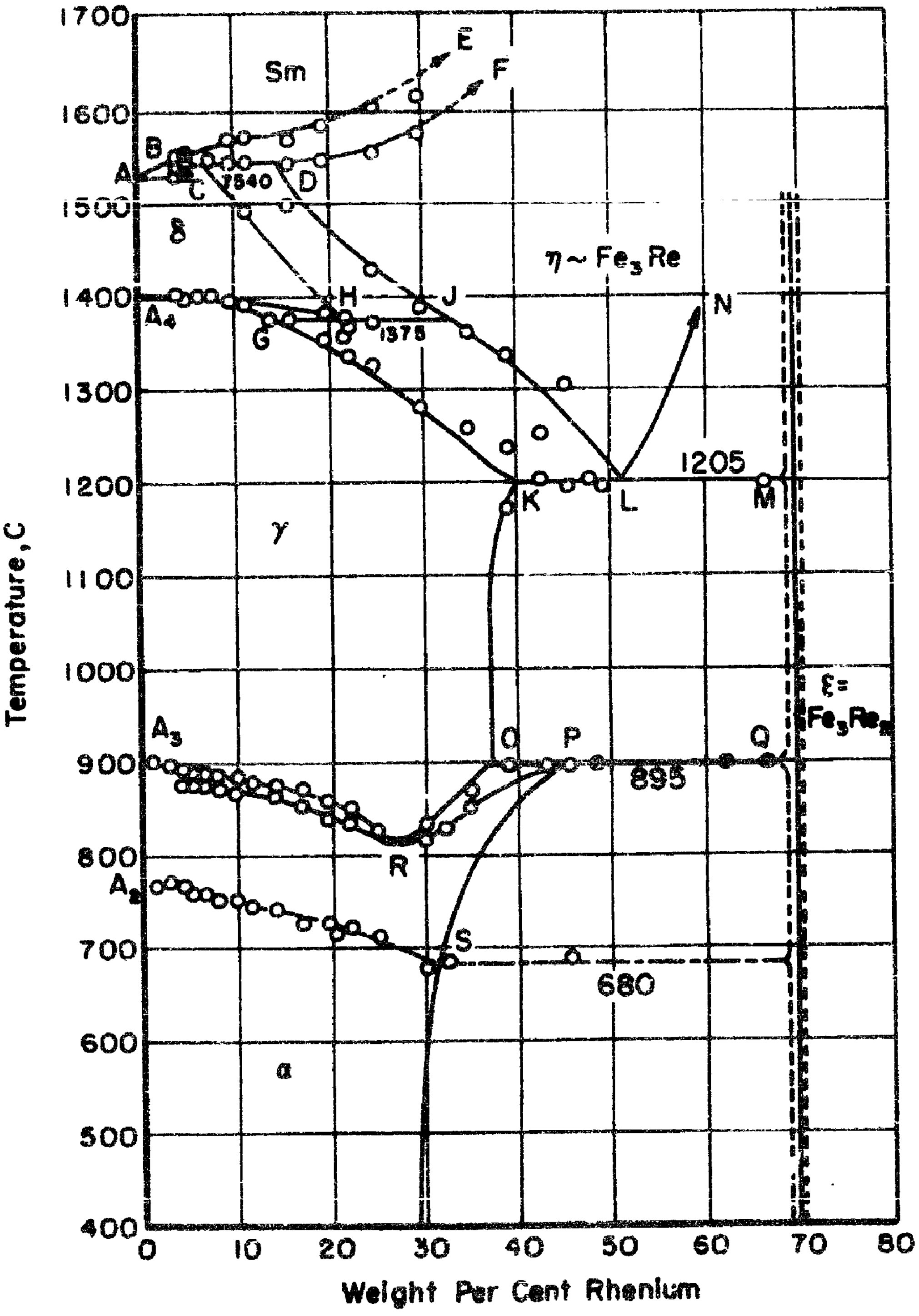


FIGURE 10. PHASE DIAGRAM OF THE IRON-RHENIUM SYSTEM
Eggers[233]

A-4008

products. Thus, rhenium behaves toward carbon as an element intermediary between tungsten and osmium. Osmium also does not form temperature-resistant carbides.

Mercury

During the electrolysis of aqueous potassium perrhenate(236), hydrated rhenium dioxide, $ReO_2 \cdot 2H_2O$, and an amalgam were deposited at the mercury cathode, indicating that rhenium does amalgamate with mercury. Druce(84) also reported that rhenium formed amalgams.

Tin

X-ray studies(237) have indicated that tin is not soluble in rhenium, and rhenium is not soluble in tin.

Zirconium

Wallbaum(238) reported on the lattice constants of the compound $ZrRe_2$.

Osmium

In his study on frictional strength, Winkler(232) prepared a few osmium-rhenium alloys which he subsequently tested for abrasion resistance. The lattice constants of these alloys, given in Table 8, show complete mutual solid solubility.

Miscellaneous Alloys

Numerous patents and papers have presented other binary, ternary, and quaternary alloys containing rhenium. These alloys were most commonly developed for thermocouples or high-wear-resistant applications.

An early patent(239) stated that rhenium will alloy with platinum, rhodium, iridium, silver, or copper. It was recommended(240) that a 3.15 per cent rhenium balance platinum versus platinum thermocouple be used to replace the common Pt/PtRh couple. According to a Fiat report(241), the use of rhenium to replace all or part of the rhodium in thermocouples in this manner evidently became fairly widespread in Germany in the 1930's.

It was also found at this time that if rhenium was added to iridium in amounts up to 10 per cent, better wire-drawing properties were obtained.(242)

Several refractory alloys were patented by Hensel and Emmert(243, 244). These alloys were reported to be fine grained, with low electrode emissivity, and excellent properties for make-and-break contacts. Their compositions were:

	I	II	III
Re	0.01-10	0.01-25	15-25
Mo	1-20	20-60	20-60
W	Bal	40-80	40-60

Hard, white alloys of 2 or more per cent rhenium with a balance of tungsten, molybdenum, chromium, tantalum, nickel, cobalt, or iron have also been patented(245), and are reportedly good for pen nibs. In addition, alloys for pen nibs containing rhenium as base metal (50 to 99.9 per cent) have been patented.(95, 96, 246) They are made by powder-metallurgy techniques and may be precipitation hardened. Three typical alloys of this latter type are:(52)

(1)	60Re	15Ni	10W	15Pt or Ru
(2)	90Re	6W	3Ta	1Ni or Co
(3)	75Re	20Pt	5Ni or Co	

Alloy (2) above is the hardest of the three listed. Many of these developments were triggered by an osmium shortage in Germany.

An alloy of 95Pt-5Re was found useful for platinum-base electrodes, as it was claimed to possess better corrosion resistance than pure platinum. If true, this alloy is extremely resistant to corrosive attack, for platinum is considered the most corrosion-resistant metal in existence. Five per cent rhenium hardened platinum better than twice as much iridium. Rhenium, it should be noted, is cheaper than iridium.(24)

Corrosion Resistance

The following information on the corrosion resistance of rhenium is classified according to corrosive media.

Atmosphere

Rhenium oxidizes in air(91), and when heated to 1000 C it oxidizes at the same rate as tungsten. When only 10 per cent oxygen is present in the ambient atmosphere, no attack occurs below 1600 C, and above 1600 C it oxidizes about 1/3 as fast as tungsten. Water vapor or carbon dioxide present in atmospheres of hydrogen or nitrogen speed oxidation, but when the metal is heated in moist hydrogen at 2000 C, passivation occurs toward the moisture-accelerated oxidation. When so passivated, it still oxidizes in dry air. Sintered rhenium, particularly, corrodes quite readily in air, and evidently suffers a more serious type of attack than has been noticed for plated or arc-melted rhenium.(89) As would be expected, the corrosion product is the heptoxide which is readily hydrolyzed to perrhenic acid, a corrosive media in its own right.

Codeposits of rhenium with nickel or iron(247, 248) were found to halt atmospheric tarnishing.

In general, rhenium is more resistant to oxidation than tungsten, and less so than osmium.

Hydrogen

Agte(91) stated that rhenium was not attacked by moist hydrogen at any temperature, although tungsten is susceptible.

Nitrogen

Moist nitrogen(91) attacked rhenium above 1900 C, and if carbon dioxide was used in place of moisture, the attack still continued. Passivation in moist hydrogen stopped this oxidation, even up to 2500 C.

Inert Atmospheres

Under argon, rhenium(91, 94) yields a slight white fog at about 1400 C, but at higher temperatures no fog and no blackening of a surrounding glass envelope occurred.

Acids

One of rhenium's more noted properties is its high resistance to corrosion by hydrochloric acid. Specimens tested in this media have remained unattacked and untarnished for days.(88) However, nitric acid readily dissolves rhenium. Sulphuric acid has little or no effect, even at elevated temperatures.(84, 89)

Codeposited nickel-rhenium platings(248) showed even more resistance to concentrated hydrochloric acid than did pure rhenium deposits, although the alloy plate did not stand up against 6N hydrochloric acid, and was also attacked by oxidizing acids.

Alkalies

Alkalies, particularly if fused and in the presence of oxidizing agents, will attack finely divided rhenium.(84) Codeposited nickel(248) aided the resistance of plated rhenium to sodium and ammonium hydroxides.

CHEMICAL PROPERTIES

Introduction

The chemical properties of rhenium are quite well known. They are presented in a highly subdivided manner in this report, so a very brief summary of the more practical chemical properties is given here for the casual reader.

In general, rhenium behaves as an element between tungsten and osmium in the periodic table is expected to behave. It is practically inert to halogen acids, but is attacked by oxidizing acids, such as nitric. It forms a long series of oxides, evidencing its wide variety of valences, from Re^{-1} to Re^{+7}. The highest oxide, rhenium heptoxide, readily forms from the action of moist air on the metal. This oxide is volatile when heated, so unprotected rhenium cannot be used at high temperatures. The heptoxide is readily soluble in water to form a strong nonoxidizing acid, $HReO_4$. Rhenium forms a wide variety of other inorganic and organic compounds, but does not form nitrides. Indications are that rhenium forms both carbides and amalgams.

The physical properties of many of the more common compounds will be found summarized in Table 9.

Valence States

Rhenium has now been found to possess all valence states from Re^{-1} to Re^{+7}. Since rhenium occurs in Group VII of the periodic table, the maximum valence of +7 is expected. Re^{+7} is also the strongest rhenium valence. According to Pauling(282), the single-bond radius of rhenium is 1.283 A.

Rulfs and Elving(283), in a study of the oxidation levels of rhenium, stated that the tendency for rhenium to exist in the Re^{+1}, Re^{+2}, or Re^{+3} valence states is very low. They determined oxidation potentials in this range which were reported as follows:

Oxidation State	Potential vs. Standard Calomel Electrode, volts
Re^{-1} to Re^{+1}	-0.50
Re^{+1} to Re^{+2}	-0.27
Re^{+2} to Re^{+3}	-0.02

Rhenium^{-1}

This is the most recent valence of rhenium observed. In 1937 Lundell and Knowles(284) reduced perrhenic acid in the Jones reductor and claimed formation of a Re^{-1} compound. According to Pauling(285) (1947), this is the only known occurrence of a metal with a negative oxidation number. Maun and Davidson(286) and Lingane(287) also prepared Re^{-1} by zinc reduction methods. These preparations of Re^{-1} all occurred in solution only and no compounds were separated, although still more recently, Rulfs and Elving(283) also asserted that some sort of compound must be formed. The following reactions are thought to occur:

$$Re^{-1} + \text{gaseous oxygen} = Re^{+1}$$

$$Re^{-1} + Cu^{+2} = Re^{+1} + Cu$$

$$3Re^{-1} + Re^{+7} = 4Re^{+1}$$

$$Re^{+1} + \text{gaseous oxygen} = Re^{+4}$$

$$Re^{+1} + Cu^{+2} = Re\ (\text{higher oxidation state}) + Cu^{+1}$$

$$Re^{+1} + Re^{+7} = 2Re^{+4}$$

Pauling's(285) explanation of the situation is that rhenium possibly exists with an electronic structure similar to Pt^{+2}, which is isoelectronic with Re^{-1}. Re^{-1} may exist with 4 covalent bonds, with 4 groups arranged in a co-planar square around it. The four groups may be water molecules. If this is the case, hydrorhenic acid, HRe, could be formed, although no one has yet isolated it.

Rhenium^{+1} and Rhenium^{+2}

Two low hydrated oxides of rhenium, $Re_2O \cdot 2H_2O$ and $ReO \cdot H_2O$, were prepared in an impure state by Young and Irvine(288). They reduced perrhenic acid with zinc and cadmium, forming $Re_2O \cdot H_2O$ and $ReO \cdot H_2O$, respectively. Both compounds were isolated.

TABLE 9. KNOWN PHYSICAL PROPERTIES OF

Compound	Name	Crystalline Form	Crystal Dimensions a, A	b, A	c, A	Physical State at 20 C	Density at 25 C, g/cc
ReO_2	Rhenium dioxide	-	-	-	-	Solid	11.4
ReO_3	Rhenium trioxide	Cubic	3.734	-	-	Solid	7.43
Re_2O_7	Rhenium heptoxide	-	-	-	-	Solid	8.2
$HReO_4$	Perrhenic acid	-	-	-	-	Liquid	2.16 (65% soln.)
$KReO_4$	Potassium perrhenate	Tetragonal	5.615	-	12.50	Solid	4.38
$NaReO_4$	Sodium perrhenate	-	-	-	-	Solid	5.24
NH_4ReO_4	Ammonium perrhenate	-	-	-	-	Solid	3.53
$AgReO_4$	Silver perrhenate	-	-	-	-	Solid	6.96
$CsReO_4$	Cesium perrhenate	Orthorhombic	5.73	5.98	14.26	Solid	4.76
$RbReO_4$	Rubidium perrhenate	Tetragonal	5.80	-	13.14	Solid	4.73
$TlReO_4$	Thallium perrhenate	Orthorhombic	5.63	5.80	13.33	Solid	6.89
ReF_6	Rhenium hexafluoride	-	-	-	-	Liquid	4.251
$ReCl_3$	Rhenium trichloride	Hexagonal	-	-	-	Solid	-
$ReCl_5$	Rhenium pentachloride	-	-	-	-	Solid	-
$ReBr_3$	Rhenium tribromide	-	-	-	-	Solid	-
ReS_2	Rhenium disulfide	-	-	-	-	Solid	7.5
Re_2S_7	Rhenium heptasulfide	Amorphous	-	-	-	Solid	4.866
K_2ReCl_6	Potassium rhenichloride	Octahedral	-	-	-	Solid	3.34^{15}
ReO_3Cl	Rhenium trioxychloride	-	-	-	-	Liquid	-
ReO_2Cl_3	Rhenium dioxytrichloride	-	-	-	-	Solid	3.359^{35}
$ReOF_4$	Rhenium oxytetrafluoride	-	-	-	-	Solid	4.032
$Re(CO)_5$	Rhenium pentacarbonyl	Pseudo-tetragonal	-	-	-	Solid	-
$Re(CH_3)_3$	Trimethylrhenium	-	-	-	-	Liquid	1.0+
$K_3[ReO_2(CN)_4]$	Potassium rhenoxycyanide	Monoclinic	-	-	-	Solid	2.704^{40}

Notes: d. = decomposed; s. = soluble; est. = estimated

SOME SELECTED RHENIUM COMPOUNDS

Melting Point, C	Boiling Point, C	Color	Magnetic Susceptibility at 20 C, CGS units $\chi \times 10^6$	Solubility Cold Water, g/l	Solubility Hot Water, g/l	References
d.	-	Brown	+101	-	-	128, 249
d.	-	Red	+94	-	-	128, 250, 251, 252, 253
297	363	Yellow	+90	Very soluble		35, 128, 251, 254
-	-	Colorless	-	Very soluble		255, 256
555	1370	White	+90	3.6	22.2^{40}	128, 257, 258, 259, 37, 260, 261
414	-	White	-	654	$1100^{50.3}$	260, 262
580^est.	-	White	-	17	s., d.	260
455	-	White	-	4.3	27.1^{50}	263, 264
616	-	White	-	2.44	$18.16^{50.3}$	260, 262
598	-	White	-	2.73	$24.6^{50.3}$	260, 262
525	-	White	-	1.15	5.55^{30}	259, 262, 264, 265
18.8	47.6	Yellow	-	s., d.	s., d.	35, 266, 267, 268
Sublimes 500 to 550		Violet	+75	Very soluble		35, 128
-	d.	Brown	+1225	s., d.	s., d.	128, 269
Sublimes 450		Dk. green	+12	-	-	128, 270
-	d.>1000	Black	+62	Insoluble		128, 271
-	d.>470	Black	-	Insoluble		272
-	-	Yellow green	-	Slight Insoluble		273, 274
[illegible]	[illegible]	Yellow	-	-	-	275
[illegible]	[illegible]	Red brown	-	s., d.	s., d	35, 276
[illegible]	[illegible]	Colorless	-	s.	s.	35, 277
	[illegible]	Colorless	-	Insoluble		278, 279
		[illegible]	-	-	-	280
			-	s.	s.	281

Rhenium^{+3}

Trivalent rhenium compounds are fairly common; Re^{+3} was probably first prepared in solution by Manchot, Schmid, and Düsing(289). It was later verified by the separation of halides such as rhenium trichloride, $ReCl_3$, and rhenium tribromide, $ReBr_3$. $ReCl_3$ has been studied by Biltz, Geilmann, and Wrigge(290) and can be prepared by electrolytic reduction of potassium rhenichloride solutions(291, 292) or by reduction of perrhenic acid with a hot hydrochloric acid solution of chromium dichloride.(293) Oxidation of Re^{+3} solutions to higher valence states occurs very readily(291).

Rhenium^{+4}

Re^{+4} has been known since early in rhenium history. Turkiewicz(294) reduced potassium perrhenate with chromium and an iodine catalyst to give Re^{+4}. The reduction of potassium perrhenate by iodine alone proceeds in two stages:

$$Re^{+7} + 2I^{-1} = Re^{+5} + 2I$$

$$Re^{+5} + I^{-1} = Re^{+4} + I$$

Other methods for preparation involve reduction of perrhenic acid by the chlorides of Sn^{+2}, Cr^{+2}, Ti^{+3}, or V^{+3} in hydrochloric acid solution.(293, 295, 296). Re^{+4} ion is responsible for the formation of the so-called "Burgundy Red"(161) and has an ionic diameter of 0.68 A.(297) Some of the more common tetravalent compounds are rhenium dioxide, rhenium disulfide, rhenium tetrafluoride, double halides (as K_2ReCl_6) etc.

Rhenium^{+5}

Re^{+7} reduces easily in hydrochloric acid to Re^{+5} by electrolytic procedures. Re^{+5} is usually an intermediate in the formation of Re^{+4}. It hydrolyzes easily(298) and is unstable in acid solutions, decomposing to Re^{+4} and Re^{+7}.(293, 299) Jakob and Jezowska(300) prepared compounds of the type X_2ReOCl_5. The pentachloride, $ReCl_5$, and a few other pentavalent compounds exist, but Re^{+5} is not so common as Re^{+4} or Re^{+7}.

Rhenium^{+6}

Re^{+6} exists in compounds such as rhenium trioxide, rhenium hexafluoride, and the oxytetrahalides like $ReOCl_4$. The Noddacks(251, 301) reduced rhenium heptoxide with zinc to produce the trioxide in solution, and Biltz, et al.,(252) later prepared it in a free state. Re^{+6} has an ionic radius of 0.58 A.

Rhenium+7

This is the highest and most common of all rhenium valences. Re^{+7} was present in the starting compounds from which virtually all of the compounds mentioned previously in this valence section were prepared. Heptavalence is characteristic of Group VII and is evidenced by rhenium heptoxide, Re_2O_7, perrhenic acid, $HReO_4$, and the salts of perrhenic acid such as potassium and ammonium perrhenates, $KReO_4$ and NH_4ReO_4, respectively.

Oxides of Rhenium

If rhenium metal is fused with sodium hydroxide, there is no color change immediately noticed. However, if oxygen is added[302] to a water solution of the fused material in greater and greater quantities, a series of color changes will occur in this order: dark brown, light brown, yellow, olive green, dark green, brown, bright red. These colors all correspond to varying oxidation states of rhenium, and of course, simultaneously represent the valences listed above.

About 9 or 10 rhenium oxides in these oxidation states have been reported[303], but the existence of several is quite doubtful. As might be expected, the higher oxides form acids in solution. Noddack[302] originally noted the following oxides: Re_2O, ReO, Re_2O_3, ReO_2, Re_2O_5, ReO_3, and Re_2O_7. Others have reported Re_2O_8(or ReO_4) and Re_3O_8. Rhenium heptoxide forms the very strong acid, $HReO_4$. The lower oxides should form basic solutions, but the dioxide does not. These oxides are generally quite stable (the highest are more so than the corresponding manganese oxides[303]), which Noddack[304] attributed to their moderate heats of formation. Neighboring elements, such as tungsten, manganese, or osmium possess higher heats of formation. A detailed discussion of the various oxides follows.

Rhenium Suboxide, Re_2O

Young and Irvine[288], as noted previously, definitely prepared $Re_2O \cdot H_2O$ in the Jones reductor, although Noddack[302] reported it as early as 1933. The compound was black, insoluble in hydrochloric acid, and unattacked by alkaline chromate or acid ferric sulfate. It was soluble in nitric acid and bromine water.

Rhenium Monoxide, ReO

This was also first reported by Noddack[302], but later produced by Young and Irvine[288] in the same manner as $Re_2O \cdot H_2O$. Rhenium monoxide appeared as the double hydrate, $ReO \cdot 2H_2O$, and possessed the same properties noted above for the suboxide.

Rhenium Sesquioxide, Re_2O_3

Impure black Re_2O_3 has been prepared with difficulty by Geilmann and Wrigge.[305]

$$2\,ReCl_3 + 3H_2O\ (\text{alkaline}) = Re_2O_3 + 6HCl$$

Air must be excluded, as the sesquioxide oxidizes readily to perrhenate. It decomposes to Re^{+2}, Re^{+4}, and Re^{+7} in the presence of alkalies.

Rhenium Dioxide, ReO_2

Any high rhenium oxide may be reduced to ReO_2 if treated strongly. The Noddacks[251, 301] prepared it by heating sodium or potassium perrhenate with hydrogen. However, the simplest technique was that of Biltz[249], who heated the heptoxide and rhenium for a day at about 650 C:

$$3\,Re + 2\,Re_2O_7 = 7ReO_2$$

The dioxide is a dark brown or black solid which reduces easily to the metal.[301] Oxidation to perrhenic acid also occurs readily. It will not fuse with barium oxide, but will do so with alkaline sodium and barium perrhenates, and sodium or potassium hydroxides.[302] In the absence of air, rhenites (as Na_2ReO_3) are formed, and with excess alkali, the hyporhenites (as Na_3ReO_4). With air, the perrhenates are formed.

Hydrogen chloride will cause formation of oxychlorides from the dioxide, and the dioxide will also precipitate quantitatively as the disulfide from acid solution when treated with hydrogen sulfide.[306] This is important analytically. The thermite reaction can be performed with ReO_2 to yield rhenium metal.[93] Decomposition of the dioxide occurs at elevated temperatures in vacuum as follows:

$$7ReO_2 = 2Re_2O_7 + 3Re$$

Treatment with sulfur dioxide causes formation of $ReSO_4$.[306]

Rhenium Pentoxide, Re_2O_5

Briscoe, et al.,[307] reduced Re_2O_7 with rhenium metal in a sealed tube, producing a reddish substance claimed to be Re_2O_5:

$$4\,Re + 5\,Re_2O_7 = 7\,Re_2O_5$$

Roth and Becker[308] also formed this oxide as partial product from heating rhenium metal and paraffin oil in a combustion tube. Re_2O_5 was insoluble in cold water, hydrochloric and sulfuric acids, and alkaline solutions, but was soluble in warm water and nitric acid. Chlorine probably converted the oxide to oxytetrachloride.

Tri-Rhenium Octoxide, Re_3O_8(?)

This oxide was formed by the reaction:

$$3\ Re_2O_7 + 5SO_2\ (\text{or } CO) = 2\ Re_3O_8 + 5SO_3$$

as stated by the Noddacks[251]. However, they later surmised it to be compounds of ReO_2 with ReO_3 or Re_2O_7, so its existence is somewhat questionable. It appeared as a black or violet compound to them, although others thought it was blue.[30]

Rhenium Trioxide, ReO_3

Rhenium trioxide was also first noticed by the Noddacks[297, 301], who prepared it from perrhenic acid and zinc. It was unstable and impossible to isolate, but salts of ReO_4^{-2} were similar to manganates, forming bright yellow solutions. Heating caused decomposition to the heptoxide.[251] Biltz[252, 309] formed it from rhenium metal powder and rhenium heptoxide by a long heating process at about 300 C. It was not originally claimed by him as ReO_3, but evidence for this formula was good:

$$3\ Re_2O_7 + Re = 7\ ReO_3$$

Biltz[249] later definitely claimed that he prepared the trioxide by heating weighed amounts of the dioxide and heptoxide for over a week:

$$ReO_2 + Re_2O_7 = 3\ ReO_3$$

and then found it identical with "rhenium blue"[310] found by earlier investigators[30]. It can also be prepared from the heptoxide and dioxane[253, 311]:

$$Re_2O_7 + xC_4H_8O_2 = 2\ ReO_3 + \text{decomposition products}$$

It is a red cubic crystalline solid[252, 312] not affected by water or dilute caustic. Its heat of formation[313] is 82.5 ± 8 kg-cal. The trioxide will liberate iodine from potassium iodide, but no chlorine from hydrochloric acid. In excess of potassium hydroxide and sodium oxide it will fuse to form perrhenates or perrhenites.

Rhenium Heptoxide, Re_2O_7

This is the most common of the oxides, and is readily formed by exposure of the metal to moist air, or by heating. Oxidation of any of the lower oxides also produces the heptoxide.[253]

$$4\ Re + 7O_2 = 2\ Re_2O_7$$

$$4\ ReO_2 + 3O_2 = 2\ Re_2O_7,\ etc.$$

It is a yellow, crystalline substance[251] and is readily soluble in water, hydrolyzing to form the strong acid, $HReO_4$. It is also soluble in alcohol and acetone, but not in ether. It can be reduced by hydrogen, carbon monoxide, sulfur dioxide, and other reducing agents to lower oxides or the metal. It is precipitable from solution with hydrogen sulfide as the heptasulfide.

The heptoxide has a density of 8.2 and melts at 297 C. It sublimes at 363 C[128], so is a completely unprotective coating for massive rhenium above 300 C. Roth and Becker[313] found the heat of formation to be 297.5 ± 2 kg-cal.

Rhenium Tetroxide, Re_2O_8 or ReO_4(?)

The Noddacks[301] originally assumed falsely that the highest oxide possible for rhenium was Re_2O_8, and isolated a white substance claimed to be this compound. Druce[306] also claimed such an oxide. However, its existence was soon questioned by Briscoe, Robinson, and Rudge[314] who tried to make it. They found that moisture lowered the melting point of the heptoxide to the value found by the Noddacks, and furthermore, the sublimate was white. A careful check proved the substance was only Re_2O_7, so the existence of Re_2O_8 (or ReO_4) is highly improbable.

Acids and Their Salts

Acids of Rhenium

Perrhenic Acid, $HReO_4$. This is a stable, colorless acid. It is prepared in several simple ways, the most common of which is by the combination or solution of the very common heptoxide with water:[301]

$$Re_2O_7 + H_2O = 2\ HReO_4.$$

It can also be produced[255] by the oxidation of rhenium metal with nitric acid:

$$3\ Re + 7HNO_3 = 3\ HReO_4 + 7NO + 2\ H_2O.$$

In addition, oxidation of the lower rhenium oxides, such as ReO_2[315], by hydrogen peroxide, chlorine water, and other oxidizing agents produces the acid:

$$2\ ReO_2 + 3\ H_2O_2 = 2\ HReO_4 + 2H_2O.$$

Druce[316] suggested that oxidation of a sul , such as Re_2S_7, to perrhenic acid would be a means of recovery of rhenium after analysis when the sulfide was formed.

Roth and Becker[317] measured the conductivity of perrhenic acid, and found the mobility of ReO_4^{-1} at 18 C was 44 ± 1. Thus, $HReO_4$ is considered a strong acid, although it is not an oxidizing one. It neutralizes bases and its heat of neutralization with potassium hydroxide is 13.5 ± 0.1 kg-cal at infinite dilution. It is usually yellow in color when concentrated, unless very pure when it appears colorless. The densities of aqueous solutions of perrhenic acid were found by Feit[256] and are reported in Table 10.

Perrhenic acid will dissolve zinc, iron, and manganese.[301] It reacts with hydrates of aluminum, zinc, and iron to form perrhenates:

$$Fe + 2HReO_4 = Fe(ReO_4)_2 + H_2$$

$$Fe(OH)_3 + 3HreO_4 = Fe(ReO_4)_3 + 3H_2O.$$

Although not usually an oxidizing agent, additions of various metals and acids cause the formation of oxides:[288, 301]

$$2HReO_4 + Zn + H_2SO_4 = 2ReO_3 + ZnSO_4 + 2H_2O.$$

Perrhenic acid will react with hydrogen sulfide or ammonium polysulfide in acid solution to produce rhenium disulfide, ReS_2.[301] If the solution is dilute, the thioderivatives are apt to be first found.[318] With hydrogen peroxide alone, it gives a red color, which Hagen and Sieverts[319] claimed showed the presence of a "per-acid of rhenium heptoxide".

It can be seen, from the reactions of perrhenic acid with metals and bases, that many metal salts of the acid are formed. They are discussed below.

Other Acids, H_2ReO_4 and H_3ReO_5. Druce[255] reported rhenic acid, H_2ReO_4, as existing in a solution containing perrhenic acid after sulfur

TABLE 10. SPECIFIC GRAVITY OF AQUEOUS SOLUTIONS OF PERRHENIC ACID (AFTER FEIT)

Specific Gravity	Per Cent $HReO_4$	Grams $HReO_4$ per Liter
1.00	0.0	0
1.025	2.93	30
1.05	5.71	60
1.075	8.37	90
1.10	10.91	120
1.15	15.65	180
1.20	20.00	240
1.25	24.40	305
1.30	28.46	370
1.35	31.85	430
1.40	35.00	490
1.45	37.93	550
1.50	40.67	610
1.55	43.23	670
1.60	45.94	735
1.65	48.18	795
1.70	50.29	855
1.75	52.57	920
1.80	54.44	980
1.85	56.22	1040
1.90	57.90	1100
1.95	59.49	1160
2.00	61.00	1220
2.05	62.44	1280
2.10	63.81	1340
2.15	65.12	1400

dioxide was passed through it. The Noddacks[302] claimed the formation of meso-perrhenic acid, H_3ReO_5, and some of its salts from a reaction between barium perrhenate and sodium hydroxide. They stated that it was weaker than carbonic acid.

Salts of Perrhenic Acid

The ReO_4^{-1} ion derived from perrhenic acid forms many salts with metals, positive radicals, and organics. A discussion of all of these with the exception of organics follows. It might be noted that Fonteyne[320] found that the rhenate ion is octahedral in solution, but has a slightly deformed tetrahedral structure in the crystalline state. The valency forces increase when proceeding from the tetrahedral to the octahedral state.

Potassium Perrhenate, $KReO_4$. This salt is the result of neutralization of potassium hydroxide with perrhenic acid,

$$KOH + HReO_4 = KReO_4 + H_2O,$$

or potassium chloride and the acid will react:

$$KCl + HReO_4 = KReO_4 + HCl.$$

Potassium perrhenate is the most important salt of perrhenic acid and is an article of commerce.

According to Vorlander and Dalichau[259] (through Druce[321]) the melting point is 552-3 C and boiling point about 1370 C. The melting point was later determined as 513 C by Kleese and Hölemann[261], but revised to 555 C by Smith and Long[260]. The heat of formation is 263 kg-cal and a saturated aqueous solution at 18 C is 0.0329N. The density is 4.38 and the heat of solution, according to Roth and Becker[317], is 13.80 ± 3 kg-cal at 21.7 C, but Smith and Long reported a value of 7.68 kcal/mole.

Hölemann and Kleese[261] and Pushin and Kovack[322] have determined the water solubility of this salt at various temperatures. Druce[321] has combined this with unpublished data (see Table 11). Smith[323] also determined the solubility, and his data is combined with the above in Table 11. His plot, including the data of Pushin and Kovack and Hölemann and Kleese is shown in Figure 11. Good agreement was found except for a 6 per cent variation at zero C. Pushin and Kovack also found a eutectic of 0.343 per cent perrhenate at 0.060 C, and noted that the freezing point lowering was 1.5 times the theoretical.

In general, it may be noted that the solubility of potassium perrhenate in cold water is low, and is further lowered by the presence of potassium ion. This is helpful in chemical analysis or recovery. Smith[323] studied

TABLE 11. THE SOLUBILITY OF POTASSIUM PERRHENATE (After Hölemann and Kleese, Pushin and Kovack, Druce, and Smith)

Temp, C	$KReO_4$, g/100 cc of water	Temp, C	Per Cent $KReO_4$, per 100 cc of solution
0.00	0.36*	109	12.6
2.01	0.4945	112	14.0
8.30	0.5207	154	26.3
10.20	0.5777	194	39.7
16.90	0.8350	220	50.7
23.80	1.1580	239	59.9
30.00	1.47*	290	71.9
30.90	1.5410	335	84.6
35.00	1.7920	401	89.3
38.95	2.016	445	94.4
40.00	2.22*	470	96.8
44.85	2.525	498	98.4
49.78	3.21*	518	100.0 (mp)
50.45	3.128		
65.80	5.001		
86.15	7.522		
100.30	9.484		

*Per 100 g water.

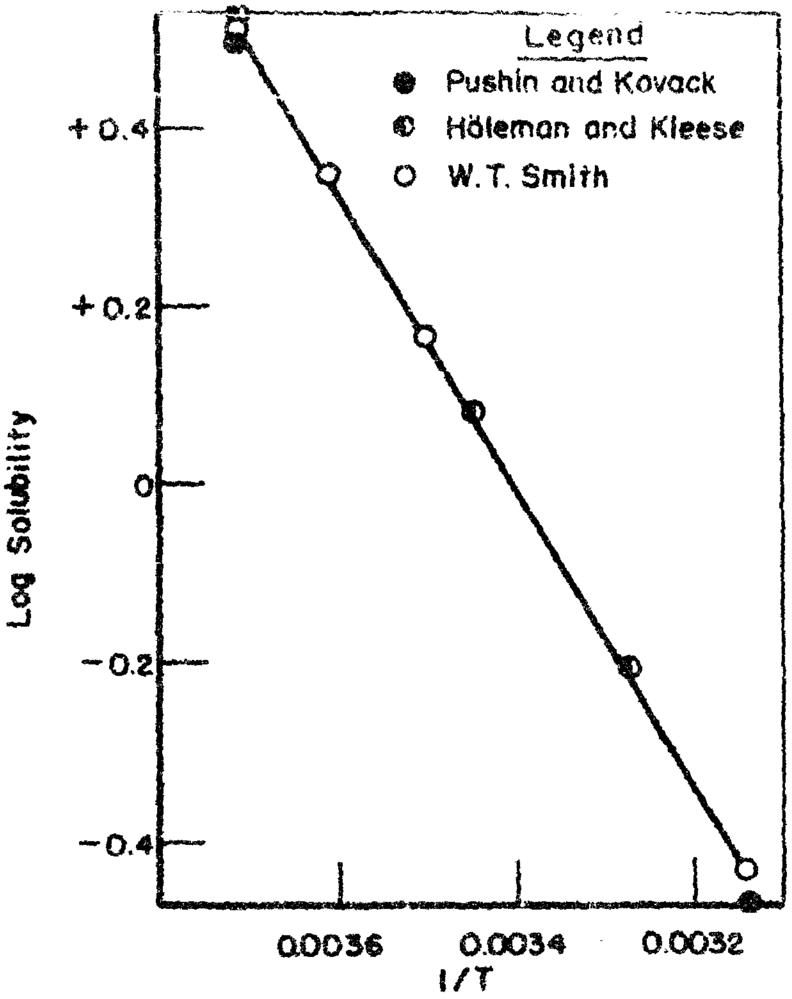


FIGURE 11. TEMPERATURE - SOLUBILITY CURVE OF POTASSIUM PERRHENATE AND WATER
Pushin and Kovack[322],
Höleman and Kleese[251],
and W.T. Smith[323]

A-4009

[illegible] system potassium perrhenate-potassium chloride-water, and found that less chloride was needed to cause effective precipitation if the temperature was depressed to about zero C. Increasing the temperature decreased the separational efficiency.

The electrolytic conductivity of potassium perrhenate solutions at infinite dilution has been determined as follows.[324]

Temperature, C	Molar Conductivity
18	115.5
25	125.7
30	141.8
40	169

Per cent dissociation of 0.02M and 0.01M solutions were also determined.[324]

Potassium perrhenate can be reduced by zinc, calcium, sodium amalgam, hydrazine hydrate, magnesium, etc.[325, 326] It will not be reduced by sulfur dioxide or hydrocarbons.

Careful reduction with zinc and cold hydrochloric acid[326] will yield step-by-step color changes: yellow, yellow green, bluish violet, brownish black, and nearly colorless. This reduction can be stopped at any time and the appropriate oxide separated. In concentrated sulfuric acid solution, Hölemann[327] found that ferrous, stannous, or titanous sulfates will reduce potassium perrhenate to Re^{+5} compounds, while chromous sulfate will reduce it to Re^{+4} compounds. Electrolytic reduction with zinc chloride in the presence of thiocyanates also produced Re^{+5}.[328] In neutral solution[327], electrolysis liberated rhenium and hydrated rhenium dioxide at the cathode.[235]

Numerous other compounds can be prepared, using potassium perrhenate as a starting material.

Ammonium Perrhenate, NH_4ReO_4. This also is an important rhenium salt. In fact, it is more satisfactory than the potassium perrhenate for reduction to very pure rhenium metal as the potassium-produced metal often contains potassium oxide or other impurities difficult to remove.[33] The salt is prepared by neutralization of perrhenic acid with ammonium hydroxide:

$$HReO_4 + NH_4OH = NH_4ReO_4 + H_2O.$$

Early determinations gave its solubility in water to be 120 g/l[301], but this has been recently revised to about 17 g/l at zero C.[260] The temperature of the 120 g/l value is unknown, but it must have been over

50 C. The density of ammonium perrhenate is 3.53 and the heat of solution 6.21 kcal/mole. It decomposes upon heating at about 365 C; but if heated in hydrogen, first the black oxide and then metal powder are produced:

$$NH_4ReO_4 + H_2 = ReO_2 + NH_4OH + H_2O$$

$$ReO_2 + 2H_2 = Re + 2H_2O.$$

As noted above, this is a common method of preparing very pure rhenium metal.

Sodium Perrhenate, $NaReO_4$. This colorless salt is also prepared by acid-base neutralization. It is stable and much more soluble than the other common perrhenates. Its water solubility is about 653 g/l at zero C.[260] Its freezing point is 414 C and density is 5.24.

Silver Perrhenate, $AgReO_4$. Perrhenic acid and silver nitrate form insoluble (4.3 g/l at zero C) silver perrhenate.[264] Its melting point is 455 C and density 6.96. It decomposes at 455 C.[259]

Manganese Perrhenate, $Mn(ReO_4)_2$. This pink salt was first obtained by Druce[329] by dissolving manganese carbonate in perrhenic acid which gave the trihydrate. On drying, the anhydrous salt appeared. The melting point is over 300 C according to Druce[265], but Smith and Maxwell[330] later found it to be much higher, 861 C. It is soluble to the extent of 3400 g/l at 27 C and has a density of 5.12.

Other Perrhenates. Copper, nickel, and cobalt perrhenates were first formed from an acid-carbonate interreaction by Briscoe, Robinson, and Rudge.[331] Addition of ammonia or ammonium hydroxide produced amines of the metal salts, such as $Cu(ReO_4)_2 \cdot 4NH_3$, $Ni(ReO_4)_2 \cdot NH_3$, or $Cu(ReO_4)_2 \cdot 4NH_3$. Smith[260, 264, 330, 332] also prepared other perrhenates. The more common anhydrous ones are given in the list on the following page.

Wilke-Dorfürt and Gunzert[333] and Neusser[334] prepared some uncommon perrhenates, the former workers to show the similarity between perrhenic acid and other Group VII acids such as $HMnO_4$, and the latter while working on the microchemical determination of rhenium. The formulas and colors of the salts are given on page 69.

Name	Formula	Color	Reference
Rubidium perrhenate	$RbReO_4$	White	260
Cesium perrhenate	$CaReO_4$	White	260
Lithium perrhenate	$LiReO_4$	White	260
Barium perrhenate	$Ba(ReO_4)_2$	-	302
Thallium perrhenate	$TlReO_4$	White	302
Beryllium perrhenate	$Be(ReO_4)_2$	-	332
Magnesium perrhenate	$Mg(ReO_4)_2$	-	332
Calcium perrhenate	$Ca(ReO_4)_2$	-	332
Stannous perrhenate	$Sn(ReO_4)_2$	-	332
Mercuric perrhenate	$Hg(ReO_4)_2$	-	332
Cuprous perrhenate	$Cu(ReO)_2$	-	332
Cupric perrhenate	$Cu_2(ReO_4)_2$	White	264
Lead perrhenate	$Pb(ReO_4)_2$	-	332
Cobalt perrhenate	$Co(ReO_4)$	Purple	330
Nickel perrhenate	$Ni(ReO_4)_2$	Yellow	330
Ferrous perrhenate	$Fe(ReO_4)_2$	Dark red	330
Ferric perrhenate	$Fe(ReO_4)_3$	Black	330
Neodymium perrhenate	$Nd(ReO_4)_3$	-	265
Lanthanum perrhenate	$La(ReO_4)_3$	-	265

Salt	Color	Reference
$[Co(NH_3)_6](ReO_4)_3$	Orange yellow	333
$[Cr(NH_3)_6](ReO_4)_3$	Yellow	333
$[Cr(Co(NH_2)_2)_6](ReO_4)_3$	Green	333
$[Zn(NH_3)_4](ReO_4)_2$	White	333
$[Cd(NH_3)_4](ReO_4)_2$	Colorless	333
$[Co(NH_3)_4](ReO_4)_2$	Purple red	333
$[Ag(NH_3)_4]ReO_4$	Colorless	333
$(NO)ReO_4$	Colorless	333
$[Co(NH_3)_6](ReO_4)_3 \cdot 1\frac{1}{2}H_2O$	Orange	334
$[Co(NH_3)_5](ReO_4)_3 \cdot 3H_2O$	Rose	334
$[Co(NH_3)_5](ReO_4)_2$	Red	334
$[Co(NH_3)_5](ReO_4)_2$	Yellow brown	334
$[Co(NH_3)_4](ReO_4)_4$	Granite red	334

Salts of Hyporhenic, Rhenic, and Mesoperrhenic Acids

According to Druce[335], very little is known concerning the rhenates, M_2ReO_4, salts of rhenic acid. However, the Noddacks[302] prepared the sodium and barium salts, Na_2ReO_4 and $BaReO_4$, from rhenium dioxide, sodium hydroxide, and the appropriate perrhenate.

Mesoperrhenates are salts of mesoperrhenic acid, H_3ReO_5, and Scharnow[336] prepared $Ba_3(ReO_5)_2$, barium mesoperrhenate, by evaporation of barium perrhenate with excess barium hydroxide. The hyporhenates, salts of unisolated hyporhenic acid $HReO_3$, have been listed by Druce[321] as:

Sodium hyporhenate	$NaReO_3$
Sodium pyrorhenate	$Na_4Re_2O_7$
Sodium ortho-hyporhenate	Na_3ReO_4

The alkali rhenites, K_2ReO_3 and Na_2ReO_3, are also known to exist.

The Halides of Rhenium

Numerous halides and related halogen compounds of rhenium have been identified. Discussion of these compounds will be presented in six sections: Halides, Double Halides, Oxyhalides, Double Oxyhalides, Double Hydroxyhalides, and Carbonyl Halides.

Rhenium Halides

Fluorides. Two compounds of fluorine, rhenium hexafluoride, ReF_6, and rhenium tetrafluoride, ReF_4, are known to exist. The former was prepared by Ruff, K 'asnik, and Ascher(277) in a fluorspar tube:

$$Re + 3F_2 = ReF_6.$$

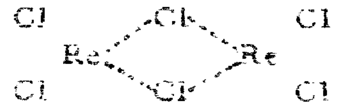
Rhenium hexafluoride sublimes easily, giving off purple clouds in air. Its properties were determined by Ruff(337), Ruff and Kwasnik(266, 267, 268, 338), and others. This hexafluoride, a yellow crystalline material, melts at 18.8 C and boils at 47.6 C. The density is 4.251, and the vapor pressure at the melting point is 261.4 mm. With quartz, the hexafluoride reacts to form oxyfluorides. It also can be oxidized to the oxyfluorides by more common oxidants. Reduction by hydrogen or sulfur dioxide produces the tetrafluoride, and hydrolysis yields rhenium dioxide, and perrhenic and hydrofluoric acids.

Rhenium tetrafluoride, with a melting point of 124.5 C(267) was prepared by reduction of the hexafluoride as stated above. Another fluoride, ReF_7, was also mentioned, but information on it is sparse. A recent attempt(339) to prepare ReF_3 has been unsuccessful.

Chlorides. Several chlorides of rhenium exist. The lowest, rhenium dichloride ($ReCl_2$) was claimed by Schacherl(102) in 1929, but evidently it does not exist, as no mention has since been made of it.

Rhenium trichloride, $ReCl_3$, was first reported by Noddack(297), who formed it from the elements. It is most common, and forms bright red solutions. Other methods of preparation were developed, such as thermal decomposition of pentachlorides or of the double chlorides (as Ag_2ReCl_6)(340), or by reaction between rhenium powder and sulfonyl chloride(341). The latter method is not recommended.

its intensely red solution contains a bimolecular complex:(290, 292, 342)



This can be assumed to be Re_2Cl_6.

The rhenium trichloride crystals are hexagonal, violet black in color and sublime at 500 to 550 C. The trichloride hydrolyzes to a hydrated oxide[343, 344] or an oxide, and can be oxidized by oxygen to give various oxychlorides:

$$6ReCl_3 + 7O_2 = 4ReO_3Cl + 2ReOCl_4 + 3Cl_2.$$

However, it is stable to any oxidation or reduction in acid solutions.[302] In basic solution, reduction will normally proceed (without lower chlorides forming) directly to metallic rhenium[302, 343], although zinc, sodium, or mercury will cause formation of Re^{+1}. Precipitation with hydrogen sulfide is possible, but not quantitatively.[344] Ammonium hydroxide causes complex reactions with rhenium trichloride[345] and tensiometric examination shows the existence of ammoniates: $ReCl_3 \cdot 14NH_3$, $ReCl_3 \cdot 7NH_3$, $ReCl_3 \cdot 6NH_3$. The addition of sodium hydroxide causes a brown precipitate, and Re^{+2}, Re^{+4}, and Re^{+7} are found to be present. Insoluble double chloride salts can be obtained by additions o   adium or cesium chloride.

Rhenium tetrachloride, $ReCl_4$, was first reported in 1926[340], but it may be nonexistent. Briscoe, Robinson, and Rudge[273] believed they had made it by the Noddacks' method of heating rhenium metal in chlorine[302], and double halides were then formed from it. This was substantiated by Yost and Shull[346], who heated measured amounts of rhenium and chlorine in evacuated tubes. These authors believed the rhenium tetrachloride had at least partially polymerized to Re_2Cl_8. The tetrachloride was thought to form brown or reddish crystals and a blue solution. It was reasonably stable.

However, Geilmann, Wrigge, and Biltz[343, 347] who worked extensively in the field of rhenium chemistry, tried to make the tetrachloride but could prepare only the pentachloride and the trichloride. Analysis showed that a mixture of the two latter chlorides and an oxychloride (also possibly present) could produce a molecular weight easily mistaken for that of rhenium tetrachloride.

As described above, rhenium pentachloride, $ReCl_5$, was prepared by the reaction of excess chlorine on rhenium metal. It is a brownish-black solid yielding dark-brown vapors. It cannot be volatilized at atmospheric pressure without decomposition. Reduction at 400 to 500 C will produce the trichloride[302, 343] and chlorine. Oxidation[306] produces oxychlorides:

$$16ReCl_5 + 14O_2 = 10ReOCl_4 + 6ReO_3Cl + 17Cl_2.$$

Alkalies cause a reaction of the type

$$3ReCl_5 + 16NaOH = 2ReO_2 \cdot 2H_2O + NaReO_4 + 15NaCl + 4H_2O,$$

although intermediate compounds may be formed. Acids cause a reaction of the type

$$10ReCl_5 + 2HCl + 3H_2O = 2HReO_4 + 8H_2ReCl_3 + 13Cl_2.$$

Neutral salts will form the rhenichloride of the metal involved when added to the pentachloride.[340] Klemm and Frischmuth[345] found ammoniates could be formed in the system $ReCl_5 - NH_3$, as with the trichloride. The specific compounds present were undetermined.

Noddack[297] claimed formation of rhenium hexachloride, $ReCl_6$, and Yost and Shull[346] reported it (along with the questionable tetrachloride) as a result of heating a 1:6 ratio of rhenium and chlorine. It was not isolated. Druce[340] doubts its formation with good reason, and no one since has produced it.

The highest possible chloride, rhenium heptachloride, $ReCl_7$, was thought formed by Druce and Loring[3, 340] from the action of hydrochloric acid and rhenium. According to Schröter[348] the Noddacks also produced a green crystalline heptachloride. However, this chloride, too, could not be separated and has not been prepared by more recent investigators.

Bromides. Rhenium tribromide, $ReBr_3$, was prepared at 500 C by combination of the elements[270]. It sublimes slowly at 450 C and forms dark-green crystals on condensation. The addition or presence of oxygen at 400 C probably produces the oxybromide. As with the chlorides, the system $ReBr_3 - NH_3$ shows formation of ammoniates: $ReBr_3 \cdot 20NH_3$, $ReBr_3 \cdot 14NH_3$, $ReBr_3 \cdot 9NH_3$, $ReBr_3 \cdot 7NH_3$.[345]

The tetrabromide, $ReBr_4$, is claimed by Druce[338] to have also been identified, but no other evidence than his claim has been uncovered.

Iodides. The Noddacks[340] were reported to have made the tetraiodide, ReI_4, but Rulfs and Elving[341] failed to produce it after attempting to do so by several methods.

Summary. As a summary of the known and the unconfirmed halides, a short tabulation is presented on the following page.

Fluorides	Chlorides	Bromides	Iodides
	$ReCl_2$(?)		
	$ReCl_3$	$ReBr_3$	
ReF_4	$ReCl_4$(?)	$ReBr_4$(?)	ReI_4(?)
	$ReCl_5$		
ReF_6	$ReCl_6$(?)		
ReF_7(?)	$ReCl_7$(?)		

Physical properties of the more important halides are reported in Table 9. The following summary also lists the common known properties of all the definitely isolated halides:

Halide	Name	Color	MP, C	BP, C	Density	Reference
ReF_4	Rhenium tetrafluoride	-	124.5	-	-	267
ReF_6	Rhenium hexafluoride	Yellow	18.8	47.6	4.251	266,267,268,387
$ReCl_3$	Rhenium trichloride	Violet black	Sublimes at 500		-	340
$ReCl_5$	Rhenium pentachloride	Brown black	Decomposes		-	340
$ReBr_3$	Rhenium tribromide	Green black	Sublimes at 500		-	270
$ReBr_4$	Rhenium tetrabromide	-	-	-	-	340

Double Rhenium Halides

Double rhenium halides, or rhenihalides, are the salts of rhenium halogen acids, such as chlororhenic acid, H_2ReCl_6. Except for this, none of these acids have been identified, but their salts do exist and are made from constituents other than the acids.

Double Fluorides. Potassium rhenifluoride, K_2ReF_6, has been reported by Ruff and Kwasnik[267] as a possible product from rhenium hexafluoride.

Double Chlorides. The afore-mentioned acid, H_2ReCl_6, was found by the Noddacks[392] to result from the interaction of hydrochloric acid and rhenium dioxide, and its most common salt is that of potassium, K_2ReCl_6, also called potassium chlororhenite.[269] It is prepared by titrating potassium perrhenate and potassium iodide with hydrochloric acid:[302, [illegible], 274, [illegible], 350]

$$2KReO_4 + 6KI + 16HCl = 2K_2ReCl_6 + 4KCl + 8H_2O + 3I_2.$$

This general type of reaction is also utilized to form other metal rhenichlorides. Potassium rhenichloride may also be prepared from the pentachloride:[351]

$$2ReCl_5 + 4KCl = 2K_2ReCl_6 + Cl_2.$$

Briscoe, Robinson, and Stoddart[273] obtained it by heating rhenium and potassium chloride in a stream of chlorine gas, and Schmid[352] by electrolytic reduction. Enk[274] found the yellow-green crystals had a density of 3.34; he also determined the equivalent and specific conductivity of water solutions of the salt. It is only slightly soluble in water[302] and dissociates according to the reaction:[274]

$$K_2ReCl_6 = 2K^{+1} + ReCl_6^{-2},$$

but it then hydrolyses. It is unstable above 25 C.[273] A quantitative precipitation occurs if a solution is boiled, and electrolysis produces Re^{+2} and Re^{+4} at the cathode.

Two other double salts of the same elements were obtained by Krauss and Steinfeld[353] and Dählmann[350]. These were K_3ReCl_6 (brown) and $K_4Re_2Cl_{11}$ (yellow orange). The latter contained both Re^{+3} and Re^{+4}.

Double chlorides with metal ions other than potassium have been prepared, usually by the reactions of the type

$$2KReO_4 + 16HCl + 6MI = 2M_2ReCl_6 + 4MCl + 8H_2O.$$

The double chlorides are here summarized:

Salt	Color	Reference
Ag_2ReCl_6	Orange	343
Ag_3ReCl_6	-	353
$RbReCl_4$	-	349, 354
Rb_2ReCl_6	Yellow orange	350, 354
$CsReCl_4$	-	354
Cs_2ReCl_6	Yellow	350, 354
Tl_2ReCl_6	Yellow	351
Tl_3ReCl_6	-	353
Hg_2ReCl_6	Yellow	351
$(NH_4)_2ReCl_6$	-	349

A few organic halides of this type also exist; they will be discussed later in this report.

Double Bromides. [illegible][351] claimed that treatment of hydrobromic acid with rhenium dioxide produced bromorhenic acid, H_2ReBr_6. Using this as a starting point, Krauss and Dählmann[350] and Krauss and Steinfeld[353] recrystallized several complex bromide salts by addition of light-metal bromides to a bromorhenic acid solution:

Salt	Color	Reference
K_2ReBr_6	Violet red	350, 353
Rb_2ReBr_6	Dark red	350
Cs_2ReBr_6	Violet red	350

Double Iodides. Biltz, et al.,[355] prepared rhenium hydropentiodic acid, $HReI_5$, by the reaction

$$K_2ReI_6 + H_2SO_4 = K_2SO_4 + HI + HReI_5$$

and extracted the acid with ether. This reaction is not possible with potassium rhenichloride or rhenibromide. The more probable acid of this type, iodorhenic acid, H_2ReI_6, has not been isolated.

This potassium salt of iodorhenic acid, K_2ReI_6, was found by Briscoe, Robinson, and Rudge[356] who heated potassium perrhenate, an excess of potassium iodide, and aqueous hydriodic acid at the boiling point of the acid. The rheniiodide separated as crystals. Decomposition of the salt occurred at 300 C. Krauss and Dählmann[350] also prepared rheniiodides in like manner, so that the known double iodides are:

Salt	Color	Reference
K_2ReI_6	Brown black	350, 356
Na_2ReI_6	Black	350
Cs_2ReI_6	Black	350

Rhenium Oxyhalides

Oxyhalides of a substance are formed when a halogen is substituted for part of the oxygen in a metal oxide. For instance, with Re^{+7}, one of the more common oxyhalides is ReO_2Cl_3. The oxide of Re+7, of course, is Re_2O_7.

Oxyfluorides. The first oxyfluoride prepared was probably $ReOF_4$, rhenium oxytetrafluoride.[277] It was prepared by hydrolysis of the hexafluoride:

$$ReF_6 + H_2O = ReOF_4 + 2HF.$$

This substance forms colorless crystals with a melting point of 39.7 C. Ruff and Kwasnik[266, 267] produced the same compound, (and others also) from rhenium hexafluoride and quartz. Recently Wiechert[357] heated potassium perrhenate with hydrofluoric acid to produce the trioxyfluoride:

$$KReO_4 + HF = ReO_3F + KOH.$$

Aynsley, Peacock, and Robinson[338] prepared two more by a reaction between fluorine (with nitrogen), rhenium dioxide, and potassium perrhenate.

The other known oxyfluorides are listed in the following tabulation:

Salt	Name	MP, C	BP, C	Color	Reference
$ReOF_5$	Rhenium oxypentafluoride	34.5	55	Cream	338
$ReOF_4$	Rhenium oxytetrafluoride	39.7	62.7	Colorless	266,267,277
$ReOF_2$	Rhenium oxydifluoride	-	-	Colorless	266,267
ReO_2F_3	Rhenium dioxytrifluoride	90-95	200	Pale yellow	338
ReO_2F_2	Rhenium dioxydifluoride	156	-	Colorless	266,267
ReO_3F	Rhenium trioxyfluoride	-	-	Colorless	266,267,357

<u>Oxychlorides.</u> The first oxychlorides were prepared by Brukl and Zeigler[275] by heating together rhenium heptoxide and rhenium tetrachloride. Fractional distillation gave rhenium trioxychloride, ReO_3Cl, as the first product. Geilmann, et al.,[343] also formed it, but by heating rhenium trichloride in oxygen. The substance is a colorless liquid, freezing at 4.5 C and boiling at 131 C. It is stable but will hydrolyze:

$$ReO_3Cl + H_2O = HCl + HReO_4.$$

A second product of the distillation is rhenium oxytetrachloride, $ReOCl_4$, which can also be prepared by heating chlorides in oxygen:

$$6ReCl_3 + 5O_2 = 4ReOCl_4 + 2ReO_3Cl,$$

or in air:

$$6ReCl_5 + 5O_2 = 4ReOCl_4 + 2ReO_3Cl + 6Cl_2.$$

Either the trichloride or the pentachloride can be used. Heating the oxytetrachloride in oxygen yields the trioxychloride:

$$2ReOCl_4 + O_2 = 2ReO_3Cl + 3Cl_2.$$

This oxytetrachloride[276] consists of brown crystals melting at about 30 C that will hydrolyze to hydrochloric acid, perrhenic acid, and hydrated rhenium dioxide. It was also found that ammonia added to the solid oxytetrachloride produced brown, stable, $ReO(NH_2)_2Cl_2$, which will hydrolyze in ice water to $ReO(OH)_2(NH_3)_2$. Heating and evacuating caused formation of $ReO_2 \cdot NH_3$.

Another oxychloride, ReO_2Cl_3, was prepared by Briscoe, Robinson, and Rudge[358]. This dioxytrichloride can be made in several ways:

$$(1)\quad 2Re + 3Cl_2 + 2O_2 = 2ReO_2Cl_3,$$

$$(2)\quad 2ReCl_4 + 2O_2 = 2ReO_2Cl_3 + Cl_2,$$

$$(3)\quad 2Re_2O_5 + 6Cl_2 = 4ReO_2Cl_3 + O_2,$$

but the authors specify (1) as the best method. The salt forms needle-like red-brown crystals and melts to a yellow-brown liquid.

Brukl and Plettinger[359] carefully solvated rhenium oxytetrafluoride in organic solvents with small amounts of moisture present. A blue precipitate occurred, having a ratio of rhenium to chlorine of 1:2, but a varying ratio of oxygen to hydroxyl ion. The product could not be isolated, but there is a good possibility that it was rhenium oxydichloride, $ReOCl_2$.

The oxychlorides and a summary of their important properties follow:

Salt	Name	Color and State	MP, C	FP, C	Reference
ReO_3Cl	Rhenium trioxychloride	Colorless liquid	4.5	131	269,275
ReO_2Cl_3	Rhenium dioxytrichloride	Red brown solution	23.9	300˚	302
$ReOCl_4$	Rhenium oxytetrachloride	Brown solution	30	223	275
$ReOCl_2$	Rhenium oxydichloride	Blue solution	-	-	359

<u>Oxybromides</u>. Three oxybromides have been reported. Brukl and Zeigler[360] treated rhenium with oxygen and excess bromide to prepare the trioxybromide, ReO_3Br. This is a white solid with a melting point of 39.5 C. The reaction is:

$$2Re + 3O_2 + 2Br = 2ReO_3Br.$$

Preparation of the dioxydibromide, ReO_2Br_2, was more difficult since the compound decomposed before it melted (60-70 C) preventing purification. This caused it to retain an excess of 1-2 per cent of bromine. It has also been reported that the oxydibromide, $ReOBr_2$, forms a red solution. No other oxybromides are known.

Salt	Name	Color and State	MP, C	FP, C	Reference
$ReOBr_2$	Rhenium oxydibromide	Red solution	-	-	67
ReO_2Br_2	Rhenium dioxydibromide	-	Decomposes at 60-70 C		360
ReO_3Br	Rhenium trioxybromide	White solid	39.5	163	360

Oxyiodides. No oxyiodides have been reported.

Double Rhenium Oxyhalides

Double halides of many of the rhenium compounds have been prepared and here reported. In like manner, double oxyhalides of the rhenium oxyhalides exist.

By the reaction of hydrochloric acid with potassium perrhenate and potassium iodide, Jakob and Jezowska[300] prepared potassium oxyrhenichloride, K_2ReOCl_5. These yellow-green crystals hydrolyzed in moist air and were soluble in dilute acid. They hydrolyzed on further dilution, and heating caused decomposition.

Ammonium oxyrhenichloride, $(NH_4)_2ReOCl_5$, was prepared in the same manner utilizing ammonium instead of potassium salts. These crystals were also greenish-yellow colored.

Several other double oxyhalides have also been found; all are listed below:

Salt	Color	Reference
K_2ReOCl_5	Yellow green	300
$(NH_4)_2ReOCl_5$	Yellow green	300
$K_4Re_2OCl_{10}$	-	349, 353
$(NH_4)_4Re_2OCl_{10}$	-	349, 353
$Ag_4Re_2OCl_{10}$	-	353
$K_2Re_2OBr_{10}$	-	302

Double Rhenium Hydroxyhalides

In the classical preparation of rhenichlorides and oxyhalides from perrhenic and hydrochloric acid and the metal iodide, intermediate salts may be formed. Some of these are rhenihalides with one or more hydroxyl groups substituted for halides. These compounds are called hydroxyhalides and exist as double salts. Actually, they may be considered to form by hydrolysis of a rhenichloride as follows:

$$K_2ReCl_6 + H_2O = K_2ReCl_5 \cdot OH + HCl.$$

Krauss and Dählmann(350), Jezowska and Jodko(349), and Jakob and Jezowska(361, 362), identified some of these substances. The latter electrolyzed hydriodic acid solutions of potassium perrhenate and iodine to form a dihydroxyhalide. The salts are:

Salt	Color	Reference
$K_2Re(OH)Cl_5$	Green	349, 350
$K_2Re(OH)_2Cl_5$	-	361, 362
$Rb_2Re(OH)Cl_5$	Yellow	349, 350
$Rb_2Re(OH)_2Cl_5$	Green	350
$Cs_2Re(OH)Cl_5$	Yellow	350
$Cs_2Re(OH)_2Cl_5$	Yellow	350
$(NH_4)_2Re(OH)Cl_5$	-	349
$Cs_2Re(OH)Br_5$	Red	350

<u>Rhenium Carbonyl Halides</u>

These are compounds of the type $Re(CO)_5X$, of which the most common is $Re(CO)_5Cl$. This was prepared by Schulten(363) by three different reactions, all at 230 C for 30 hours under 250 atmospheres pressure.

(1) $ReCl_5 + 4Cu + 9CO = Re(CO)_5Cl + 4CuCl \cdot CO$

(2) $ReCl_5 + 2Cu + 7CO = Re(CO)_5Cl + 2CuCl \cdot CO$

(3) $K_2ReCl_2 + 3Cu + 8CO = Re(CO)_5Cl + 3CuCl \cdot CO + 2KCl$

The rhenium pentacarbonyl chloride is extracted with ether, appearing as a fine grayish powder. The iodide and bromide salts can also be prepared by identical methods. All are odorless, insoluble in water, and are decomposed by hydrogen peroxide-sodium hydroxide mixtures.

Hieber, Schuh, and Fuchs(364) also tried to make rhenium carbonyls. They repeated the methods of Schulten and also derived new methods but were at first unsuccessful. Eventually they were able to prepare two compounds by the reaction:

$$Re + CuCl_2 + 6CO = Re(CO)_5Cl + CuClCO.$$

This was essentially the same as Schulten's method, occurring at high temperatures and pressures. $Re(CO)_5Cl$, $Re(CO)_5Br$, and $Re(CO)_5I$ could be made by this method. Another method was the reaction:

$$KReO_4 + CCl_4 + 8CO = Re(CO)_5Cl + KCl + COCl_2 + 3CO_2.$$

This also occurred at high temperature and pressure. One halide can also be made by another reaction:

$$2Re(CO)_5I + Br_2 = 2Re(CO)_5Br + I_2.$$

The boiling point of these compounds ranges from 90 to 140 C decreasing in order from the iodo- to the chloro-compound. This represents steps of increasing stability.

Hieber and Fuchs(279) then found that rhenium carbonyl, $Re(CO)_5$, could be prepared by two methods, neither of which involved removing halogens from the halide carbonyls. Either potassium perrhenate, rhenium heptoxide, or one of the lower oxides were treated with carbon monoxide at 200 to 250 C and 250 to 270 atmospheres:

$$2Re_2O_7 + 20CO = 4Re(CO)_5 + 7O_2.$$

The crystalline carbonyl is pseudo-tetragonal and resistant to acids and bases. It melts at 177 C, but is decomposed by nitric or sulfuric acid on heating (400 C). The presence of sulfur causes catalysis and may involve formation of compound, $ReH(CO)_5$. The carbonyl is probably dimeric, existing as $[Re(CO)_5]_2$.

Sulfur Compounds of Rhenium

Rhenium, like any other metal, forms two types of sulfur compounds, the sulfides, where the metal combines with sulfur alone and directly, and the thiosalts, which involve the metal, sulfur, and some other element.

Thio-Salts

Feit(318, 365) treated saturated potassium perrhenate solution with hydrogen sulfide. A yellow solution appeared which Feit reported as a thioperrhenate:

$$KReO_4 + H_2S = KReO_3S + H_2O.$$

This compound hydrolyzed, forming monothioperrhenic acid:

$$KReO_3S + H_2O = HReO_3S + KOH.$$

Treatment of the solution with thallium sulfate caused formation of two unstable compounds of thallium, $TlReO_3S$ and $TlReS_4$. Treatment with silver, lead, copper, and mercury compounds all caused formation of precipitates. The potassium salt of mono-thioperrhenic acid is very soluble in water and ethanol. The rubidium and cesium salts, which Feit evidently also prepared, are less soluble.

Sulfides

Noddack(297) originally reported that the action of hydrogen sulfide on rhenium produced three sulfides, Re_2S_7, ReS_3, and ReS_2. This view was supported by Schacherl(102), who stated that rhenium disulfide was the only one of the three that was stable.

Rhenium Heptasulfide, Re_2S_7. This was prepared by precipitation when perrhenate solutions were treated with hydrogen sulfide:(272, 306, 366)

$$2HReO_4 + 7H_2S = Re_2S_7 \text{ and } 8H_2O.$$

However, there was some difficulty in securing a precipitate and the reaction was not thought to be quantitative, so Briscoe, Robinson, and Stoddard(272) prepared the heptasulfide by treating potassium perrhenate with sodium thiosulfate in acid solution. They claimed this method was better than the hydrogen sulfide precipitation. Biltz and Wiebke(366) refuted the statement that the hydrogen sulfide precipitation of rhenium heptasulfide was not quantitative. They prepared the heptasulfide, and found it to be a black powder, easily oxidized in air. Its density was 4.866 and it decomposed exothermically at 460 to 480 C. It was nearly insoluble in water, and was attacked by nitric acid.

Rhenium Disulfide, ReS_2. Rhenium disulfide may be prepared by heating the heptasulfide in nitrogen or carbon dioxide; sulfur is sublimed:(366)

$$\text{(a)}\quad Re_2S_7 = 2ReS_2 + 3S.$$

The disulfide may also be prepared directly from the elements:

$$\text{(b)}\quad Re + 2S = ReS_2,$$

or by the method of Tiede and Lemke(228), who heated rhenium metal and the heptasulfide at 1400 C:

$$\text{(c)}\quad 3Re + 2Re_2S_7 = 7ReS_2.$$

In Method (b), a pressure of hydrogen sulfide must be maintained.

The disulfide is quite stable; Juza and Biltz[271] found it did not decompose until heated above 1000 C. It was black and possessed a density of 7.5. It will attack quartz. Heating in air caused decomposition by oxidation:

$$4ReS_2 + 15O_2 = 2Re_2O_7 + 8SO_2.$$

Heating in hydrogen forced reduction to the metal:

$$ReS_2 + 2H_2 = Re + 2H_2S.$$

Rhenium Trisulfide, ReS_3. The trisulfide, ReS_3, mentioned by Noddack[297] and Schacherl[102], has not been prepared since. Its existence must be considered questionable.

The sulfide compounds are valuable in the chemical analysis of rhenium, where sulfide precipitation for the separation of elements is common. This subject will be covered completely in the Analytical Chemistry section of this report. A summary of the more important rhenium sulfur compounds that have been identified follows:

Compound	Name	Color	Density	Reference
ReS_2	Rhenium disulfide	Black	7.5	102,297,366
Re_2S_7	Rhenium heptasulfide	Black	4.866	102,297,366
$HReO_3S$	Mono-thioperrhenic acid	-	-	318,363
$KReO_3S$	Potassium thioperrhenate	Yellow	-	318,363
$TlReO_3S$	Thallium thioperrhenate	Yellow	-	318
$TlReS_4$	Thallium thiorhenite	-	-	318
$Pb(ReO_3S)_2$	Plumbic thioperrhenate	Red	-	318
$Hg(ReO_3S)_2$	Mercuric thioperrhenate	Yellow	-	318

Miscellaneous Inorganic Compounds

Selenides

Two selenides of rhenium have been prepared by Briscoe, Robinson, and Stoddard.[272] Both are analagous to the sulfides and are formed in the same manner.

Rhenium Heptaselenide, Re_2Se_7. This was prepared by treating ammoniated aqueous potassium perrhenate with hydrogen selenide:

$$2KReO_4 + 7H_2Se = Re_2Se_7 + 6H_2O + 2KOH.$$

Like the sulfide, it is a black powder.

Rhenium Diselenide, $ReSe_2$. If the heptaselenide was heated for nine hours at 330 C in vacuum, reduction to the diselenide occurred:

$$Re_2Se_7 = 2ReSe_2 + 3Se.$$

Phosphides

Haraldsen[367] heated rhenium and phosphorus together and observed compound formation around and above 780 to 800 C. The possible compounds formed were:

ReP_3	Rhenium triphosphide
ReP_2	Rhenium diphosphide
ReP	Rhenium phosphide
Re_2P	Rhenium subphosphide

Silicides

Only one silicide has been reported, and that, the disilicide, $ReSi_2$, by Wallbaum.[368] The compound is isomeric with molybdenum silicide, $MoSi_2$.

Arsenides

Weichmann, Heimberg, and Biltz[369, 370] studied the system rhenium-arsenic. They reported only one compound was formed, Re_3As_7. The arsenide decomposed at 780 C and no intermediate compounds were formed. The affinity of rhenium for phosphorus is greater than the affinity of rhenium for arsenic.

Rhenides

The possibility that rhenium existed in the Re^{-1} state was discussed in the Valence States section of this report. Rulfs and Elving[371], assuming that Re^{-1} would act like a halide, attempted to separate insoluble silver, lead, or as ferric rhenides. The rhenide ion proved too strong a reducing agent to do this, so Tl^{+1}, not reduced by Re^{-1}, was assayed as the cation. Evidently TlRe was prepared in solution, but could not be precipitated because thallium chloride and thallium bromide, also present, are less soluble.

Organic Compounds of Rhenium

Alkanes

Trimethylrhenium, $Re(CH_3)_3$. This trialkylrhenium compound was prepared by Druce[280] by treating the trichloride of rhenium with a Grignard reagent:

$$2ReCl_3 + 6CH_3MgI = 2Re(CH_3)_3 + 3MgI_2 + 3MgCl_2.$$

The organic is a volatile, colorless, inflammable oil, heavier than water with an ethereal odor. It boils at 60 C.

Triethylrhenium, $Re(C_2H_5)_3$. Druce claimed[372] that he also prepared this compound in like manner to the trimethylrhenium. It had the same general properties as the methyl compound, but boiled at 30 C.

Other authors[352, 373] have also tried to formulate these organics. They were generally unsuccessful, and stated that rhenium chloride catalyzed a reaction between methyl magnesium iodide and methyl iodide, producing only methane or ethane as product. Druce's explanation of their troubles was that "impurities" caused the failure.

Pyridine Perrhenates

Copper Tetrapyridine Perrhenate, $[Cu(C_5H_5N)_4](ReO_4)_2$. Wilke-Dörfurt and Gunzert[333] isolated this compound after treating pyridine with cupric chloride and perrhenic acid. It is a blue crystalline salt, slightly soluble in water and possessing a density of 2.338.

Silver Tetrapyridine Perrhenate, $[Ag(C_5H_5N)_4]ReO_4$. This was prepared by the above investigators in the same manner. It is unstable, yielding a pyridine group, C_5H_5N, to form tripyridine perrhenate, also an unstable complex.

2,2'-Dipyridyl Perrhenate, $C_5H_5N \cdot NC_5H_5 \cdot HReO_4$, and 2,2',2"-Tripyridyl Perrhenate, $C_5H_5N \cdot C_5H_5N \cdot C_5H_5N \cdot HReO_4$. According to Druce[335, 351], these were prepared by Turkiewicz[294] and reported by Morgan[374]. The substances separate from a solution of the pyridine base in perrhenic and acetic acids.

Alkyl Oxides

Rhenium Triethoxide, $Re(OC_2H_5)_3$, and Rhenium Tri-isopropyloxide, $Re(OC_3H_7)_3$. Sodium ethoxide or sodium propoxide were treated by Druce[375] with rhenium trichloride:

$$ReCl_3 + 3NaOC_2H_5 = 3NaCl + Re(OC_2H_5)_3$$

$$ReCl_3 + 3NaOC_3H_7 = 3NaCl + Re(OC_3H_7)_3.$$

These organics are brown solids decomposed by water, acids, or alkalies. They are stable in air.

Organic Halides

Turkiewicz[294] has already been mentioned for his preparation of pyridyl perrhenates. In addition, he treated the pyridine base with chlororhenic and hydrochloric acids, causing formation of three pyridyl chlorides:

(1) 2,2'-Dipyridyl Rhenichloride, $C_5H_4N \cdot C_5H_4N \cdot H_2ReCl_6$

(2) Bis-2,2'-Dipyridyl Rhenichloride, $(C_5H_4N \cdot C_5H_4N)_2\ H_2ReCl_6$

(3) 2,2',2"-Tripyridyl Rhenichloride, $C_5H_4N \cdot C_5H_4N \cdot C_5H_4N \cdot H_2ReCl_6$

The dipyridyl salt (1) appeared as yellow needles, and the bis-salt (2) as green ones. The bis- and tri-salts, (2) and (3), are only slightly soluble in water.

Numerous authors have prepared other complex organic halides. The formulas, names and references for many of these compounds have been compiled in Table 12. Lebedinskii and Ivanov-Lmin[376] claim that their stable complexes are the first examples of rhenium in the cation.

Carbonyls

Rhenium Tricarbonyl Pyridine, $Re(CO)_3(C_5H_5N)_2$. This was prepared by Hieber and Fuchs[377] from rhenium carbonyl and pyridine:

$$Re(CO)_5 + 2C_5H_5N = Re(CO)_3(C_5H_5N)_2 + 2CO.$$

TABLE 19. SUMMATION OF THE KNOWN COMPLEX RHENIUM ORGANIC HALIDES

Formula and Name	Color	Author	Reference
$C_5H_4N \cdot C_5H_4N \cdot H_2ReCl_6$ 2, 2'-dipyridyl rhenichloride	Yellow	Morgan and Davies Turkiewicz Schmid	51 294 370
$(C_5H_4N \cdot C_5H_4N)_2H_2ReCl_6$ Bis-2, 2'-dipyridyl rhenichloride	Green	Morgan and Davies Turkiewicz	51 294
$C_5H_4N \cdot C_5H_4N \cdot C_5H_4N \cdot H_2ReCl_6$ 2, 2', 2''-tripyridyl rhenichloride	-	Turkiewicz	294
$C_2H_5Re(OH)Cl_3$ Ethyl rhenium hydroxychloride	-	Druce	375
$C_3H_7Re(OH)Cl_3$ Propyl rhenium hydroxychloride	-	Druce	375
$(C_6H_4CH_3NH_3)_2H_2ReCl_6$ Di-toluidyl rhenichloride	Yellow brown	Schmid	352
$C_9H_7N \cdot C_9H_7N \cdot H_2ReCl_6$ Di-quinodyl rhenichloride	Yellow brown	Schmid	352
$C_5H_5N \cdot C_5H_4N \cdot C_5H_4N \cdot H_2ReCl_6 \cdot H_2O$ 2, 2', 2''-tripyridyl rhenichloride hydrate	-	Morgan and Davies	51
$[ReO_2(C_2H_5(NH_2)_2)_2]Cl$ Rhenium dioxydiethylenediamine chloride	Yellow	Lebedinskii and Ivanov-Emin	376
$[ReO_2(C_2H_5(NH_2)_2)_2]I$ Rhenium dioxydiethylenediamine iodide	Yellow	Lebedinskii and Ivanov-Emin	376
$[ReO(OH)C_2H_5(NH_2)_2]Cl_2$ Rhenium oxyhydroxyethylenediamine dichloride	-	Lebedinskii and Ivanov-Emin	376
$[ReO(OH)(C_2H_5(NH_2)_2)_2]PtCl_6$ Rhenium oxyhydroxydiethylenediamine platinichloride	-	Lebedinskii and Ivanov-Emin	376
$[ReO(OH)(C_2H_5(NH_2)_2)_2]Co(NO_2)_6$ Rhenium oxyhydroxydiethylenediamine cobaltinitrite	-	Lebedinskii and Ivanov-Emin	376
$[Re(OH)_2(C_2H_5(NH_2)_2)_2]Cl_3$ Rhenium hydroxydiethylenediamine trichloride	Blue	Lebedinskii and Ivanov-Emin	376
$(C_5H_5N)_4Re_2OCl_{10}$ Tetrapyridine rhenium oxychloride	-	Jezowska and Jodko	349
$(C_5H_5N)_2Re(OH)Cl_5$ Dipyridine rhenium hydroxychloride	-	Jezowska and Jodko	349
$Re(CH_3)_5Cl$ Dimethyl rhenium chloride	-	Druce	371

Chlororhenium Tricarbonyl Pyridine, $ReCl(CO)_3(C_5H_5N)_2$. This can also be made with iodine replacing the chlorine. It is a derivative in which the organic base can be regarded as replacing some of the carbonyl radicals in compounds like rhenium pentacarbonyl chloride, $Re(CO)_5Cl$.

o-Phenanthroline also substitutes in analogous manner to pyridine. The reaction is considered simpler to accomplish than with pyridine itself.

Oxycyanides

In 1935, Morgan(374) produced a complex organic cyanide, potassium rhenium oxycyanide, $K_3[ReO(CN)_4]$, from potassium perrhenate. The dioxy-salt was prepared next by Klemm and Frischmuth(281) from potassium rhenichloride, potassium cyanide, and hydrogen peroxide. This salt, $K_3[ReO_2(CN)_4]$, occurred as red monoclinic crystals. It was soluble in water and stable up to 300 C. The density at 40 C was 2.704. The thallium salt, $Tl_3[ReO_2(CN)_4]$, was also made by the same process. Later, Morgan and Davies(51) made the hydrated salt of sodium, $Na_3[ReO_2(CN)_4] \cdot 2H_2O$, and also potassium sodium rhenium dioxycyanide, $K_3Na[ReO_2(CN)_4] \cdot 6H_2O$. Morgan(374) had already prepared the monoxy-salt of this series. Druce(371) reported that Turkiewicz made a partially hydrated compound, $K_3[ReO(CN)_4 \cdot OH]$, from rhenium dioxide and potassium cyanide.

Hölemann(378) produced many of this type of complexes, but never analyzed them. He did, however, report that the average valence of rhenium was about 5, and evidently prepared rhenium oxycyanide salts of silver, copper, mercury, and lead in addition to those light-metal salts already reported.

Tribalat(379) studied the reduction of perrhenates with potassium thiocyanate and stannous chloride, a reaction typical of the type leading to preparation of these salts. She found that:

$$HReO_4 + HCl + SnCl_2 + KCNS = Re^{+4}.$$

The reaction is quantitative if the hydrochloric acid is four normal. At this point, the stannous chloride reduces the Re^{+7} to Re^{+4}. If the acid is one normal and excess $SnCl_2$ is used, both Re^{+4} and Re^{+5} are present.

The oxycyanides are summarized in the tabulation on the following page.

Salt	Color	Reference
$K_3[ReO(CN)_4]$	-	374
$K_3[ReO(CN)_4]OH$	-	281
$K_2Na[ReO(CN)_4]$	Pink	371
$K_3[ReO_2(CN)_4]$	Red	371
$K_2Na[ReO_2(CN)_4]6H_2O$	Red	51
$Na_3[ReO_2(CN)_4]2H_2O$	Yellow	51
$Tl_3[ReO_2(CN)_4]$	-	281
$(C_{19}H_{15}N_2H)_3[ReO_2(CN)_4]4H_2O$	-	51
$(C_{13}H_9NH)_3[ReO_2(CN)_4]2H_2O$	-	51
$(C_{13}H_9NH)_2H[ReO_2(CN)_4]$	-	51
$(C_{10}H_8N_2H_2)_3[ReO_2(CN)_4]_23H_2O$	-	51
$(C_{10}H_8N_2H_2)_3H[ReO_2(CN)_4]_24H_2O$	-	51

Thiocyanates

Druce(380) and Miller(381) prepared the only reported compounds of this type by the following reactions:

$$2HReO_4 + 10HCl + SnCl_2 = 2ReOCl_4 + SnCl_4 + 6H_2O$$

$$ReOCl_4 + 4KCNS = ReO(CNS)_4 + 4KCl.$$

Rhenium oxythiocyanate, $ReO(CNS)_4$, is a dark-red crystalline material which decomposes to a yellow organic sublimate and residue when heated. Organic salts may be easily prepared, so Druce made the double derivatives of pyridine and quinoline, analogous to uranyl salts of the same type:

Salt	Color	Reference
$ReO(CNS)_4$	Dark red	380, 381
$(C_6H_5N \cdot HCNS)_2ReO(CNS)_4$	-	380
$(C_9H_7N \cdot HCNS)_2ReO(CNS)_4$	-	380

THE ANALYTICAL CHEMISTRY OF RHENIUM

Qualitative Analysis

Microchemical Reactions (Spot Tests)

Noddack[297] first suggested that rhenium could be distinguished from molybdenum by the formation of a yellow-red color when potassium thiocyanate was added to a rhenium-containing solution.

Geilmann and Brünger[382] then showed that cesium and rubidium perrhenates would be dyed red if precipitated in the presence of MnO_4^{-1}. They claimed that 0.00025 mg of rhenium could be detected in 0.00035 cc of solution by this method.

Nitron is an organic precipitant often used in both qualitative and quantitative determinations of rhenium. Kronman and Bibikova[383] added nitron acetate to a drop of acid potassium perrhenate. Gelatin was superimposed on this, and titanium trichloride added on top of the gelatin. The titanium trichloride diffused down through the gelatin and caused the nitron perrhenate crystals to be dyed brownish yellow. Another author[384] found that hydrogen iodide and an iodine crystal will give dark cyrstalline precipitates of the form M_2ReI_6 if added to ReO_4^- ion. Salts of potassium, rubidium, cesium, thallium, mercury (ous), or silver are those which, of course, must be present to provide the M^+ cation. Molybdenum and tungsten interfere.

One of the earlier methods was the borax bead test, to which rhenium imparted a black color if heated in a reducing flame.[385] Yagoda[386] used a sodium carbonate bead. If more than 50 per cent manganese was present, rhenium caused a black to yellow to white color change in the reducing flame. Any flame was usable if there was no manganese present, and tungsten or molybdenum did not interfere. 0.015 mg of rhenium could be detected.

Stannous chloride will reduce tellurates, such as Na_2TeO_4, if rhenium is present to catalyze the reaction. A black precipitate or color will result. Poluektov[387] detected as little as $.025 \times 10^{-6}$ gram in .05 cc by this method, but molybdenum and other elements interfered. This problem can be solved by first distilling the rhenium from the impurities as the heptoxide.[388] Anisimov[389] used the same type of reaction, but added potassium thiocyanate to the stannous chloride. Molybdenum interference was eliminated by decolorizing with $NH_2OH \cdot HCl$, and tungsten interference eliminated by adding phosphoric acid.

Organics are popular for spot tests. For example, [illegible] added to perrhenate produced an orange cobaltammine perrhenate, $Co(NH_3)_6(ReO_4)_3 \cdot 1\frac{1}{2}H_2O$, which will detect 1.4×10^{-6} gram of rhenium.[334] Toluene-3, 4-dithiol and potassium thiocyanate form green complexes, effective to as low as 5×10^{-6} gram of rhenium, but these reagents do the same with molybdenum.[381] Dilute iodine gives a green color with molybdenum, but the color is much stronger with rhenium. Zwikker's reagent[390] or thallium nitrate will detect small amounts of rhenium as bluish crystals. Acridine is also used, but pyridine is better.[391]

Wenger and Duckert[392], in a general evaluation of qualitative data, found that two tests, that with stannous chloride and sodium tellurate or another with stannous chloride and DMG (dimethylglyoxime) which produced a yellow color, were the only fully satisfactory methods of detection.

Several authors[393, 394] have suggested methods for preparation of rhenium salts, followed by confirmation of their occurrence by microscope. Hurd, in Scott's Standard Methods of Chemical Analysis[395], recommended the following procedure:

(1) Precipitate rhenium heptasulfide by acid hydrogen sulfide.

(2) Remove molybdenum by addition of sodium sulfide to (1). In this step the molybdenum will be extracted, the rhenium sulfide remaining insoluble.

(3) Digest sulfide in sodium hydroxide and hydrogen peroxide; a soluble sodium perrhenate will now be present.

(4) Filter off any hydrated oxides. Concentrate by evaporation.

(5) Add solid cesium chloride to one drop of Solution (4).

(6) Identify the resultant crystals of $CsReO_4$ microscopically.

Several other final precipitants can also be used, such as rubidium chloride. Geilmann and Wrigge[394] precipitated and identified the crystals characteristic of double chlorides, prepared from acid solutions of rhenium trichloride by addition of rubidium, cesium, pyridine, quinoline, acridine, and others. Salts of the type K_2ReCl_6, $CsReCl_4$, and $C_6H_5NHReCl_4$ are produced. Photomicrographs of a few of these crystals are reproduced in Figure 12.

General Qualitative Tests

Closed- and open-tube reactions were studied at an early date by Geilmann and Wrigge.[396] The closed-tube reactions were unsatisfactory,

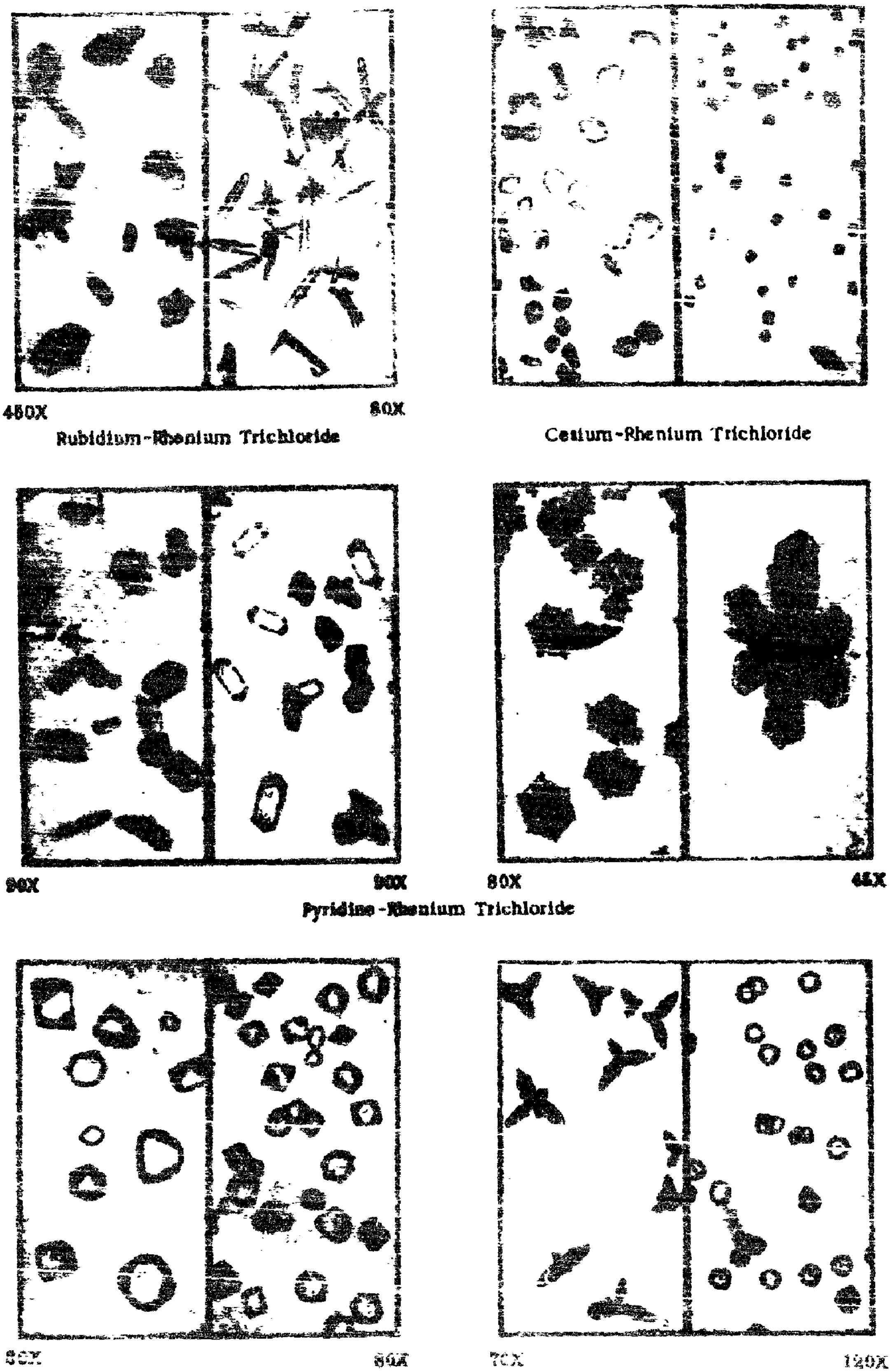
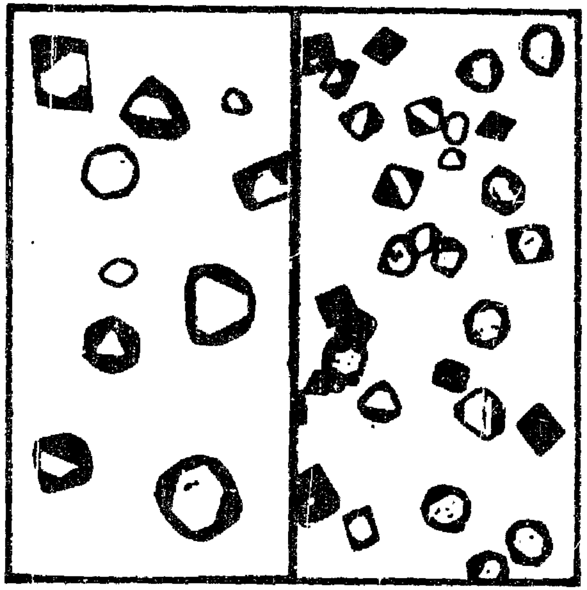


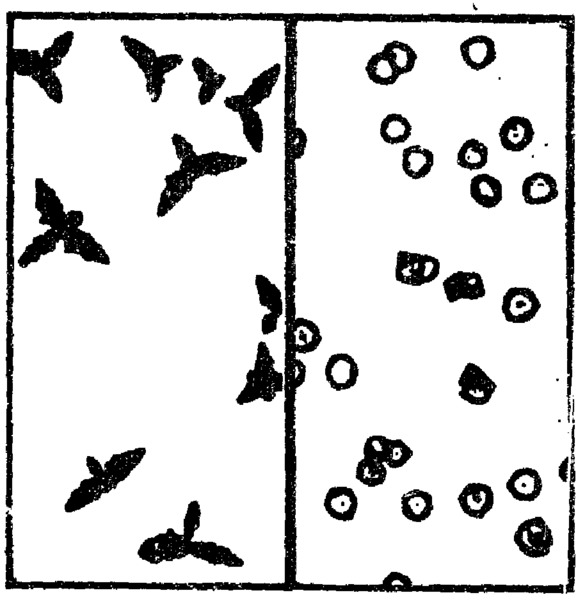
FIGURE 12. PHOTOMICROGRAPHS OF COMPLEX RHENIUM HALIDE CRYSTALS SUITABLE FOR COMPOUND IDENTIFICATION

Geilmann and Wrigge[illegible]



80 × *a* *b* 80 ×

Fig. 7. Kalium-Rheniumhexachlorid

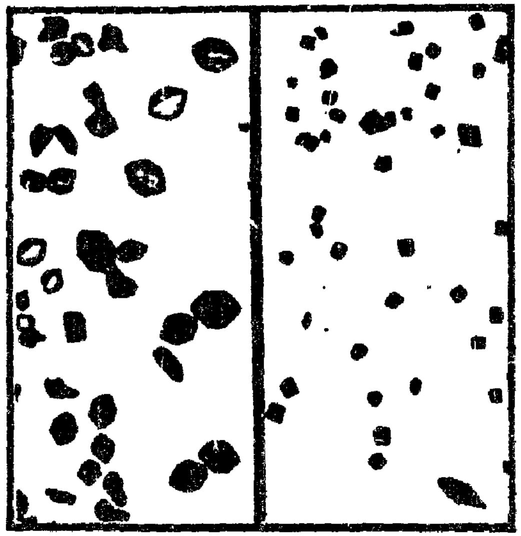


70 × *a* *b* 120 ×

Fig. 8. Rubidium-Rheniumhexachlorid

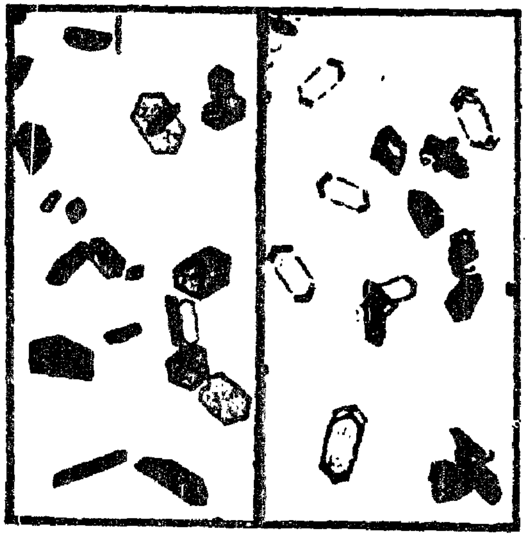
450 × a b 80 ×

Fig. 1 Rubidium-Rheniumtrichlorid



a b

Fig. 2. Caesium-Rheniumtrichlorid



90 × a b 90 ×

Fig. 3 Pyridin-Rheniumtrichlorid

80 × a b 45 ×

Fig. 4

but those with the open tube were evaluated as good. Very small quantities of rhenium can be determined. If a test tube containing rhenium is heated, the following will occur:

(1) A bluish oxide will form near the test substance, particularly if sulfur dioxide is added. Druce[385] suggested that this was the oxide Re_3O_8.

(2) Farther away, yellow hygroscopic crystals of rhenium heptasulfide form.

(3) White drops, possibly impure rhenium heptoxide, appear on the coolest part of the tube.

(4) White, odorless fumes at the open end of the tube color the Bunsen flame yellowish green.

(5) The oxide deposit can be dissolved in water, perhydrol, and ammonia. Treatment with potassium or rubidium chloride yields potassium or rubidium perrhenate.

If rhenium compounds are placed on charcoal in an oxidizing flame[385], fumes, a green color, and a bronze-red deposit are formed. Geilmann and Wrigge said this and other flame tests were poor.

Yoe[397] added the following reagents to rhenium solutions in the order given, and noted the color changes. The solution was first prepared with hydrochloric acid and ammonium acetate. Then "aluminon" (the ammonium salt of aurintricarboxylic acid) was introduced, causing formation of a red solution. Ammonium hydroxide turned the solution pale yellow, and ammonium carbonate destroyed all color.

Potassium thiocyanate and stannous chloride were presented as reagents by Geilmann, Wrigge, and Weibke.[398] As little as 0.5×10^{-6} gram of rhenium could be detected. The thiocyanate was added to an acid solution containing stannous chloride. The presence of rhenium was indicated by a yellow color: ether extraction removed the yellow complex and evaporation of the extracted solution left a red solid. This reaction was modified by Hurd and Babler[399] and, in a general study, was later stated by Hurd[400] to be the best laboratory test for the detection of Re^{+7}. Hurd also found that ethyl xanthate would separate molybdenum from rhenium by formation of a molybdenum complex, removable by carbon tetrachloride extraction. The rhenium is then free to be detected if present. This reaction separates Group III elements in the analysis system developed by Wenger, Duckert, and Ankajdio.[401]

Hurd[400] discovered that rhenium will appear in the test for arsenic using the system of Prescott and Johnson. Their text[402], noting that rhenium belongs to the hydrogen sulfide group, suggested detection by fusion of the heptasulfide with sodium hydroxide. In the absence of chromium, manganese, rubidium, and osmium, a yellow color appeared. Water extraction and precipitation of ammonium or potassium perrhenate give further proof if desired.

Rhenium can be determined in Noyes and Bray's system, although much rhenium is thought to be lost in acid hydrogen sulfide precipitations.[403, 404] However, this can be avoided, and final detection by stannous chloride, potassium thiocyanate, and hydrogen sulfide is recommended.

Geilmann and Bode[405, 406] have recently compiled extensive information on the techniques of separating rhenium from the hydrogen sulfide group and other metal ions. Some of the methods for cation removal follow:

(1) Ag^{+1}-Precipitate as a chloride or metal from basic solution.

(2) Hg^{+2}-Precipitate as Hg by hydrogen peroxide from basic solution, or by reduction with hydrazine.

(3) Pb^{+2}-Separate as the chromate, thiocyanate, or thiosulfate.

(4) Bi^{+3}-Remove as the oxychloride or phosphate.

(5) Cu^{+2}-Precipitate by hydrogen peroxide from basic solution or remove by electrolysis.

(6) Cd^{+2}-Precipitate by 8-hydroxyquinoline.

(7) As^{+5}-Remove as $(NH_4)_3AsO_4 \cdot 3H_2O$.

(8) Sb^{+3}-Remove with thionalide, or separate the rhenium by hydrogen sulfide.

(9) Sn^{+4}-Separate by boiling in a buffered acetate solution.

(10) Au^{+1}-Separate wit sulfur dioxide, hydroquinone, or oxalic acid.

(11) Mo^{+3}-Precipitate with oxime.

(12) Ge^{+2}-Separate as Mg_2GeO_2.

(13) Se^{+4}-Remove by reducing agents. Not usually harmful.

(14) Te^{+4}-Precipitate with hydrazine and sulfur dioxide.

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(13) Se^{+4}-Remove by reducing agents. Not usually harmful.

(14) Te^{+4}-Precipitate with hydrazine and sulfur dioxide.

Special Methods

Heyrovsky[6,407], who originally laid a claim to the discovery of rhenium with his polarograph, later stated the instrument would detect a 1×10^{-6} molar solution. The rhenium must be present as the sulfide. This work of Heyrovský's was separate from the discovery claim (which was later abrogated) and is considered fully accurate.

Electrolysis and spectroscopy were utilized by Schleicher[408], who electrolyzed a small volume of solution with a copper wire as cathode. The anode was a platinum crucible lid which contained the solution. After electrolysis the residue and solution were evaporated in an electric arc giving rhenium spectral lines.

Summary

Table 13 lists a number of characteristic qualitative reactions, including spot tests, special methods, and some of the general methods. A few reactions not discussed in the text are also reported. Where possible, the test is evaluated.

Many of the qualitative methods presented herein are either inaccurate or too complicated. However, most authors agree that the microscopic identification of crystals is a positive, straightforward method. The chemical reactions are simple and few, and a permanent pictorial record of the crystals can readily be maintained.

Quantitative Analysis

Chemical Methods

The first significant step in the development of chemical methods of quantitative analysis was taken by Geilmann and Voigt[86,412] in 1930 when they applied the organic base, nitron (1,4-diphenyl-3,5-endo-anilino-4,5-diphenyl-1,2,4-triazole), formerly used for determination of nitrates, to the analysis of perrhenates. Slightly acid potassium perrhenate, treated with nitron, formed very insoluble precipitates in water (0.18 mg/l) and even less soluble ones in the presence of nitron acetate. The rhenium is normally determined gravimetrically as Re^{+7} and can be recovered. If molybdenum is present, it interferes, but can be removed with 8-hydroxyquinoline.[413,414] Many methods[405] for the quantitative analysis of rhenium use nitron for the final determination, no matter what the prior steps. Melaven[33], however, currently producing rhenium metal at the University of Tennessee, does not recommend nitron, and prefers the organic precipitate tetraphenyl arsonium chloride, to be discussed below.

One common method of the nitron type is that of Russian chemists[415], who first separated both rhenium and molybdenum from acid solutions as sulfides. The precipitate was then oxidized with alkaline hydrogen peroxide to cause conversion to perrhenates and molybdates. Care must be taken here as the peroxide may contain nitrate.[416] Molybdenum was removed by 8-hydroxyquinoline, and the rhenium determined with nitron.

It was long believed that if rhenium could be precipitated from basic instead of acid solution, separation from molybdenum would occur in that step. This had been considered impossible until Muller and LaLande[417] claimed that treatment of perrhenate solutions with hydrogen sulfide under pressure produced a slow but practically quantitative precipitation. This was done only with difficulty. Recently, however, it has been shown that rhenium heptasulfide is appreciably soluble in alkaline sulfide solutions, refuting the claim of Müller and LaLande.[418]

More recently, acid sulfide precipitations have been carried out under pressure.[419] Geilmann and co-workers[420] summarized sulfide precipitations from various types of rhenium solutions:

$\underline{Re^{+3}}$ - Precipitate from 0.05-1.0N hydrochloric acid solutions at room temperature. A mixture of sulfides results.

$\underline{Re^{+4}}$ - Stronger acid solutions can be used. Rhenium disulfide precipitates.

$\underline{Re^{+7}}$ - Add warm ammonium polysulfide, then add acid. If desired, rhenium of other valences can be oxidized to Re^{+7} prior to precipitation. However, this method is considered poor, as the precipitation may be sulfur contaminated.

$\underline{Re^{Any}}$ - Saturate with hydrogen sulfide at room temperature, then heat the closed flask to 100 C. Rhenium sulfide will precipitate under the pressure generated.

Geilmann and Bode[421] have also devised a sodium thiosulfate type of sulfide precipitation. Reduction of rhenium sulfides with hydrogen at elevated temperatures has been suggested.[422]

Krauss and Steinfeld[423] found that thallium acetate, $TlC_2H_3O_2$, would separate insoluble thallium perrhenate from Re^{+7} solution. The determination was gravimetric and chlorides interfered. However, thallium perrhenate is soluble in cold water to the extent of 1.15 g/l[264] and, on this basis, the method cannot be recommended for quantitative analysis.

The volatility of rhenium heptoxide is useful for separation from molybdenum. Volatilization was originally obtained by heating the perrhenates with sulfuric acid in air. This was objectionably slow, so hydrogen

TABLE 13. SOME SIMPLE TESTS FOR RHE

Reagent or Procedure	Color or Result if Rhenium Present	Amount Detectable, ppm	Interfering Elements (if mentioned)
Potassium thiocyanate	Yellow red	-	-
Precipitate rhenium as: (1) $KReO_4$ (2) $RbReO_4$ (3) $CsReO_4$ in presence of MnO_4^{-1}	 - Red Red	 0.25 0.10 -	 Mo Mo Mo
Open-tube reactions	Bluish oxide Yellow crystals White droplets White fumes	-	-
$SnCl_2$ and KCNS	Yellow	0.5	Mo
HCl and NH_4Ac plus: (1) Aluminon (2) NH_4OH (3) $(NH_4)_2CO_3$ in that order.	 Red Pale yellow Colorless	-	-
Nitron, Na_2S, gelatin plus: $TiCl_3$	 Brownish yellow	-	-
HI and I crystal	Dark precipitate	-	Mo, W
(1) $SnCl_2$ + Ferrocyanide (2) $SnCl_2$ + Dimethylgyloxime (3) Heat (2)	Red Yellow Green	100	-
H_2O_2, $KMeO_4$, RbCl	Identify crystals by microscope	-	-
$SnCl_2$ and Na_2TeO_4	Black	0.025	V, W, As, Os, Mo
Na_2CO_3 bead, >50% Mn, heat in reducing flame	Black to yellow to white	15	-
Roseochloride	Orange	1.4	-
HCl plus: Rb, Cs, pyridine quinoline, acridine, aniline, brucine	Identify crystals by microscope		-
Toluene-3,4-dithol and KCNS	Green	5	Mo
Zwikker's Reagent and Vaseline or $TlNO_3$ and Vaseline	Identify blue crystals by microscope	10# or 10	-
Polarograph	No step, no Re	10^{-8} molar solution	-
Spectrograph	Characteristic lines	-	Fe, Mn, Mo
X-ray spectra, L_{α_1} and L_{β_1}	Characteristic lines	0.72	Mo for L_{α_1}
α-benzildioxime and H_2SO_4	Colored complex	5	

Evaluation by Wenger and Duckert(392) For ReO_4^{-1}	For Re^{+7}	Evaluation by Hurd(385, 405)	Author	Reference
			Noddack	297
			Geilmann and Brünger	389
Poor				
Poor				
			Geilmann and Wrigge	395
	Poor	Best lab test for Re^{+7}	Geilmann, Wrigge, and Weibke	39b
			Yoe	397
	Poor		Kronman and Bibikova	383
Poor			Kronman and Berkman	384
Poor				
Good	Good		Tougarinoff	409
Good	Good			
Good	Good		Kao and Chang	393
Good	Good		Poluektov	388
			Yagoda	386
			Neusser	334
Cs, Rb acridine good	Rb, acridine good	Ca good	Geilmann and Wrigge	[illegible]
			Miller	381
			Graf	390
Poor				
			Heyrovsky	8
		Good for large [illegible]	[illegible]	408
			Prévot	410
			Tribalat	411

chloride was passed through the perrhenate-sulfuric acid solution, causing a rapid distillation.[424, 425] Further developments occurred[426], and now the method is to acidify the test solution with nitric and hydrochloric acids, partially evaporate, treat with sulfuric acid, and steam distill.[427, 428]

Still other methods have been reported for securing a rhenium-molybdenum separation. Hoffmann and Lundell[429] reduced the molybdenum to an ether-soluble complex with mercury and potassium thiocyanate. The ether extract was used to determine molybdenum. Stannous chloride then reduced the rhenium to an ether-soluble state, which was extracted and determined. Hurd and Hiskey[430] varied this procedure slightly by extracting molybdenum and rhenium together with ether, then removing the rhenium by distillation. Geilmann and Bode[431, 432] studied these ether separation methods, and recommended that the molybdenum be removed by 8-hydroxyquinoline. In this case, it was suggested that potassium xanthate be added and the molybdenum then be extracted as a molybdenum xanthate complex with chloroform.[414, 430, 432, 433]

Melaven and Whelsel[434] and Geilmann and Bode[432] suggested that α-benzoinoxime be substituted for 8-hydroxyquinoline. Melaven had also evaluated the foregoing methods. He found that the molybdenum xanthate-chloroform extraction of Hurd[430] was satisfactory for qualitative but not quantitative work. Ether extraction with steam distillation was satisfactory for rhenium determinations in manganese ores, but not in molybdenite. The mercury reduction method of Hoffmann and Lundell[429] was satisfactory, but long and detailed.

In the α-benzoinoxime method, the molybdenum was precipitated from solution with the reagent and separated by filtration, leaving rhenium in solution. Potassium thiocyanate and stannous chloride were added. These caused formation of a rhenium thiocyanate color complex, the transmittance of which was measured with a photoelectric spectrophotometer and compared with a blank, thus determining the rhenium content. The method is not recommended if the sample contains large amounts of molybdenum.

Willard and Smith[435] found that tetraphenyl arsonium ion, $(C_6H_5)_4As^{+1}$, formed the complex $(C_6H_5)_4AsReO_4$ with perrhenates. This is a white, crystalline solid, insoluble in cold water. From 0.43 to 133.0 milligrams of ReO_4^- can be determined gravimetrically in a moderate excess of the reagent. A potentiometric-type determination can be substituted if desired. Precipitation is usually carried out in hot sodium chloride solution. Nitrate must be avoided, but molybdenum does not interfere if a few simple precautions are taken. A few other ions such as MnO_4^{-1}, I^{-1}, Hg^{+2}, and Sn^{+2} interfere. This method is presently used and recommended by those[33] working on rhenium at the University of Tennessee. However, consistently low results were at first obtained, so W. Smith and Long[260] suggested a modification of Willard and G. Smith's method. Normally the accumulated precipitate containing rhenium was washed with water. The modification involved substitution of a saturated solution of tetraphenyl arsonium perrhenate for washing, which corrected this difficulty. Tribalat[436, 437, 438], an active French worker in rhenium chemistry, also has used this method recently with considerable success.

Another organic base, sodium diethyldithiocarbamate, has also been suggested as a possible reagent.[439]

After separation of the rhenium from interfering elements, determination may be accomplished by gravimetric methods (as above) or by volumetric or colorimetric methods. In general, colorimetric methods seem to have been the most popular. Color-producing reducing agents such as bromine[427, 430] or stannous chloride with thiocyanates[429, 431, 433, 436] are reacted with the unknown, standards are prepared, and measurements taken by comparison in Nessler tubes. Recently, photoelectric spectrophotometers, which measure the transmittance of light, have been introduced.[433, 434]

Titration methods have been used extensively in rhenium determinations, but recently have yielded to more rapid methods such as the colorimetric determinations. Geilmann and Hurd[440], for instance, dissolved the lower oxides of rhenium by oxidation with perhydrol, and then titrated the resultant perrhenic acid with a base. Although this method of oxidation of the lower oxides has now been declared unreliable,[441] ferric sulfate, potassium dichromate, or ceric sulfate can be used for oxidation purposes if desired.[442] Excess oxidizer may be titrated with permanganate. Perrhenates have also been titrated with silver nitrate, using potassium chromate as an indicator.[443]

Geilmann and Hurd[444] found it possible to determine chlororhenic acid in the presence of perrhenic acid with tetron (N, N'-tetramethyl-o-tolidine) which precipitated a weighable complex containing Re^{+4}.

Special Methods

Electrolytic methods have been developed. The Tomiceks[445] cathodically reduced perrhenate ion in sulfuric acid solution causing the rhenium to deposit completely on the cathode; it was then oxidized and titrated. Voigt[446] varied this method by forming cathodic deposits from ammoniacal solutions. Mercury served as the cathode and was distilled off, leaving a rhenium residue which was examined polarographically.[447]

This polarographic method has been studied extensively by Lingane.[287, 448] Using hydrochloric or perchloric acid as the supporting electrolyte, the perrhenate was reduced to Re^{+4} at the dropping-mercury cathode. The diffusion current was well defined and directly proportional to the concentration of perrhenate ion. The half-wave potential in 4N perchloric acid is

-0.4 v and in 2N and 4.2N hydrochloric acid is -0.45 v and -0.31 v, respectively, versus the standard calomel electrode. A double wave was produced in neutral unbuffered potassium chloride solutions. The first part of this wave was caused by a reduction to Re^{-1}, and the second part by hydrogen discharge. In a phosphate buffer of pH 7, ReO_4^{-1} produced a catalytic wave at -1.6 v.

Polarograms of Re^{-1} solutions in 1-2N sulfuric acid at zero C showed three anodic waves. Their half-wave potentials were α = 0.54 v, β = 0.34 v, γ = 0.07 v. A similar polarogram was obtained in 1N perchloric acid with some modifications, including separation of the β-wave into two components. In each medium the corresponding waves pertained to the same oxidation states. The α-wave represented oxidation of Re^{-1} to Re^{+2}, the β'-wave to Re^{+3}, the β''-wave to Re^{+5}, and the γ-wave to Re^{+7}.

Reduction of rhenium in alkaline, neutral, and acid solutions were observed by Geyer(449), who found that six steps occurred. The steps are listed below. Geyer recommends that Steps (1), (5), and (6) are analytically valuable.

Step	Acidity	Potential, volts	Characteristic Reaction
(1)	Alkaline to weak acid	-0.9 to -1.5	$ReO_4^{-1} \rightarrow Re$
(2)	Alkaline to weak acid	-1.3 to -1.7	$Re \rightarrow Re^{-1}$
(3)	Normal acidity	0.0 to -0.3	$Re^{+7} \rightarrow Re$
(4)	Normal acidity	-0.5 to +0.9	$Re \rightarrow Re^{-1}$
(5)	High acidity	+0.4 to +1.0	$Re^{+7} \rightarrow Re^{+4}$
(6)	High acidity	-0.1 to -0.3	$Re^{+4} \rightarrow Re$

Hölemann(328) found that hot perrhenate solutions reduced so smoothly with stannous chloride that ReO_4^{-1} could be determined potentiometrically. In 4N $HClO_4$ and 2N KCl, these perrhenate reductions have been found to be irreversible.(450)

The catalytic properties of rhenium can be utilized for a semiquantitative determination, as they control reduction of sodium tellurate by stannous chloride(451) to tellurium metal. If a protective colloid is used, the tellurium will remain suspended in solution and can be determined "colorimetrically" to give a measure of the rhenium present. The accuracy is only about 10 to 20 per cent.

Analysis of rhenium in materials such as meteorites has been accomplished by irradiation of the specimens in an atomic pile.(28) The substance was compared with a standard and the relative radioactivity gave a measure of the rhenium present.

Summary

For general determinations of rhenium, the method of Willard and G. Smith(435) using tetraphenyl arsonium chloride is recommended and used by most researchers today. The modification of W. Smith and Long is, of course, mandatory.

In conclusion it should also be noted that the work of Geilmann (with numerous co-workers) presents almost a step-by-step history of the analytical chemistry of rhenium, from 1930 to the present, in his series, "The Analytical Chemistry of Rhenium". There are no less than 20 sections in this splendid series, published in Germany in the Z. anorg. allgem. Chem. and in the Z. anal. Chem.

ELECTRODEPOSITION

Hölemann(87) foreshadowed successful plating of rhenium in 1933 when he precipitated pure rhenium metal by the electrolysis of acid solutions containing perrhenate and fluoride ions. He claimed both high current and high material efficiency, but was unable to produce a satisfactory plate. A year later, Fink and Deren(88) obtained hard, bright, compact deposits of rhenium from acid, neutral, and alkaline baths, by controlling the pH very carefully. The pH value depended upon the electrolytes (other than rhenium) present. Plating temperature was important and can be considered to increase with the pH. Four baths are given as examples in Table 14. In addition to these, an oxalate bath of pH 1.2 to 1.5 and a sodium bicarbonate-ammonium sulfate bath of pH 7.5 to 3.5 were developed.

The plate obtained was found to be mirror bright if deposited on a polished surface. It was highly resistant to hydrochloric acid attack. The rhenium was deposited on several metals such as brass, copper, and tungsten and could be codeposited with other metals such as nickel and cobalt. Lundell and Knowles(284) claimed satisfactory electrodeposition of rhenium from dilute sulfuric acid solutions at much lower current densities, i.e., 0.25 amp/dm^2.

Young(452) somewhat disagreed with Fink and claimed the sulfuric acid concentration must be raised to give a bright plate. Young could not plate rhodium over rhenium but found that if he flash-plated rhodium onto the base metal first, then deposited the rhenium, he could finally plate rhodium that would adhere satisfactorily.

Netherton and Holt(89) also reviewed Fink's work, particularly with respect to current efficiency. They found that the CCE (cathode-current efficiency) was generally quite low. Bath No. 3 in Table 14 was recommended as the most satisfactory, where, if a current density of 8 amps/dm^2

TABLE 14. FOUR RHENIUM-PLATING BATHS SUGGESTED BY FINK AND DEREN

Bath No.	Perrhenates	Other Electrolytes	pH	Temp, C	Current Density, amp/dm²
1	$KReO_4$ 11 g/l	H_2SO_4 [illegible] g/l (Sp. gr. 1.84)	0.9	[illegible]	10-14
2	$HReO_4$ 20 g/l	H_2SO_4 5 g/l (Sp. gr. 1.84)	0.7-1.2	25-30	10-15
3	$KReO_4$ 10-15 g/l	H_2SO_4 90 g/l (Sp. gr. 1.84)	0.80-1.00	25-45	10-16
		NH_4OH 100 cc (28% NH_3)			
4	$KReO_4$ 12 g/l	H_3PO_4 48 g/l (Sp. gr. 1.7)	2.1	80-90	13-17
		Na_2HPO_4 66 g/l			

at 70 C was used, the CCE was 15 per cent. These authors also developed an ammoniacal citrate bath, found to be the best for thin plates. The rhenium deposits tarnished in air but possessed good resistance to hydrochloric and sulfuric acids.

Recently these authors[247, 248] investigated the conditions for co-deposition of other metals with rhenium, using nickel, cobalt, and iron. Ammoniacal citrate baths were most commonly utilized. Compositions of the most successful baths are recorded in Table 15. pH variations markedly affected the alloy composition and were carefully controlled. The corrosion resistance of the alloys plated was evaluated and is reported in the Corrosion Resistance section of this report.

TABLE 15. PLATING BATHS FOR THE CODEPOSITION OF NICKEL, COBALT, OR IRON WITH RHENIUM AS RECOMMENDED BY NETHERTON AND HOLT

Plate	Bath Composition	pH	Temp, C	Current Density, amp/dm^2	CCE, %	Per Cent Rhenium
Re-Ni	$KReO_4$, 10 g/l Citric acid, 66 g/l $NiSO_4 \cdot 6H_2O$, 56 g/l NH_4OH to pH of 12	12	70	5	90	70
Re-Co	$KReO_4$, 10 g/l Citric acid, 66 g/l $CoSO_4 \cdot 7H_2O$, 60 g/l NH_4OH to pH of 7	7	70	5	85	75
Re-Fe	$KReO_4$, 10 g/l Citric acid, 66 g/l $FeSO_4 \cdot 7H_2O$, 59.4 g/l NH_4OH to pH of 7	7	70	5	65	85

BIOLOGICAL PROPERTIES

Toxicity

Rabbits were dosed with 200 milligrams of potassium perrhenate[453] per kilogram of body weight. No unusual effect was observed, even though the lethal dose of manganese in analogous experiments was 5 to 6 mg/kg of body weight. Repeated doses of rhenium also had no ill effect. The lethal dose[454] for rats, injected intraperitoneally as sodium perrhenate, is about 1000 mg/kg of body weight. Molybdates are roughly tenfold more poisonous than perrhenates, and rhenium chlorides are somewhat more toxic also, due to hydrochloric acid liberation.

Physiological Effects

Rhenium has no effect on the blood pressure of rats and has no hemopoietic action.[454] Radioactive rhenium was found to concentrate in the thyroid, but practically all of it was excreted through the urine within two days.

Botanological Properties

Druce[455] reported that cress seedlings watered with a 0.1 per cent solution of potassium perrhenate did not grow quite as well as the control seedlings watered with rain water, but the rhenium-watered seedlings grew better than those watered with a 0.1 per cent solution of potassium permanganate. Geraniums watered with perrhenate solutions cast off leaves that were found to contain rhenium, and specimens of mullein (Verbascum thapsus) were found to do poorly, compared with the control plants when treated similarly.

USES OF RHENIUM

Rhenium, to date notably a rare and expensive metal, has found use only in such specialized applications as catalysis, thermometry, and pen-point alloys. It is in great part due to prospective catalytic properties that the chemistry of rhenium has been so well developed. Metallurgical applications have remained in the background, probably due to lack of cheap massive metal, and the paucity of information on rhenium's metallurgical properties bear this fact out. Electronic and lamp applications of rhenium have been slow in development also, but show great future promise.

The general situation may be well summed up by the words of Ida and Walter Noddack[24], discoverers of rhenium and still active in its chemistry: "Rhenium can never be made into massive articles in industry, but it will find application where it possesses a singular property of special value, as in the case of the platinum metals".

Past and Present Applications

Catalysis

Rhenium was first suggested for catalytical use in 1929 by the Noddacks[456, 459] for oxidation processes. Free or combined rhenium on a tungsten and quartz carrier promoted oxidation of sulfites to sulfates, nitrites to nitrates, and aniline to aniline black. The heats of formation of rhenium oxides are small, so rhenium is a good oxygen transmitter. Oxidation of ammonia[458] was conducted utilizing a rhenium-platinum alloy or rhenium plated on platinum. These catalysts were all in the form of gauze.

Other investigators, meanwhile, found rhenium valuable for destructive and constructive hydrogenation, the refinement of anti-knock fuels, and desulfurization.[459,460,461] Shortly, Anisimov, Krasheninnikova, and Platonov[462,463,464], who commenced a series of articles on the catalytic properties of rhenium, claimed that rhenium was poor for hydrogenation and oxidation, but an effective dehydrogenation agent. In the dehydrogenation of ethanol to acetaldehyde, maximum yields of about 12 per cent occurred at 300 and 600 C, with a minimum yield at 400 C. Propanol gave 20 per cent propionaldehyde at 400 C. The propionaldehyde formed was practically undecomposed and the propanol was not dehydrated. Much better results were obtained in the dehydrogenation of isopropanol to acetone. At 400 C the yield was a maximum of 85 per cent. Chloroform was also produced by the catalytic action of rhenium at this time.[465] Finely divided rhenium metal failed to hydrogenate either maleic acid or cyclohexene effectively, but if the metal was prepared by hydrogen reduction of ammonium perrhenate, catalytic action was improved for all uses, including both hydrogenation and dehydrogenation.[466,467] However, a copper-rhenium catalyst was just as effective as rhenium alone and considerably less expensive.

The Russians continued their work on a wide scope and carried out a number of additional organic reactions by rhenium catalysis, a summation of which is given in Table 16. Eventually their best rhenium-metal catalyst was prepared by dissolving the rhenium metal in nitric acid, neutralizing with ammonium hydroxide, and then evaporating to dryness. This product was reduced in hydrogen for 1 to 2 hours at 150 to 170 C, 1 hour at 170 to 250 C, 2 hours at 400 C, and a final 2 hours at 400 C.[473]

Colloidal rhenium catalysts are considered the best rhenium catalysts at the present time.[474] Zenghelis and Stathis[475,476] prepared catalytic rhenium in a colloidal form by treating potassium perrhenate with protalbinic acid and chloroform, or by treating potassium rhenium chloride with gum arabic, hydrazine, and formaldehyde. The colloidal solution catalyzed the decomposition of hydrogen peroxide and hydrogenated maleic acid. These authors[477] also moistened rhenium metal with sulfuric acid and found it possible to synthesize ammonia from its elements thereby. The decomposition of ammonia over rhenium has also been studied.[478] However, Zenghelis and Stathis evaluated rhenium as a catalyst and found it just fair, compared with ruthenium, palladium, and platinum.

Rhenium can be alloyed with these and other elements to form effective catalytical alloys.[479] The metal or its compounds can also be adsorbed on powdered, activated charcoal or coal. In the latter state it was claimed

TABLE 16. THE EFFECT OF RHENIUM CATALYSTS ON A FEW ORGANIC REACTIONS
(Compiled from the data of Anisimov, Krashemikova, and Platonou)

Starting Compound	Product	Temp, C	Yield, %	Catalyst	Reference
$CH_3(CH)_2OH$ (ethyl alcohol)	CH_3CHO (acetaldehyde)	300 600	11 14	NH_4ReC_4	462, 463
NO	N_2	-	Good	NH_4ReC_4	463
$CH_3(CH)_2OH$ (n-propyl alcohol)	CH_3CH_2CHO (propionaldehyde)	200-400	21	Re metal	464
$(CH_3)_2CHOH$ (iso-propyl alcohol)	$CH_3(CO)CH_3$ acetone	400	85	Re metal	464
$CH_3(CH_2)_3OH$ (n-butyl alcohol)	$CH_3(CH_2)_2CHO$ (n-butyraldehyde)	350-450	-	Re metal	467
$(CH_3)_2CHCH_2OH$ (isobutyl alcohol)	$CH_3(CO)CH_2CH_3$ (methyl ethyl ketone)	350	-	Re metal	467
HCO_2H (formic acid)	CO_2	230	100	Re metal	468
CH_3OH (methyl alcohol)	HCOH (formaldehyde)	-	Good	Re poisoned by H_2S or As_2O_3	469
Cyclohexanol	Cyclohexanone	250-	Good	Re metal	470
Cyclohexanol	Phenol	500	79	ReS_2	470, 471
Alcohols	Aldehydes or ketones	400-500	Good	ReS_2	471, 472

to be valuable for hydrogenation, desulfurization, or conversion of phenols, cresols, etc., organics commonly found in coal tar and mineral oil.[480]

Recently, Tribalat[481] catalyzed the following reductions with perrhenate ion so that they occurred quantitatively. The oxidation potentials for these reactions are listed below, but the abstract consulted did not indicate the products formed.

Reduction	Oxidation Potential, v
NO_3^{-1} (by $SnCl_2$)	1.05
NO_3^{-1} (by $FeSO_4$)	1.00
NO_3^{-1} (by $HAsO_3$)	1.03
HNO_2 (by $SnCl_2$)	1.29
NH_2OH (by $SnCl_2$)	1.35
HNO_2 (by NH_4OH)	-0.05
HNO_2 (by N_2H_4)	-1.87

If the evaluation of Zenghelis and Stathis is correct, rhenium is not of great worth as a catalyst. At the present time its price does not compare favorably with certain other metals more commonly used for these purposes. Rhenium evidently is effective catalytically, but so are many other metals and materials. Rhenium is not unique as a catalyst, but merely good.

Thermocouples

Rhenium was early recommended[240] as a replacement for rhodium in rhodium-platinum thermocouples. Three to fifteen per cent rhenium was suggested, and it was also found that three or more per cent rhenium prevents brittleness in these wires. Schulze[482] and Goedecke[483] extensively investigated the properties of rhenium for thermoelectric use. Rhenium produced a potential three times as great as rhodium when equal percentages of each were tested as platinum alloys against pure platinum. The comparison is shown in Figure 13. Characteristics of the couples Pt8Re/Pt and Pt4.5Re5Rh/Pt are plotted in Figure 14. These couples produced voltages as high as those of Chromel-Alumel couples. More recent literature[52] indicated use of a Pt5.4Re3.5Rh/Pt couple in Germany. The couple Ir/60Re40Ir produced a remarkably straight characteristic curve (Figure 15).

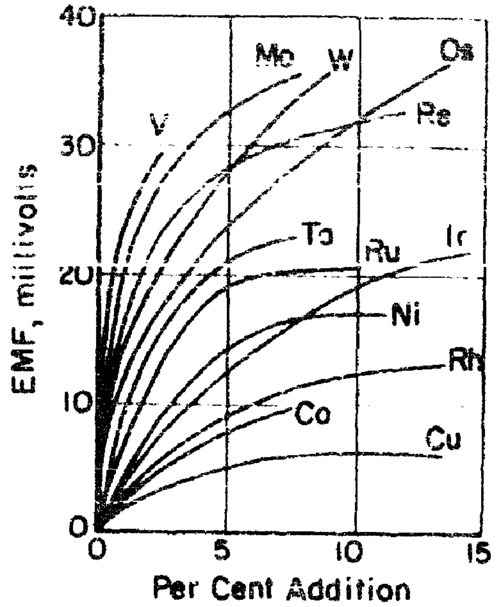

FIGURE 13. EMF PRODUCED BY ADDITION OF VARIOUS ALLOYING ELEMENTS TO PLATINUM IN ALLOY-PLATINUM VERSUS PLATINUM THERMOCOUPLES AT 1200 C
Schulze(482)

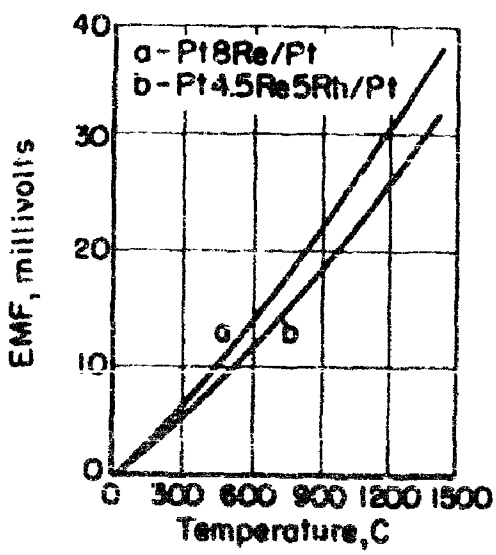

FIGURE 14. EMF PRODUCED BY PLATINUM ALLOY THERMOCOUPLES
Schulze(482)

A-40II

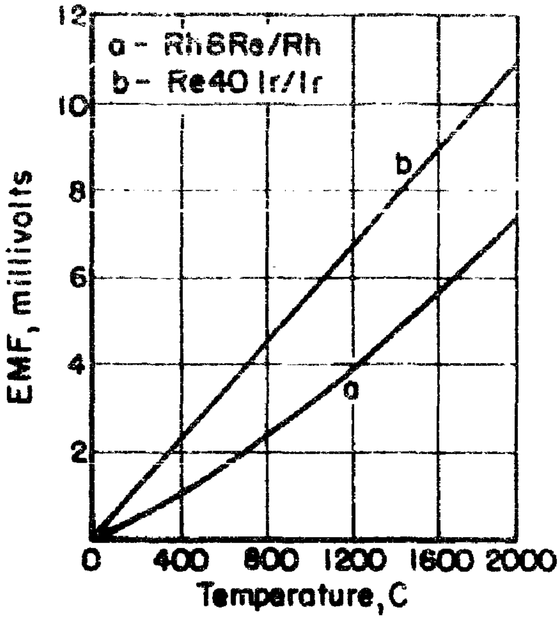

FIGURE 15. CHARACTERISTICS OF IRIDIUM-RHODIUM-RHENIUM THERMOCOUPLES
Schulze[482]

A-4012

Due to these properties, attempts were made to replace at least part of the critical rhodium in platinum-rhodium couples with rhenium in German thermocouple wires.[54] However, it was claimed[241] that excessive volatilization of the rhenium above 1000 to 1100 C (a result of oxidation followed by volatilization of the oxide) caused changes in the thermocouple emf, precluding the use of rhenium above this temperature. The Pt8Re/Pt couple definitely did this, but Goedecke claimed that the Pt4.5Re5Rh wire did not.

Some reports[24] stated that rhenium thermocouples (alloys unspecified) were good up to 1900 C and for long time periods. Goedecke and Schulze did specify the alloy: it was Rh8Re/Rh and possessed an emf of 7.2 mv at that temperature. If volatilization occurs, this high-temperature usability is questionable, but the presence of a neutral atmosphere would eliminate all trouble.

Contact Materials

Several patents have been issued[243, 244, 484] for rhenium-containing electrical contact alloys, previously mentioned in the metallurgical section of this review. In general, rhenium comprised about 10 per cent of the composition; the balance consisted of about 1 to 20 parts molybdenum or vanadium and the remainder tungsten. These materials could be prepared by powder-metallurgy techniques and very fine-grained hard compacts with melting points over 2900 C resulted. They were excellent for make-and-break contacts, due to innate toughness and low electrode emissivity. According to Weiger[485] there was little tendency for arcing, pitting, oxidation, or transference of the metal during operation, and small amounts of impurities did not interfere with their properties. They were also valuable as refractory bases suitable for impregnation with copper, silver, or gold.

The Noddacks[24] explained that the excellency of rhenium for make-and-break contact alloys is a result of oxygen absorption by the reduced metal. The oxygen combines with rhenium to form lower oxides which are good conductors and can be thermally decomposed.

Wear-Resistant Alloys

Several alloys of rhenium possessing high wear resistance have been developed in Germany.[245, 246] Their primary use has been to replace the alloys containing osmium formerly used for pen points.[52] Several typical compositions have been recorded in the section under alloys. The rhenium content varied widely, but in most of the alloys it was present from 50 to 99 per cent. Many other metals were contained in the compositions, the most prevalent being tungsten, nickel, cobalt, molybdenum, and platinum. These alloys were usually prepared by powder-metallurgy methods, crushed, seived, and hand-tweezer picked for suitable pen points. Far more worthwhile uses for rhenium than in wear-resistant types of alloys for pen points have been suggested, but evidently not yet applied. These will be discussed below.

Lamp Filaments

Since rhenium has been found to be readily deposited on tungsten filaments by the halide-thermal-decomposition processes, early suggestions were forthcoming for its use as a lamp filament.[486] The Noddacks[487] found that rhenium volatilized less in vacuo than tungsten and thus could be used up to 2550 C. They also suggested[488] forming filaments by working up rhenium and ammonium perrhenate into a plastic mass, forcing it through nozzles or dies as a filament, and finally reducing the perrhenate binder in the resultant filament with hydrogen.

Agte[235] recalled that attempts to coat tantalum carbide on a tungsten wire base were unsuccessful. Tantalum carbide is a better filament material than tungsten, but more brittle. The filaments were unsuccessful because the tungsten core became carburized and the tantalum carbide lost its fine filament properties. Agte claimed that rhenium formed no carbides (which is not wholly accurate) so he developed a layer of tantalum carbide on a rhenium instead of a tungsten core. No diffusion of carbon occurred and the carbide was properly active. The carbide could also be prepared effectively on rhenium-alloy cores, or on tungsten cores first coated with a layer of rhenium. In all cases, tantalum was vapor deposited as the final coating, then carburized in methane.

Photographic Emulsions

Halide salts of rhenium, of the type R_2ReX_6 (where R is a metal and X is a halide), were found to be excellent fog inhibitors.[489] A fog inhibitor of this type was added to the emulsion after final digestion or following the after-ripening during preparation of the plate. A time lag after processing improved the fog-inhibiting properties.

Potential Uses for Rhenium

Facts and data show that rhenium has been used but little to date. The literature seems to indicate that a low German production of about 2 to 400 pounds a year for 10 to 12 years (time period estimated) after 1930 probably went to three sources: (1) research, (2) thermocouples, and (3) pen points. The first source undoubtedly took the lion's share. The other uses so far suggested for rhenium have been largely confined to experimental applications. U. S. production from the University of Tennessee[33] in the main part has been sent to universities and institutions for research. In the Western World today, rhenium is 99 per cent a laboratory metal.

This situation should not last much longer. So far, its development has been retarded by the exceedingly high price, its scarcity, and a lack of knowledge about some of its very interesting properties. It appears, for instance, that rhenium should be able to do most of the things tungsten does in electron tubes, and should be able to do some of them better. Other possible uses are also known, but all applications, including the electronic ones, must stand on a firmer foundation of physical, metallurgical, and electronic knowledge than is presently available. Simultaneously with the advent of this information, the potential uses of rhenium will have crystallized, and with utility and markets for the metal in sight, the present excessively high cost will be reduced.

The following is a discussion of some of the possible future uses of rhenium.

Electronic Uses

Physical and Electrical Properties for Electron-Tube Applications. Rhenium has several properties which indicate that it would be more desirable for certain electron-tube applications than tungsten or other metals. The melting point of rhenium has been generally accepted to be 3440 ± 60 K.[118] Evidence from the literature indicates that the resistance of rhenium to attack by residual gases in evacuated containers is much greater than that of tungsten.[88] These properties would be a very important factor in increasing the life of electron-tube heaters.

Rhenium is more ductile after being heated to high temperatures than tungsten.[91, 94] This property would give a filament constructed from rhenium greater resistance against mechanical shock than the usual tungsten filament. The electrical resistivity is about four times that of tungsten.[120] This would permit filaments of rhenium to be constructed with a larger cross section than tungsten filaments but with no change in the total resistance of the filament. The larger cross section of a rhenium filament would give added ruggedness to the filament, while the higher resistivity would permit use of the same voltage source for heater power which is required for a tungsten filament with a smaller cross section.

The spectral emissivity of rhenium has been reported to be about 0.366.[119] This would make the use of pure rhenium as an anode material in high-power tubes undesirable since other materials would dissipate more heat by radiation.

Application of Rhenium for Electron-Tube Heaters. The cathodes in vacuum tubes may be classified as directly heated and indirectly heated cathodes. The directly heated cathode is, as the name implies, a cathode whose emitting surface is heated by the passage of the heater current directly through the emitter material. The indirectly heated cathode is one in which the emitter material is coated on a sleeve, or cap, which encloses the heater element. The sleeve, or cap, is heated indirectly by radiation and conduction from the heater element. As a rule, the directly heated type cathode is used in tubes where the power and/or voltage requirements are very high. They are also employed in battery-operated tubes in which it is desired to employ the minimum amount of power to heat the filament. The indirectly heated cathodes are used where the power requirements are not unusually high and where efficiency is fairly important.

The materials which are most commonly employed in directly heated cathodes are tungsten and thoriated tungsten. It appears that pure rhenium may be as good as, or better than, tungsten as an electron emitter. If it is a comparable emitter, rhenium should be considered as a replacement for tungsten for directly heated cathodes. Rhenium cathodes are particularly interesting since they may be safely operated at a temperature higher than tungsten with no more evaporation of material, as a result of the lower vapor pressure of rhenium. Deterioration of the cathode is from evaporation, sputtering by residual gases, and chemical attack. Operation at higher temperatures would also increase the total emission current from the cathode.

With directly heated cathodes, a larger diameter of rhenium cathode of a given length will have the same resistance as smaller diameter cathode of tungsten. This requires a basic redesign of tubes which employ directly heated cathodes in order for the desired operating temperature to be obtained from a balance between the radiated energy and the energy input from the filament supply.

A possible application for a directly heated rhenium cathode might be in filament X-ray tubes which are employed for X-ray analysis. In this type of tube, the evaporation of tungsten poses a serious problem. When the target of the X-ray tube becomes coated with evaporated tungsten, the X-ray diffraction lines of tungsten appear in the diffraction patterns. These lines seriously interfere with the interpretation of the analyses. Since rhenium is reported not to deposit to any great degree on the walls of tubes in which it is heated, this problem would be minimized by the use of rhenium filaments.

The possibility of the use of rhenium for application in indirectly heated cathodes is fairly good. The physical and electrical properties of rhenium indicate promise as a heater for this type of cathode. Since the resistivity in ohm-cm of rhenium is higher than that of tungsten, a filament for operation on the same voltage would have a larger cross section, and consequently be more resistant to shock and vibration. The increased cross section and the ductility of rhenium would give added ruggedness to the heater. The low volatility and resistance to attack by residual gases of rhenium should increase the life of a rhenium heater over that of tungsten. It is also probable that the possibility of contamination of the emitting surface of the cathode by evaporation or migration of the heater material to the cathode-emitting material would be minimized by the use of rhenium as a heater element.

Thoriated Rhenium Emitters. In high-voltage tubes which require large emission currents, thoriated tungsten is usually employed. Since this cathode is seriously damaged by positive-ion bombardment, it is limited to application in tubes having operating potentials of less than about 10,000 volts.

Tungsten is thoriated by adding a small amount of thorium oxide to the tungsten before it is drawn into the desired size of wire. The cathode formed from the wire is flashed at a high temperature to reduce the thorium oxide to the metal. The cathode is activated by operating at a temperature which allows the thorium metal to diffuse to the surface of the tungsten wire more rapidly than it is evaporated. This permits the formation of patches of thorium on the surface of the cathode. The operating temperature is maintained at a value which permits the thorium that is evaporated to be replaced by diffusion of thorium to the surface of the cathode.

Several factors are involved in the preparation of a thoriated rhenium emitter. The success of such an emitter would depend largely upon the rate of diffusion of thorium to the surface of rhenium. If the rate of diffusion were too low, then patches of thorium could not be maintained on the surface of the rhenium. There are reports, however, that thoriated rhenium emitters have been constructed and have promising operating characteristics. The possibilities of a thoriated rhenium emitter warrant investigation, since thoriated tungsten emits about 1000 times as much current as is obtained from pure tungsten. The mechanical properties of rhenium are such that thoriated rhenium should be more rugged than thoriated tungsten.

Use of Rhenium in Electron-Tube Elements Other Than Heaters. On the basis of the indicated physical, electrical, and mechanical properties of rhenium, it appears to be promising for other elements in vacuum tubes in addition to cathodes. Since the other components are either grids or plates, the requirements for each will be considered with respect to the characteristics of rhenium.

The materials which are employed as anodes for high-power tubes must be capable of dissipating the heat which they receive as a result of the current flowing through the tube. This heat is dissipated almost entirely by radiation from the anode surface. For the dissipation of the same energy, the anode material with the spectral emissivity nearest 1 will be the coolest. Anodes are often coated on the outer surface with some material which approaches 1. The spectral emissivity of 0.366, which has been reported for rhenium(119), indicates that this metal would not be a good heat radiator. The high melting point and ductility do, however, not exclude the possibility of using rhenium for such an application. If employed, the outside surface would probably increase the emissivity, and consequently, increase the radiation of heat. The only advantage of coated rhenium over other refractory metals would be its strength at high temperatures. This does not appear too important for most applications.

As a grid material for electron tubes, rhenium appears to be little better than materials which are now in use. The material from which grids are constructed should have a low secondary-electron emission coefficient in order to reduce the grid current. For high-power tubes, the grid material must be physically strong and should have a low rate of sputtering under ion bombardment. The secondary-emission yield of rhenium is 1.30, which is only slightly less than the 1.38 reported for tungsten. Since the secondary-emission coefficient for all metals in this atomic weight range is about the same, rhenium has no marked advantage over other materials from this standpoint. The secondary emission from grid wires is frequently reduced by coating the metal which forms the grid structure with gold, or nickel. As a rule, the wires of the grid structure are of tungsten when high power is involved. The objective is to obtain strength at high temperatures. In low-power tubes, the grid is usually made of nickel, which is easier to fabricate and has a low secondary-electron emission coefficient. It is possible that rhenium would fulfill most of the requirements for a good grid material, particularly in high-power tubes. Certainly it would compete with tungsten since it is believed to have a lower vapor pressure and a higher resistance to attack by residual gases.

Powdered Rhenium in Cermet-Type Heaters. In the past few years, work has been carried on in the development of cermet cathodes. Cermets are mixtures of a metal and refractory insulating materials, which are first pressed to shape and then sintered. Cermets for cathodes contain just enough metal to give the cermet the desired electrical conductivity, since an excess of metal reduces the electrical resistance and increases the danger of cracking on repeated heating and cooling cycles. The cermet cathode is heated by passing current through it. The materials for cermets on which the most work has been performed are tungsten, or molybdenum mixed with thorium oxide. In 1950, G. A. Espersen made some tests on a cermet composed of rhenium and thorium oxide.[490] The emission constants which were determined for the rhenium and thorium oxide cermets were a work function of 2.83 electron-volts when the Richardson constant was 11.7 amp cm^{-2} K^{-2}. The emission current which was obtained from the rhenium and thoria cermet was about twice that obtained from a similar cermet formed from tungsten and thoria. It was also reported that there was less deposit on the glass bulb after 150 hours of life test at 2040 K from the rhenium and thoria cermet than from the tungsten and thoria cermet.

Although the cermet-type cathode is not in general use in electron tubes at the present time, it appears that it will find widespread use in applications where a high-power, rugged cathode is needed. It appears that rhenium is adaptable for the construction of cermets of promising materials. From the available data it appears that rhenium will be even better than tungsten for this application.

Lamp Filaments

Numerous suggestions[37, 473, 486, 487] indicate the possible use of rhenium for incandescent lamp filaments. Undoubtedly, rhenium would be excellent in this application. It can be operated at higher filament temperatures, should be stronger than tungsten, and does not enter into the deleterious water cycle as does tungsten. Druce[491] has never heard of or seen incandescent lamp bulbs with rhenium filaments on the open market, so the field is evidently virgin. Patents developed to cover this property were drawn in the early 1930's, so it is probable that they have now expired or are about to expire. Probably the only reasons for lack of rhenium filaments on the market are their scarcity and high price.

High Temperature Construction Material

Rhenium should possess excellent high-temperature structural properties. It has a melting point almost as high as tungsten, and it probably does not become as embrittled as does tungsten. Rhenium or rhenium alloys might be used above 2500 C if protected from oxidation, and Arend[492] has suggested it for use in aircraft-mounted gas turbines. However, it is probable that high cost and low production volume of rhenium preclude large-scale use of the massive metal, but for certain critical applications, utilizing small amounts of metal, rhenium might be used for construction purposes for service at extremely high temperatures. Cladding or coating to prevent oxidation is, of course, mandatory.

Thermocouples

Because of the high emf produced in thermocouples due to the presence of rhenium as an alloying ingredient, its use in this field may become widespread. Some accounts[241] claim that excessive oxidation and volatilization of the oxide of the rhenium above 1100 C prevents use of the couple Pt8Re/Pt except at low temperatures. However, the Pt4.5Re5Rh/Pt thermocouple does not do this and other alloys yet to be developed may not also. These thermocouples can be used for long periods and produce three to four times the potentials of usual noble metal couples. The couple Rh8Re/Rh[482, 483] can be used up to 1900 C, an extremely high thermocouple temperature. The Noddacks[24] state that the following thermoelements have distinct possibilities:

PtRe/Pt	PtRe/Pd
PtRe/Rh	RhRe/Rh
IrRe/Ir	

They further declared that in their opinion, the best future use for rhenium lies in this field.

Electrical Contacts

The several patents and papers on this subject indicate good potentialities for make-and-break electrical contact materials of rhenium, rhenium alloys, and/or sintered compacts which contain rhenium. These could be used as facings in large circuit breakers, or in smaller contacts such as internal-combustion engine distributor points. Rhenium content of the alloys recommended in the past has been low (usually around 10 per cent) and no objections to the performance of the alloys have been recorded in the literature. Evidently they perform very well, but the expense of rhenium has so far stifled their development.

Wear-Resistant Alloys

The use of pen-nib tips composed of rhenium alloys developed to replace scarce osmium alloys may be but a preview of the applications of rhenium in this field. Pivot bearings and wear-resistant surfaces of all types should be developed as an outgrowth of the limited German pen-point business. Watch bearings, compass bearings, scale edges, and other high-use parts of instruments and machinery could be made of rhenium alloys. The watch industry, balance makers, and all types of precision instrument manufacturers should be interested in wear-resistant applications for both civilian and military consumption.

It is possible that rhenium alloys might be highly resistant to erosion corrosion by abrasive fluids, although no tests on this type of wear have been conducted. Application would be found in needle valves and similar fluid-control devices.

Corrosion Resistance

Rhenium has been noted as possessing remarkable ability to withstand the ravages of hydrochloric acid. This acid is a notably bad actor and construction materials for containing hydrochloric acid are hard to find. Stainless steels, for instance, have a tendency to be pitted by the acid, despite their over-all high corrosion resistance in this medium. If rhenium should show no tendency to pit in hydrochloric acid, its use is a distinct possibility. It probably would be present as an electroplate or cladding on less expensive base metals.

Catalysis

Catalysis was amply covered in the Past and Present Applications section of this survey. The information presented therein stands as fair evidence that rhenium is little better as a catalyst than either less expensive metals (copper, nickel), or equally dear but more abundant metals (platinum). However, catalytic uses where no other catalysts are satisfactory are a possibility.

Miscellaneous Metallurgical Applications

The [illegible](24) point out the fact that rhenium is one of the very few alloying additions that hardens iridium without causing embrittlement.

Rhenium also improves other mechanical properties of iridium markedly. It has been reported that very thin foil and very fine wire can be prepared from iridium-rhenium alloys. Additions to platinum will improve the corrosion resistance of electrodes. Such alloys might have application in electronic or corrosion-resistant fields.

EVALUATION OF THE DATA

This section of the report presents a general commentary on the veracity and value of the data and information compiled in this survey.

It should be noted that this report has been based only on published, nonclassified type information. If it had been possible to add certain confidential data to the survey, the picture drawn might have been colored differently, particularly from the production and resources point of view.

Occurrence, Abundance, and Production

It is obvious that rhenium is rare and costly, but its potential is sufficiently great to warrant considering it as a special-purpose material. The information on world deposits is quite confusing. The concentrations of rhenium reported by various investigators have not been placed on a comparable basis, i.e., reduced to percentage of rhenium in the whole native ore. Rather, the percentages reported are often at some advanced stage of ore concentration, resulting in figures like the 25 per cent on Swedish molybdenite reported by Aminoff[43, 44]. If rhenium comes into high demand, a survey of the mineral deposits should be made to ascertain their true value. In any case, rhenium produced in this country would come from native molybdenite, relatively easily recovered and yielding an appreciably high production.[55B]

Extraction and Reduction

From the literature and from personal observation of the Tennessee process, two modern processes appear to have economical and practical merit: the Tennessee Process and the French Process. As described in the text, both are simple and direct, and both are operating at the present time.

Two other methods deserve mention. The ion-exchange procedure developed at the University of Wisconsin (in laboratory scale only) shows great promise, but its economic worth has not been proven. In addition, the Russians are probably using Feit's old process or a modern adaptation thereof. Since they are undoubtedly actively recovering rhenium, Feit's process must be considered as a practical one.

The most widely used reduction methods for the final recovery of rhenium are the reduction of heated perrhenates and the thermal-dissociation processes. If rhenium is desired directly in a consolidated form, the thermal-dissociation method will produce "hot-wire" rhenium crystal bar from rhenium halides in one step. This method has been widely used for research production of rhenium filaments. Most common, however, is the reduction of heated potassium or ammonium perrhenates with hydrogen. These are simple reactions to conduct and result in a pure powder suitable for pressing and sintering.

Consolidation and Fabrication

Little real work has been done along these lines by previous investigators, so their sparse data can be considered only a vague guide for future work.

Physical Properties

Some of the physical properties are fairly well established. Others are only phantoms, the dimensions of which have hardly been even estimated. The atomic weight, crystal structure, melting point, magnetic properties, optical and X-ray spectra, and nuclear properties seem to have been fairly well determined. Unless future experimentation indicates serious flaws in these properties, they should not have to be redetermined.

However, due to conflicting data or lack of sufficient verification, numerous physical constants come under question. Among these are the density, boiling point, specific heat, thermal expansion, electrical resistivity, and spectral emissivity. No attempt has been made to determine the vapor pressure or any of the other physical properties not mentioned in the text.

Electronic Properties

The electronic properties have been determined in part, but those evaluated have not been adequately verified. The thermionic-emission constants have been determined by only two investigators, and these two disagree. The photoelectric threshold and Hall effects have been measured by only one investigator apiece. In general, the electronic properties appear promising, but they require verification and amplification.

Metallurgical Properties

The metallurgical constants so far reported are subject to great question. The basic properties of tensile strength and elongation have been reported by only one writer, and the material used was only a fine wire in the as-deposited condition.

In the field of rhenium alloys, little is known about any alloys except those with tungsten, osmium, and iron. There is no reason to suspect the accuracy of the data for these systems, but even here the data available are sketchy.

Chemical Properties

A great deal of disagreement occurred early in the history of rhenium over the various chemical properties. With time, these disagreements seem to have been largely settled. Thus, the chemistry of rhenium is now fairly well known, although numerous minor mistakes are apparent in present-day literature. Where observed, these mistakes were filtered out of this report; great care should be exercised when reading literature on the chemistry of rhenium, as previous reviewers have often misquoted the original source.

Analytical Chemistry

Much work has also been done in this field of chemistry. After evaluation of the methods proposed for both types of analysis by the many investigators, it is suggested that microscopic identification of characteristic crystals is perhaps the most positive way to qualitatively determine the presence of rhenium. The tetraphenyl arsonium chloride method of Willard and Smith for rhenium seems to be a very widely accepted method of quantitative analysis.

Electrodeposition

Most of the experimentation in this field seems to have been ultimately successful and reasonably unchallenged. There is little other comment that can be made on it.

BIBLIOGRAPHY

References to Rhenium Cited in the Text

1. Noddack, W., Tacke, I., and Berg, O., "Eka-manganese: I. Chemical Part; II. X-Ray Part", Naturwissenschaften, 13, 567-71 (1925).

2. Noddack, W., and Tacke, I., "Rhenium and Masurium", Oesterr. Chem.-Ztg., 28, 127-30 (1925).

3. Druce, J., "Search for Element 93: I. Examination of Crude Manganese Compounds and the Isolation of Element of Atomic Number 75", Chem. News, 131, 273-77 (1925).

4. Loring, F., "Notes on New Elements", Chem. News, 132, 407-10 (1926).

5. Dolejšek, V., and Heyrovský, J., "The Presence of Dvi-Manganese (At. No. 75) in Manganese Salts", Nature, 116, 782 (1925).

6. Heyrovský, J., "A Sensitive Polarographic Test for the Absence of Rhenium in Manganese Salts", Nature, 135, 870-71 (1935).

7. Noddack, W. and I., "Recent Investigations of the Elements Masurium and Rhenium", Continental Met. and Chem. Eng., 1, 109-111 (1926).

8. Berg, O., "The Röntgen Spectrum of Element 75", Physik Z., 28, 864-66 (1927).

9. Druce, J., "Dvi-Manganese", Continental Met. and Chem. Eng., 1, 111-12 (1926).

10. Druce, J., "Discovery of Eka-and Dvi-Manganese (Masurium and Rhenium)", Chem. Weekblad, 23, 318-20 (1926).

11. Friend, J., and Druce, J., "Davyum, A Possible Precursor of Rhenium (Element 75)", Nature, 165, 819 (1950).

12. Heyrovský, J., "The Occurrence of Dvi-Manganese (At. No. 75) in Manganese Salts", Nature, 117, 16 (1926).

13. Dolejšek, V., Druce, G., and Heyrovský, J., "The Occurrence of Dvi-Manganese in Manganese Salts", Nature, 117, 159 (1926).

14. Dolejšek, V., and Heyrovský, J., "Presence of Dvi-Manganese (Element 75) in Manganese Salts", Chem. Listy, 20, 4-12 (1926).

15. Zvjaginstsev, O., "Dvi-Manganese in Native Platinum", Nature, 118, [illegible] (1926).

16. Zvjaginstsev, O., Korsunskii, M., and Selyakov, N., "Dvi-Manganese in Platinum Ores", Z. angew. Chem., 40, 256-59 (1927).

17. Prandtl, W., "The Search for Manganese Homologs, Nos. 43 and 75", Z. angew. Chem., 39, 1049-51 (1927); ibid., 40, 561-64 (1927); Ber., 60, 621-23 (1927).

18. Herszfinkiel, M., "The Elements of Atomic Numbers 43, 61, 75, 85, 87", Compt. rend., 184, 968-70 (1927).

19. Noddack, I. and W., "The Preparation and Some Chemical Properties of Rhenium", Z. physik. Chem., 125, 264-74 (1927).

20. Weeks, E., The Discovery of the Elements, J. Chem. Education, Easton, Pa., pp 519-24 (1945).

21. Von Hevesy, G., "The Use of X-Rays for the Discovery of New Elements", Chem. Rev., 3, 321-29 (1927).

22. Hurd, L., "The Discovery of Rhenium", J. Chem. Education, 10, 605-608 (1933).

23. Druce, J., Rhenium, Dvi-Manganese, the Element of Atomic Number 75, 92 pp. University Press, Cambridge, 1948.

24. Noddack, I. and W., "Rhenium and Its Present Technical Uses", Werkstoffe und Korrosion, 2, 296-98 (1951).

25. Suess, H., "Cosmic Nuclear Abundances: II. Singularities in the Abundance Distribution in Medium-Heavy and Heavy Nuclei.", Z. Naturforsch., 2a, 604-608 (1947).

26. Frank, F., "An Isotopic-Abundance Rule and its Bearing on the Origin of the Nuclei" Proc. Phys. Soc. (London), 60, 211 (1948).

27. Brown, H., and Goldberg, E., "A New Determination of the Relative Abundance of Rhenium in Nature", Phys. Rev., 76, 1260-61 (1949).

28. Goldbert, E., and Brown H., "Radiometric Determination of Gold and Rhenium", Anal. Chem., 22, 308-11 (1950).

29. Loring, F. H., "The Optical Spectrum of Rhenium (Dvi-Manganese) and Attempts to Identify this Element in the Stars", Chem. News, 142, 321-22 (1931).

30. Meggers, W. F., "Rhenium", Sci. Monthly, N. Y., pp 413-1[illegible] (November, 1931).

31. [illegible] "[illegible] of the [illegible] Fraunhofer Lines of the Solar Spectrum", Naturwissenschaften, 19, 310 (1931).

32. Noddack I. and W., "The Geological Chemistry of Rhenium", Z. physik. Chem., Abt. A, 154, 207-44 (1931).

33. Personal Interview, Dr. A. D. Melaven.

34. Kronman, E., "Geochemistry of Rhenium", Z. physik. Chem., Abt., A, 161, 395-96 (1932).

35. Handbook of Physics and Chemistry, 27th Ed., p 303, Cml. Rubber Publishing Co., Cleveland, Ohio, 1943.

36. Kroll, W., "Production and Uses of Rare Metals", Mining and Met., 27, 262-66 (1946).

37. Noddack, I. and W., Rhenium, 72 pp, Verlag von Leopold Voss, Leipzig, 1933.

38. Aartovaara, G., "The Occurrence of Rare Elements in Finland", Tek. Fören.i Finland Förh., 52, 157-61 (1932).

39. Anon., "Minor Metals", Mineral Ind., 40, 594-603 (1931).

40. Anon., "Minor Metals", Mineral Ind., 42, 614-26 (1933).

41. "Minor Metals - Rhenium", Minerals Yearbook, U. S. Gov't Printing Office, 1940.

42. "Minor Metals - Rhenium", Minerals Yearbook, U. S. Gov't Printing Office, 1946.

43. "Minor Metals - Rhenium", Minerals Yearbook, U. S. Gov't Printing Office, 1948.

44. Aminoff, G., "A Molybdenite Rich in Rhenium", Geol. Fören. Förh., 65, No. 1, 71-72 (1946).

45. Druce J., "Sources of Rhenium", Ind. Chemist and Chem. Mfr., 25, 348 (July, 1949).

46. Works, L., "Rhenium - Bearing Molybdenite in Northern Wisconsin", Rocks and Minerals, 16, 92-93 (1941).

47. Geilmann, W., Lange, G., and Berttlingck, H., "The Rhenium Content of Some Molybdenum Minerals", Neues Jahrb. Mineral., Geol., Monatsch., A. 1945-48, pp 5-9.

48. [illegible], "Rhenium - Recent Developments and Possible Applications", Indust. Chemist, 24, No. 285, 683-684 (1948).

49. Stepanov, I., "Rhenium - A Commercial Metal", Tsvetnye Metal., 19, No. 5, 66-67 (1946).

50. Bibikova, V., "Rhenium in Dusts of the Molybdenum Division of Balkhash Works", Tsvetnye Metal., 19, No. 4, 44-48 (1946).

51. Morgan, G., and Davies, G., "Residual Affinity and Coordination: XL. Some Complex Compounds of Rhenium", J. Chem. Soc., 1938, pp 1858-61.

52. Duchart, W., Lotz, H., Fröhlich, K., and Holzmann, H., Rhenium, Hensel, F. (ed.)., Office of Military Gov't for Germany (U.S.), FIAT Final Report No. 697 (5 February 1946).

53. "University of Utah to Get Atomic Pile", New York Times, p 21, September 22, 1952.

54. Anon., "Minor Metals", Mineral Ind., 44, 628-41 (1935).

55. Hopkins, B. S., Chapters in the Chemistry of the Less Familiar Elements, p 463, Stipes Publishing Co., Champaign, Ill., 1939.

55A. Personal Communication, Dr. B. W. Gonser.

55B. Gonser, B., "The Promise of Rhenium", Resources for Freedom, IV, A Report to the President by the Presidents' Materials Policy Commission, p 109, U. S. Government Printing Office, Washington (June, 1952).

56. Feit, W., "Technical Preparation of Rhenium", Z. angew. Chem., 43, 459-62 (1930).

57. Druce, J., Rhenium, p 6, University Press, Cambridge, 1948.

58. Noddack, I. and W., "Preparation of One Gram of Rhenium", Z. anorg. allgem. Chem., 183, 353-75 (1929).

59. Noddack, I. and W., "Preparation of Rhenium", Brit. Pat. 317,035 (July 28, 1930).

60. Noddack, I. and W., "Progress in the Preparation and Uses of Several Rare Elements", Metallborse 21, 603-604, 650-52 (1931).

61. Noddack, I. and W. (to Siemens - Halske A. G.), "Rhenium", Ger. Pat. 606, 448 (December 3, 1934).

62. Noddack, W. (to Siemens-Halske A. G.), "Rhenium Compounds", Ger. Pat. [illegible] (September [illegible], 19[illegible])

63. Noddack, I. and W., "Rhenium", Z. angew. Chem., 44, 215-26 (1931).

64. Doenhardt, W., "Rhenium and Other Rare Elements Obtained in Working up Mansfeld Copper Schists", Jahrb. Hall. Verb., 15, 29-34 (1936).

65. Doenhardt, W., "Rhenium and Other Rare Elements Obtained in Working up Mansfeld Copper Schists", Neues Jahrb. Mineral., Geol., Ref II, 1939, p 194.

66. Feit, W. (to Kaliwerke Aschersleben), "Rhenium", Ger. Pat. 575, 801 (May 3, 1933).

67. Feit, W., "The Technical Extraction of Rhenium and Gallium and of Some of Their Compounds", Angew. Chem., 46, 216-18 (1933).

68. Barth, O., "Metallurgical Processing of Bituminous Shales in Mansfeld", Tek. Tid., 77, 423-28 (1947).

69. Driggs, F. (to Westinghouse Elec. Co.), "Recovery of Rhenium", U. S. Pat. 1,911,943 (May 30, 1933).

70. Kronman, E., Bibikova, V. and Aksenova, M., "Recovery of Rhenium from Molybdenite", Z. anorg. allgem. Chem., 214, 143-44 (1933).

71. Bibikova, V., "Rhenium in the Manufacture of Ammonium Molybdate", Redkie Metal., 5, No. 5, 25-28 (1936).

72. Melaven, A., and Bacon, J. (to Univ. of Tennessee Research Corp.) "Recovery of Rhenium from Flue Dusts", U. S. Pat 2,414,965 (January 28, 1947).

73. Bertolus, M., "Extracting Rhenium", Fr. Pat. 963,610 (July 17, 1950).

74. Bertolus, M., "Extracting Rhenium", Fr. Pat. 965,206 (September 6, 1950).

75. Bertolus, M., "Extracting Rhenium", U. S. Pat. 2,579,107 (December 18, 1951).

76. Fisher, S., and Meloche, V., "Ion Exchange Separation of Rhenium from Molybdenum", Anal. Chem., 24, 1100-1106 (1952).

77. Anon., "The Technical Recovery of Rhenium [illegible]", Metallbörse, [illegible] (19[illegible]).

78. Alimarin, I., and Ivanov-Emin, B., "Concentration of . . . . Rhenium . . in its Determination in Oxide and Sulfide Ores", J. Appl. Chem. (U.S.S.R.), 9, 1124-28 (1936) (In French, [illegible]).

79. Voigt, A., "Separation of Rhenium from Molybdenum", Ger. Pat. 697,0?7 (September 5, 1940).

80. Hixson, A., and Miller, R. (to the Chemical Foundation, Inc.) "Selective Extraction of Metal Values, Such as Uranium, Rhenium, and Tungsten from Ores, Etc.", U.S. Pat. 2,227,833 (January 7, 1941).

81. Kanatani, M., Murakami, S., and Ogawa, E., "Distribution of Metallic Elements in the Residue of Zinc Smelting and Leaching and Their Extraction: I.", Bull. Inst. Phys. Chem. Research (Tokyo), 22, 775-80 (1943).

82. Alexander, G., "The Chromatographic Separation of Perrhenic and Molybdic Acids", J. Am. Chem. Soc., 71, 3043-46 (1949).

83. Powell, A., "Problems in the Production of Some of the Rarer Metals", Inst. Mining and Met. (London), Symposium on Refining Non-Ferrous Metals, 1949, pp 51-66 (1950).

84. Druce, J., Rhenium, pp 12-15, University Press, Cambridge, 1948.

85. Trzebiatowski, W., "Reactions of Rhenium with Carbon", Z. anorg. allgem. Chem., 233, 376-84 (1937).

86. Geilmann, W., and Voigt, A., "Notes on the Analytical Chemistry of Rhenium: I. Determination of Soluble Perrhenates with the Aid of Nitron", Z. anorg. allgem. Chem., 193, 311-15 (1930).

87. Hölemann, H., "Chemistry and Electrochemistry of Rhenium: II. Electrochemical Reduction Products in Solutions which Contain Chlorine or Fluorine Ions, and the Chemical Mode of Formation of Lower Valence Stages in Sulfuric Solutions", Z. anorg. allgem. Chem., 211, 195-203 (1933).

88. Fink C. G., and Deren, P., "Rhenium Plating", Bull. Amer. Electrochem. Soc., 66, 381-84 (1934).

89. Netherton, L., and Holt, M., "Electrodeposition of Rhenium from Aqueous Solutions", J. Electrochem. Soc., 95, 324-328 (1949).

90. Van Arkel, A., Reine Metalle, p 296, J. Springer, Berlin, 1939.

91. Agte, C., Alterthum, H., Becker, K., Heyne, G., and Moers, K., "Physical and Chemical Properties of Rhenium", Z. anorg. allgem. Chem., 196, 129-59 (1931).

91A. Moers, K., (to Patent-Treuhand-Gesellschaft für Electrische Glühlampen), "Coating High-Melting Metals With Rhenium", Ger. Pat. 537,936; Brit. Pat. 364,502 (June 4, 1931).

92. Van Arkel, A., "Production of High-Melting Metals by Thermal Dissociation of Their Compounds", Metallwirtschaft, 13, 405-408 (1934).

93. Druce, J., "Thermite Reaction With Rhenium (Dvi-Manganese) Dioxide", Chem. News, 144, 247 (1932).

94. Agte, C., Alterthum, H., Becker, K., Heyne, G., and Moers, K., "The Physical Properties of Rhenium", Naturwissenschaften, 19, 108-109 (1931).

95. Kurtz, J., and Williams, H., "High-Density Refractory Metal Alloys", U. S. Pat. 2,467,675 (April 19, 1949).

96. Kurtz, J., and Williams, H. (to Callite Tungsten Corp.), "Alloys of High Density", Can. Pats. 442,725 and 442,726.

97. Bridgman, P., "Effects of High Shearing Stress Combined with High Hydrostatic Pressure", Phys. Rev., 48, 825-47 (1935).

98. Loring, F., "New Elements: I-V.", Chem. News, 132, 407-410 (1926).

99. Washburn, E., "A Method of Estimating Atomic Weights With the Aid of the Periodic Law", J. Am. Chem. Soc., 48, 2351 (1925).

100. Jaeger, F., and Rosenbohm, E., "Exact Measurement of the Specific Heats of Metals at Higher Temperatures: XII. Specific Heat of Metallic Rhenium", Proc. Acad. Sci. Amsterdam, 36, 786-88 (1933).

101. Noddack, I., "Some Physical Constants of Rhenium", Z. Electrochem., 34, 629-31 (1928).

102. Schacherl, F., "The Homologs of Manganese", Chem. Listy, 23, 632-35 (1929).

103. Hönigschmid, O., and Sachtleben, R., "Revision of the Atomic Weight of Rhenium. Analysis of Silver Perrhenate", Z. anorg. allgem. Chem., 191, 309-17 (1930).

104. Bodenstein, M., Hahn, O., Hönigschmid, O., and Meyer, R., "Report of the German Atomic Weight Commission", Ber., 64B 1-21 (1931).

105. Aston, F., "Constitution of Rhenium", Nature, 127, 591 (1931).

106. Goldschmidt, V., "The Crystal Structure of Rhenium", Naturwissenschaften, 17, 134 (1929).

107. Goldschmidt, V., "The Crystal Structure, Lattice Constants, and Density of Rhenium", Z. physik. Chem., Abt. B, 2, 244-52 (1929).

108. Moeller, K., "The Lattice Constants of Rhenium", Naturwissenschaften, 19, 575 (1931).

109. Stenzel, W., and Weertz, J., "Precision Determination of Lattice Constants of Non-Cubic Substances", Z. Krist., 84, 20-44 (1933).

110. Biltz, W., and Meissel, K., "Molecular and Atomic Volumes: XXXI. The Volumes of the Elements at Absolute Zero", Z. anorg. allgem. Chem., 198, 191 (1931).

111. Smithells, C., Tungsten, p 198, Chapman and Hall, London, 1952.

112. Richardson, D., "Boiling Point Determinations by Spectroscopic Methods", Proc. of the 5th Summer Conference (at MIT) on Spectroscopy and Applications, 1937, pp 64-70 (Published 1938).

113. Metals Handbook, p 20, The American Society for Metals, Cleveland, Ohio, 1948.

114. Briscoe, H., Robinson, P., and Rudge, A., "Parachor of Rhenium", J. Chem. Soc., 1932, 2673-76.

115. Tyler, P., "Rhenium (and Masurium)", U. S. Bur. Mines Information Circ. No. 6475, 17 pp (1931).

116. Perry, J. (ed.), The Chemical Engineer's Handbook, 2nd Ed., p 483, McGraw-Hill Book Co., New York, 1941.

117. Meissner, W., and Voigt, E., "Measurements With the Aid of Volatile Helium: XI. Resistance of Rhine Metal at Low Temperatures", Ann. Phys., 7, 915 (1930).

118. Becker, K., and Moers, K., "On the Melting Point of the System Tungsten-Rhenium", Metallwirtschaft, 9, 1063 (1930).

119. Levi, R., and Esperson, G., "Preparation of Rhenium Emitters and Measurements of Their Thermionic Properties", Phys. Rev., 78, 231-34 (1950).

120. Mellor, J., "The Physical Properties of Masurium and Rhenium", A Comprehensive Treatise on Inorganic Chemistry, 12, p 469.

121. Albrecht, W., and Wedekind, E., "Magnetic Measurements on Rhenium", Naturwissenschaften. 19. 20-21 (1931).

122. Perakis, N., Capatos, L., and Kyriakedes, P., "Paramagnetic Constant of Rhenium", Praktika (Akad. Athenon), 8, 163-69 (1933).

123. Perakis, N., and Capatos, L., "The Constant Paramagnetism of Metallic Rhenium", Compt. rend., 196, 611-12 (1933).

124. Perakis, N., and Capatos, L., "The Magnetochemistry of Rhenium: Metallic Rhenium and Septivalent Rhenium", Praktika (Akad. Athenon), 9, 121-25 (1934).

125. Perakis, N., and Capatos, L., "Magnetochemistry of Metallic and Septivalent Rhenium", Compt. rend., 198, 1905-1907 (1934).

126. Perakis, N., and Capatos, L., "Magnetochemistry of Rhenium", J. Phys. radium, 6, 462-68 (1935).

127. Perakis, N., Karantassis, T., and Capatos, L., "(Magnetic) Atomic Moment of Quadrivalent Rhenium", Compt rend., 206, 1369-71 (1938).

128. Schüth, W., and Klemm, W., "Magnetochemical Invesitgations: XI. The Magnetic Behavior of Some Rhenium Compounds", Z. anorg. allgem. Chem., 220, 193-98 (1934).

129. Klemm, W., and Frischmuth, G., "Magnetochemical Investigations: XXIII. Further Magnetic Investigations on Rhenium Compounds", Z. anorg. allgem. Chem., 230, 220-22 (1937).

130. Alder, F., and Yu, F., "Magnetic Moments of Magnesium^{25}, Rhenium^{185}, Rhenium^{187}, and Beryllium^{9}", Phys. Rev. 82, 105 (1951).

131. Schmidt, F., "Magnetic Moment of $_{63}Eu^{151}$, $_{63}Eu^{153}$, $_{75}Re^{185}$, $_{75}Re^{187}$, $_{35}Br^{79}$, $_{35}Br^{81}$", Z. Phys., 108, 408-20 (1938).

132. Meidinger, W., "Measurement of the Arc Spectrum of Rhenium", Z. Physik, 68, 331-43 (1931).

133. Schober, H., "The Spectra of Rhenium: II. The Arc Spectrum From Copper Electrodes in the Visible Region Between 5400 and 8000 Å", Sitzber. Akad. Wiss. Wien, Math.-naturw. Klasse, Abt. IIa, 140, 629-46 (1931).

134. Schober, H., "The Spectra of Rhenium: I. The Arc Spectra in the Photographic Region", Sitzber. Akad. Wiss. Wien, Math.-naturw-Klasse, Abt. IIa, 140, 79-98 (1931).

135. Schober, H., and Birke, J., "The Raies Ultimes in the Arc Spectrum of Rhenium", Naturwissenschaften, 19, 211-12 (1931).

136. Meggers, W., "The Arc Spectrum of Rhenium", Bur. Standards J. Research 6, 1027-60 (1931).

137. Meggers, W., "Optical Spectra of Rhenium", Phys. Rev., 37, 219-20 (1931).

138. Meggers, W., "The Infra-Red Arc Spectra of Manganese and Rhenium", Bur. Standards J. Research, 10, 757-69 (1933).

139. Piña de Rubies, S., and Dorronsoro, J., "Arc Spectra of Rhenium at Normal Pressures Between 2500 and 2320 A, Anales soc. españ. fís. quím., 31, 412-15 (1933).

140. Schober, H., "The Spectra of Rhenium: IV. The Arc Spectrum from Copper Electrodes in the Ultra-Violet Region Between 4000 and 2400 Å", Sitzber. Akad. Wiss. Wien, Math-naturw. Klasse, Abt. IIa, 142, 35-70 (1933).

141. Velasco, R., "Structure of the Arc Spectrum of Rhenium", Anales soc. españ. fís. y quím., 45A, 215-18 (1949).

142. King, A., "Lines of Tungsten and Rhenium Appearing in the Spectrum of the Electric Furnace", Astrophys. J., 25, 379-85 (1932).

143. Piña de Rubies, S., "Analytical and Quantitative Rhenium Spectra", Anales soc. españ. fís. quím., 30, 918-21 (1932).

144. Borovik, S., and Gudris, N., "Examination of the Extreme Spectrum Lines of Rhenium in the Presence of Large Quantities of Molybdenum", J. Appl. Chem. (USSR), 9, 937-42 (1936).

145. Engelmann, A., "Determination of the Photoelectric Threshold (Long-Wave Limit) for Rhenium", Ann. Physik, 17, 185-208 (1933).

146. Wennerlöf, I., "Precision Measurements in the L-Series of the New Element 75, Rhenium", Z. Physik, 47, 422-25 (1928).

147. Beuthe, H., "The L-Series of Rhenium", Z. Physik, 46, 873-77 (1928).

148. Beuthe, H., "Further Röntgen Spectroscopy Measurements in the L- and M-Series of Rhenium", Z. Physik 50, 762-68 (1928).

149. Cauchois, Y., "L-Spectrum of Rhenium in Emission and Absorption and the Characteristic Levels", Compt. rend., 203, 169-71 (1936); J. phys. radium, 8, 267-72 (1937).

150. Cauchois, Y., "L_α Satellites of Hafnium, Rhenium, Bismuth, Thorium, and Uranium", Compt. rend., 202, 2068-69 (1936).

151. Cauchois, Y., "Weak Lines in the L Spectrum of Rhenium", Compt. rend., 204, 255-57 (1937).

152. Cauchois, Y., "L_α Satellites of Some Heavy Elements and Rare Earths", Compt. rend., 205, 519-21 (1937).

153. Lindberg, E., "Measurements of the M-series in the Röntgen Spectra of the Elements From Uranium to Gadolinium", Z. Physik, 50, 82-96 (1928).

154. Lindberg, E., "M- and N-Series", Nova Acta Regiae Soc. Sci. Upsaliensis, 7, No. 7, 7-74 (1931).

155. Ingelstam, E., "The K-Spectra of the Heavy Elements", Nova Acta Regiae Soc. Sci. Upsaliensis, 10, 7-116 (1937); Chem. Zentr., 1937, I, 4735-36.

156. Klinkenberg, P., "New Classifications in Re I and Structure of the Spectrum", Physica, 14, 269-84 (1948).

157. Voth, G., "The Intensity Relationships of the K-Series Lines of the Heavy Elements Re (75) to Pb (82)", Ann. Physik, 41, 375-408 (1942).

158. Polland, B., "Absorption Limit of the K-Series of the Element of At. No. 75", Compt. rend., 183, 737-38 (1926).

159. Manescu, I., "The K-Absorption Spectra of Elements With Atomic Numbers 72 (Hf), 73 (Ta), 74 (W), 75 (Re), 76 (Os), and 77 (Ir)", Compt. rend., 216, 732-34 (1943).

160. Sandström, A., "Röntgenspectroscopic Measurements of the L-Absorption of Elements 74 to 92", Z. physik. Chem., 65, 632-55 (1930).

161. Manescu, I., "Effect of the Valence State of Rhenium on its X-Ray Absorption Spectrum", Compt. rend., 226, 1010-12 (1948).

162. Aston, F., "Isotopic Constitution and Atomic Weight of Rhenium", Proc. Roy. Soc. (London), A132, 496-97 (1931).

163. Zeeman, P., Gisolf, J., and de Bruin, T., "Magnetic Resolution and Nuclear Moment of Rhenium", Nature, 128, 637 (1931).

164. Meggers, W., King, A., and Bacher, R., "Hyperfine Structure and Nuclear Moment of Rhenium", Phys. Rev., 38, 1258-59 (1931).

165. Sommer, L., and Karlson, F., "The Nuclear Moment of Rhenium", Naturwissenschaften, 19, 1021 (1931).

166. Schüler, H., and Schmidt, T., "Deviations of Atomic Nuclei From Spherical Symmetry". Z. Physik, 94, 457-68 (1935).

167. Schüler, H., and Korshing, H., "Regularities in the Demolition of Atom Nuclei", Naturwissenschaften, 24, 796-97 (1936).

168. Schüler, H., and Korsching, H., "A Rule Relating to the Structure of the Atomic Nucleus and the Determination of the Quadrupole Moments of $_{75}Re^{187}$ and $_{75}Re^{185}$", Z. Physik, 105, 168-74 (1937).

169. Solomon, J., "Origin of Quadrupole Moments of Atomic Nuclei", Compt. rend., 204, 1933-38 (1937).

170. Hill, R., "Nuclear Quadrupole Moments and Shell Structures", Phys. Rev., 76, 998 (1949).

171. Naldrett, S., and Libby, W., "Natural Radioactivity of Rhenium", Phys. Rev., 73, 487-96, 929 (1948).

172. Seliger, H., and Bradt, H., "Stability of Os^{187} against K-Capture", Phys. Rev., 73, 1408-09 (1948).

173. Sugarman, N., and Richter, H., "Note on the Natural Radioactivity of Rhenium", Phys. Rev., 73, 1411-12 (1948).

174. De Benedetti, S., and McGowan, F., "A Metastable State of Half-Life about 10^{-6} Seconds in Re^{187}", Phys. Rev., 71, 380-81 (1947).

175. De Benedetti, S., and McGowan, F., "Short-Lived Isomers of Nuclei", Phys. Rev., 74, 728-35 (1948).

176. McGowan, F., De Benedetti, S., and Francis, J., "The Measurement of Short-Lived Isomers of Nuclei", Phys. Rev., 75, 1761 (1949).

177. Bunyan, D., Lundby, A., and Walker, D., "Experiments With the Delayed Coincidence Method, Including a Search for Short-Lived Nuclear Isomers", Proc. Phys. Soc. (London), 62A, 253-63 (1949).

178. Sullivan, W., "Decay Scheme for Isotopes W^{187} and W^{185}", Phys. Rev., 68, 277 (1945).

179. Schwarz, W., and Pool, M., "γ-Rays from Tungsten and Molybdenum", Phys. Rev., 71, 122-23 (1947).

180. [illegible] "Internal Conversion in Rhenium", Phys. Rev., 59, 406 (1941).

181. Perlman, M., and Friedlander, G., "Relative Yields of (γ, n) Reactions", Phys. Rev., 72, 1272 (1947).

182. Amaldi, E., D'Agostino, O., and Segré, E., "Artificial Radioactivity Produced by Neutron Bombardment", Ricerca sci., 5II, 381-82 (1934); Chem. Zentr., 1, 2492-93 (1935).

183. Amaldi, E., D'Agostino, O., Fermi, E., Pontecorvo, B., Rasetti, F., and Segré, E., "Artificial Radioactivity Produced by Bombardment With Neutrons: VIII", Ricerca sci., 6, 123-25 (1935).

184. Kurchatov, I., Latuisher, G., Nemenov, L., and Selinov, I., "Artificial Radioactivity Induced by Neutrons", Phyzik. Z. Sowjetunion, 8, 589-94 (1935).

185. Sinma, K., and Yamasaki, F., "β- Radioactive Isotopes of Rhenium", Phys. Rev., 55, 320 (1939).

186. Yamasaki, H., and Sinma, K., "β- Radioactivities of Rhenium", Sci. Papers Inst. Phys. Chem. Research (Tokyo), 37, 10-16 (1940) (In English).

187. Fajans, K., and Sullivan, W., "Induced Radioactivity of Rhenium and Tungsten", Phys. Rev., 58, 276 (1940).

188. Creutz, E., Barkas, W., and Furman, N., "γ- Radiation From Rhenium", Phys. Rev., 58, 1008 (1940).

189. Miller, L., and Curtiss, L., "β- and γ-Ray Energies of Several Radioactive Isotopes", Phys. Rev., 70, 983 (1946).

190. Hess, D., Hayden, M., and Ingraham, M., "Mass-Spectrographic Assignment of Activities to Re^{186} and Re^{188}", Phys. Rev., 72, 730 (1947).

191. Goodman, L., and Pool, M., "Radioactive Isotopes of Rhenium, Osmium, and Iridium", Phys. Rev., 71, 288-93 (1947).

192. Wattenberg, A., "Photoneutron Sources and the Energy of the Photoneutrons", Phys. Rev., 71, 497-507 (1947).

193. Cork, J., Shuffler, R., and Fowler, C., "Converted γ-Radiation From....,and ρ....Rhenium", Phys. Rev., 74 1657-59 (1948).

194. Mandeville, C., Scheil, M., and Keighton, W., "Study of the Radiations From Cb^{95}, Re^{188}, Os^{191}, and Os^{193}", Phys. Rev., 74, 888-93 (1948).

195. Wilkinson, G., and Hicks, H., "Some New Radioactive Isotopes of ... and Rhenium", Phys. Rev., 74, 1733-34 (1948).

196. Perlman, M., and Friedlander, C., "Relative Yields of Some X-Ray-Induced Nuclear Reactions", Phys. Rev. 74, 442-48 (1948).

197. Cork, J., "γ-Rays and Internal Conversion", Nucleonics, 4, No. 1, 24-34 (1949).

198. Beach, L., Peacock, C., and Wilkinson, R., "The Radiations of Ta^{182}, $Re^{186, 188}$, and Au^{199}", Phys. Rev., 76, 1585-91 (1949).

199. Langer, L., and Price, H., "β-Spectra of Forbidden Transitions", Phys. Rev., 76, 641-46 (1949).

200. Grant, P., and Richmond, R., "Decay of $Thulium^{170}$ and $Rhenium^{186}$", Nature, 163, 840 (1949); Proc. Phys. Soc. (London), 62A, 573-80 (1949).

201. Butement, F., "Radioactive Isotopes Produced by Nuclear Photo-disintegration", Nature, 165, 149 (1950).

202. Lindner, M., and Coleman, J., "New β-Emitting Isotopes in the Region of Tungsten", Phys. Rev., 78, 67 (1950).

203. Chu, T., "New Radioactive Isotopes of Iridium", Phys. Rev., 79, 582-88 (1950).

204. Wilkinson, G., and Hicks, H., "Neutron-Deficient Radioactive Isotopes of Rhenium", Phys. Rev., 77, 314-18 (1950).

205. Metzger, F., and Hill, R., "Disintegration Scheme of $Rhenium^{186}$", Phys. Rev., 82, 646-50 (1951).

206. Lindner, M., and Coleman, J., "Identification of $Tungsten^{188}$ Found in Neutron-Activated Tungsten by a Chemical Separation of $Rhenium^{188}$", J. Am. Chem. Soc., 73, 1610-11 (1951).

207. Steffen, R., "Dual Decay of $Rhenium^{186}$", Phys. Rev., 82, 827-31 (1951).

208. Turner, S., and Morgan, L., "Products of the High-Energy Helium-Ion and Deuteron Bombardment of Tungsten", Phys. Rev., 81, 881-82 (1951).

209. Stover, B., "$Osmium^{182}$ and $Osmium^{184}$, New Radioactive Isotopes", Phys. Rev., 80, 99 (1950).

210. McGowan, F., "An 8 x 10^{-10} Second Isomeric State of $Osmium^{186}$", Phys. Rev., 81, 1066-67 (1951).

211. Miller, M., and Wilkinson, R., "The Ratio of L to K Electron Capture for $Osmium^{185}$", Phys. Rev., 83, 1050-51 (1951).

212. Gile, J., Garrison, W., and Hamilton, J., "Carrier-Free Radioisotopes From Cyclotron Targets: IX. Preparation and Isolation of $Rhenium^{183, 184}$ From Tantalum", J. Chem. Phys., 18, 995-96 (1950).

213. Gile, J., Garrison, W., and Hamilton, J., "Carrier-Free Radioisotopes From Cyclotron Targets: XI. Preparation and Isolation of Os^{185}, $Re^{183, 184}$ From W", J. Chem. Phys., 18, 1419-20 (1950).

214. Goldhaber, M., "Slow-Neutron Reactions", Brookhaven Conf. Rept., BNL-C-9, Nuclear Fission Radiochem. Research Assoc'd. Nuclear Reactors, Chem. Conf. No. 3, pp 96-104 (1949).

215. Goldsmith, H., and Rasetti, F., "The Resonance Capture of Slow Neutrons", Phys. Rev. 50, 328-31 (1936).

216. Sinma, R., and Yamasaki, H., "Capture Cross Sections for Slow Neutrons", Sci. Papers Inst. Phys Chem. Research (Tokyo), 38, 167-73 (1941); Phys. Rev., 59, 402-403 (1941).

217. "Thermal-Neutron Absorption Cross Section for Elements", AECU-2040.

218. Seren, L., Friedlander, H., and Turkel, S., "Thermal Neutron Activation Cross Sections", Phys. Rev. 72, 888-901 (1947).

219. Hibdon, C., and Muehlhause, C., "Neutron Cross Sections at 115 e.v. and 300 e.v.", Phys. Rev., 7[illegible], 100-103 (1949).

220. Harris, S., Muehlhause, C., Rasmussen, S., Schroeder, H., and Thomas, G., "Pile-Neutron Absorption Cross Sections", Phys. Rev., 80. 342-44 (1950).

220A. Pomerance, H., "Thermal Neutron Capture Cross Sections", Phys. Rev. 83, 641-5 (1951).

221. Muehlhause, C., "Neutron-Capture γ-Ray Multiplicity", Phys. Rev., 79, 277-79 (1950).

222. Scherrer, P., and Zingg, E., "Stability of the Isobars Cd^{113}-In^{113}, In^{115}-Sn^{115}, Sb^{123}-Te^{123}, Re^{187}", Helv. Phys. Acta 12, 283-5 (1939).

223. Harris, S., Muehlhause, C., and Thomas, G., "Low-Energy Neutron Resonance Scattering and Absorption", Phys. Rev., 79, 11-18 (1950).

224. Arizumi, T., "Thermionic Constants of Polycrystalline Metal", J. Phys. Soc. Japan, 3, 1-7 (1948) (in English).

225. Farnsworth, H., and Lun, M., "Secondary Emission of Nickel-Barium Mixtures and Rhenium When Bombarded by Electronics With Energies From 50 to 8000 Electron-Volts", J. Appl. Phys., 22, 77-79 (1951).

226. Aschermann, G., and Justi, E., "Electrical Conductivity, Magnetic Increase of Resistance, Hall Effect, and Superconductivity of Rhenium", Physik. Z., 43, 207-12 (1942).

227. Alterthum, H., Krebs, K., and Rompe, R., "The Ionization of Sodium and Cesium Vapor on Glowing Tungsten and Rhenium Surfaces", Z. Physik., 92, 1-18 (1934).

228. Tiede, E., and Lemke, H., "Preparation and Detector Effect of the Sulfides of Tungsten, Molybdenum, and Rhenium", Ber., 71B, 582-88 (1938).

229. Kohl, H., Materials Technology for Electron Tubes, pp 177-228, Reinhold Publishing Co., New York, 1951.

230. McKay, L., Advances in Electronics: I, p 68, Academic Press, New York, 1948.

231. International Critical Tables.

232. Winkler, O., "The Frictional Strength of Noble Metals and of Base Metals Having High Melting Points", Z. Electrochem., 49, 221-28 (1943).

233. Eggers, H., "The Binary System Iron-Rhenium", Mitt. Kaiser-Wilhelm-Inst. Eisenforsch., Düsseldorf, 20, 147-52 (1938); Stahl und Eisen, 58, 1010 (1938).

234. Schenk, R., Kurzen, F., and Wesselkock, H., "A Study of Carbides Prepared With Methane", Z. anorg. allgem. Chem., 203, 159-87 (1931).

235. Agte, K. (to The General Electric Co.), "Electric Lamp Filaments (With a Core Containing Rhenium and a Coating of Tantalum Carbide)", U. S. Pat. 1,854,970 (April 19, 1932).

236. Hölemann, H., "Electrochemistry of Rhenium: I. A Few Reduction Products in the Electrolysis of Water Solutions of Potassium Perrhenate", Z. anorg. allgem. Chem., 202, 277-91 (1931).

237. Nial, O., "X-Ray Studies on Binary Alloys of Tin With Transition Metals: I. Binary Systems of Tin With . Rhenium. . . (V), Re-Sn and Cr-Sn", Svensk Kem. Tid., 59, 165-70 (1947).

238. Wallbaum, H., "Some New Zirconium Compounds With Transition Elements", Naturwissenschaften, 30, 149 (1942).

239. Ges, G., "Rhenium Alloys", Brit. Pat. [illegible] 859 (June 22, 1931).

240. Ges, G., "Platinum Alloys", Brit. Pat. 381,137 (June 20, 1931).

241. Fröhlich, K., and Ruthardt, K., "Noble Metals and Their Alloys: I. Development of New Alloys", FIAT Rev. Ger. Sci.1939-46; Non-Ferrous Metallurgy: II, pp 17-35 (1948).

242. Feussner, O., "Iridium and Rhodium", Ger. Pat. 626,586 (February 28, 1936).

243. Hensel, F., and Emmert, K., "Refractory Alloys of Tungsten, Molybdenum, and Rhenium", U. S. Pat. 2,157,935.

244. Hensel, F., and Emmert, K., "Refractory Alloys of Tungsten, Molybdenum, and Rhenium", U. S. Pat. 2,157,936.

245. Feussner, O., and Jedele, A., "Alloys Containing Rhenium", Ger. Pat. 608,342 (January 21, 1935).

246. Fröhlich, K., "Noncorroding, Hard, Wear-Resistant Alloy", Ger. Pat. 729,862 (December 3, 1942).

247. Netherton, L., and Holt, M., "Electrodeposition of Rhenium-Cobalt and Rhenium-Iron Alloys", J. Electrochem. Soc., 99, 44-47 (February, 1952).

248. Netherton, L., and Holt, M., "Electrodeposition of Rhenium-Nickel Alloys", J. Electrochem. Soc., 98, 106-109 (1951).

249. Biltz, W., "Rhenium Trioxide and Rhenium Dioxide", Z. anorg. allgem. Chem., 214, 225-38 (1933).

250. Meisel, K., "Rhenium Trioxide: III. The Crystal Structure of Rhenium Trioxide", Z. anorg. allgem. Chem., 207, 121-128 (1932).

251. Noddack, I. and W., "Oxygen Compounds of Rhenium", Naturwissenschaften, 17, 93-94 (1929).

252. Biltz, W., Lehrer, G., and Meisel, K., "Rhenium Trioxide: I.", Nachr. Ges. Wiss. Göttingen, Math. - physik. Klasse, 1931, 191-98.

253. Nechamkin, H., Melaven, A., et al., "Rhenium (VI) Oxide and Rhenium (VII) Oxide", Inorganic Syntheses 49, 50, McGraw-Hill Book Co., New York (1950).

254. Ogawa, E., "The Vapor Pressure of Rhenium Heptoxide, Vapor Pressure and Dissociation Pressure of Rhenium Octoxide", Bull. Chem. Soc. Japan, 7, 265-73 (1932).

255. Druce, J., Rhenium, pp 36-37, University Press, Cambridge, 1948.

256. Feit, W., "Densities of Aqueous Solutions of Perrhenic Acid", Z. anorg. allgem. Chem., 199, 271-72 (1931).

257. Machatschki, F., "Crystal Structure of Potassium Perrhenate", Z. Krist., 72, 541-42 (1930).

258. Broch, E., "Crystal Structure of Potassium Perrhenate", Z. phys. Chem., Abt. B6, 22-26 (1929).

259. Vorlander, D., and Dalichau, G., "The Melting Point and Boiling Point of Potassium Perrhenate (and Melting Points of Thallium and Silver Perrhenates)", Ber., 66B, 1534-36 (1933).

260. Smith, W., and Long, S., "The Salts of Perrhenic Acid: I. The Alkali Metals and Ammonium", J. Am. Chem. Soc., 70, 354 (1948).

261. Hölemann, H., and Kleese, W., "Chemistry and Electrochemistry of Rhenium: VI. Solubility of Potassium Perrhenate in Water Between 10 and 518 C", Z. anorg. allgem. Chem., 237, 172-76 (1938).

262. Jaeger, F., and Beintma, J., "Crystal Structure of Perrhenates", Proc. K. Akad. Wet. Amst., 36, 523-28 (1933).

263. Vorländer, D., Hollatz, J., and Fischer, J., "Alkali Fluoborates, Alkali Fluorosulforrates, and Potassium Perrhenate", Ber., 65B, 535-58 (1932).

264. Smith, W., "The Salts of Perrhenic Acid; III. Univalent Heavy Metals", J. Am. Chem., Soc., 73, 77 (1951).

265. Druce, J., Rhenium, pp 42-43, University Press, Cambridge, 1948.

266. Ruff, O., and Kwasnik, W., "Rhenium Fluorides", Angew. Chem., 47, 480 (1934).

267. Ruff, O., and Kwasnik, W., "Rhenium Fluorides (Especially ReF_6, $ReOF_4$, ReO_2F_2, ReF_4, and K_2ReF_6)", Z. anorg. allgem. Chem., 219, 65-81 (1934).

268. Ruff, O., and Kwasnik, W., "Rhenium [illegible]", Z. anorg. allgem. Chem., 220, [illegible] ([illegible]).

269. Hurd, L., "Metallic Rhenium", Inorganic [illegible], McGraw-Hill Book Co., New York, 1939.

270. Hagen, H., and Sieverts, A., "Rhenium [illegible]", Z. anorg. allgem. Chem., 215, 111-12 (1933).

271. Juza, R., and Biltz, W., "Contribution to the Doctrine of Systemic Affinity: LII. Affinity of Sulfur for Rhenium. I. Rhenium Disulfide", Z. Electrochem., 37, 498-501 (1931).

272. Briscoe, H., Robinson, P., and Stoddart, E., "The Sulfides and Selenides of Rhenium", J. Chem. Soc., 1931, 1439-43.

273. Briscoe, H., Robinson, P., and Stoddart, E., "Rhenium Tetrachloride and the Rhenichlorides", J. Chem. Soc., 1931, 2263-68.

274. Enk, F., "Potassium Rhenium Acid Chloride (or Potassium Chlororhenate)", Ber., 64, 791-97 (1931).

275. Brukl, A., and Zeigler, K., "Rhenium Oxychlorides", Ber., 65B, 916-18 (1932).

276. Druce, J., "Rhenium, p 54, University Press, Cambridge, 1948.

277. Ruff, O., Kwasnik, W., and Ascher, E., "The Fluorination of Rhenium", Z. anorg. allgem. Chem., 209, 113-22 (1932).

278. Druce, J., "Rhenium, p 61, University Press, Cambridge, 1948.

279. Hieber, W., and Fuchs, H., "Metal Carbonyls: XXXVIII, Rhenium Pentacarbonyl", Z. anorg. allgem. Chem., 248, 256-68 (1941).

280. Druce, J., "Trimethylrhenium", J. Chem. Soc., 1934, 1129.

281. Klemm, W., and Frischmuth, G., "Complex Rhenium Oxycyanide", Z. anorg. allgem. Chem., 230, 215-19 (1937).

282. Pauling, L., "A Resonating-Valence-Bond Theory of Metals and Intermetallic Compounds", Proc. Royal Soc. (London), A196, 343-62 (1949).

283. Rulfs, C., and Elving, P., "Oxidation Levels of Rhenium: II. Oxidation of Rhenide at the Dropping Mercury Electrode. Nature of the Rhenide Species in Hydrochloric Acid Media", J. Am. Chem. Soc., 73, 3287-92 (1951).

of Rhenium", J.
(1937)

Chemistry", Chem.

286. Chemistry of
Soc., 72,
3502-1

287. Lingane, J.
II. Oxidation
Potential of the
mpounds:
the
64, 2182-
90 (1942).

288. Young, R., and
Rhenium", J. Am.
Oxides of

289. Manchot, W., Schmid,
Its Behavior on Oxidation
64B, 2905-2908 (1931)

290. Biltz, W., Geilmann, W., and Wrigge, F., "Rhenium Trichloride", Ann., 511, 301-303 (1934).

291. Manchot, W., and Düsing, J., "The Lowest Valences of Rhenium and Ruthenium, - Trivalent Rhenium and Univalent Ruthenium", Z. anorg. allgem. Chem., 212, 21-31 (1933).

292. Manchot, W., and Düsing, J., "The Lower-Valence Stages of Rhenium", Ann., 509, 228-40 (1934).

293. Tribalat, S., "The Valences IV and V of Rhenium", Compt. rend., 222, 1388-90 (1946).

294. Turkiewicz, E., "Lower Degrees of Oxidation of Rhenium", Roczniki Chem., 12, 589-97 (1932).

295. Tribalat, S., "Study of Certain Physico-Chemical and Analytical Properties of Rhenium", Ann. Chim., 4, 289-351 (1949).

296. Maun, E., and Davidson, N., "Investigations in the Chemistry of Rhenium: I. Oxidation States IV, V, and VII", J. Am. Chem. Soc., 72, 2254-60 (1950).

297. Noddack, W., "The Chemistry of Rhenium", Z. Elektrochem., 34, 627-29 (1928).

298. Jezowska, B., "Reduction of Perrhenic Acid", Roczniki Chem., 14, 1061-87 (1934).

299. Tribalat, S., "Valence V of Rhenium", Compt. rend., 220, 881-83 (1945).

300. Jakob, W., and Jezowska, B., "Quinquevalent Rhenium", Z. anorg. allgem. Chem., 220, 16-30 (1934).

301. Noddack, I. and W., "Oxygen Compounds of Rhenium", Z. anorg. allgem. Chem., 181, 1-37 (1929).

302. Noddack, I. and W., "Oxygen and Halogen Compounds of Rhenium", Z. anorg. allgem. Chem., 215, 129-84 (1933).

303. Druce, J., Rhenium, p 29, University Press, Cambridge, 1948.

304. Noddack, I., "The Development of the Chemistry of Rhenium", IX Congr. intern. quim. pura aplicada, Madrid, 3, 334-40 (1934).

305. Geilmann, W., and Wrigge, F., "Rhenium Sesquioxide - Re_2O_3", Z. anorg. allgem. Chem., 214, 239-43 (1933).

306. Druce, J., "The Preparation and Properties of Some Compounds of Rhenium", Chem. News, 143, 66-67 (1931).

307. Briscoe, H., Robinson, P., and Rudge, A., "A New Oxide of Rhenium. Rhenium Pentoxide", J. Chem. Soc., 1931, 3087-88.

308. Roth, W., and Becker, G., "Rhenium Pentoxide", Ber., 65B, 373 (1932).

309. Biltz, W., Lehrer, G., and Meisel, K., "Rhenium Trioxide: II.", Z. anorg. allgem. Chem., 207, 113-20 (1932).

310. Biltz, W., Wrigge, F., and Meisel, K., "Rhenium Blue", Nachr. Ges. Wiss. Göttingen, Math. - physik. Klasse, Fachgruppen III. (N.F.) 1, 161-73 (1936).

311. Nechamkin, H., Kurtz, A., and Hiskey, C., "The Preparation of Rhenium (VI) Oxide", J. Am. Chem. Soc., 73, 2828-31 (1951).

312. Naray-Szabo, I., "The Structure of Compounds ABO_3 'Sister Structures'", Naturwissenschaften, 31, 466 (1943).

313. Roth, W., and Becker, G., "Heats of Formation of Rhenium Oxides", Z. Physik Chem., A159, 415-16 (1932).

314. Briscoe, H., Robinson, P., and Rudge, A., "The Highest Oxide of Rhenium", Nature, 129, 618 (1932).

315. Dobbins, J., and Colehour, J., "Preparation of Perrhenic Acid", J. Am. Chem. Soc., 56, 2054 (1934).

316. Druce, J., Rhenium, p 64, University Press, Cambridge, 1948.

317. Roth, W., and Becker, G., "Physical Chemistry of Rhenium", Z. physik. Chem., A159, 27-39 (1932).

318. Feit, W., "Sulfur (Thio-) Derivatives of Perrhenic Acid", Z. angew. Chem., 44, 65-66 (1931).

319. Hagen, H., and Sieverts, A., "A Color Reaction Between Rhenium Heptoxide and Hydrogen Peroxide and (a Note) Regarding Rhenium Peroxide", Z. anorg. allgem. Chem., 208, 367-68 (1932).

320. Fonteyne, R., "Raman Spectrum and Structure of Perrhenic Acid and the Perrhenate Iron", Natuurw. Tidjschr., 20, 20-30 (1938).

321. Druce, J., Rhenium, pp 39-40, University Press, Cambridge, 1948.

322. Pushin, N., and Kovack, D., "Solubility of Potassium Perrhenate in Water, and Some Physicochemical Constants of its Solution", Bull. soc. chim. roy. Yougoslav, 2, No. 1, 25-31 (1931); Z. anorg. allgem. Chem., 199, 369-73 (1931).

323. Smith, W., "The System Potassium Perrhenate - Potassium Chloride-Water", J. Am. Chem. Soc., 68, 394 (1946).

324. Pushin, N., and Tutundzic, P., "Electrolytic Conductivity of Potassium Perrhenate Solutions", Z. anorg. allgem. Chem., 193, 420-24 (1930).

325. Briscoe, H., Robinson, P., and Stoddart, E., "The Reduction of Potassium Perrhenate", J. Chem. Soc., 1931, 666-9.

326. Krauss, F., and Steinfeld, H., "Preparation of Pure Rhenium Compounds", Z. anorg. allgem. Chem., 193, 385-90 (1930).

327. Hölemann, H., "Chemistry and Electrochemistry of Rhenium: IV. The Action of Reducing Agents Upon Sulfuric Acid Solutions of Potassium Perrhenate", Z. anorg. allgem. Chem., 220, 33-42 (1934).

328. Hölemann, H., "Chemistry and Electrochemistry of Rhenium: III. Reduction of Perrhenates With Zinc Chloride and Potentiometric Method of Determination for Septivalent Rhenium", Z. anorg. allgem. Chem., 217, 105-12 (1934).

329. Druce, J., "Manganese [illegible] and Perrhenate", J. Chem. Soc., 1938, 966.

330. "The Salts of Perrhenic Acid: II. The Iron Family and Manganese", Smith, W., and Maxwell, G., J. Am. Chem. Soc., 71, 578 (1949).

331. "The Perrhenates of Copper, Nickel, and Cobalt", Briscoe, H., Robinson, P., and Rudge, A., J. Chem. Soc., 1931, 2211-13.

332. Smith, W., and Maxwell, G., "The Salts of Perrhenic Acid: IV. The Group II Cations, Copper (II) and Lead (II)", J. Am. Chem. Soc., 73, 658 (1951).

333. Wilke-Dörfurt, E., and Gunsert, T., "New Salts of Perrhenic Acid", Z. anorg. allgem. Chem., 215, 369-87 (1933).

334. Neusser, E., "Perrhenates of a Few Cobalt-Ammonia Complex Salts", Z. anorg. allgem. Chem., 230, 253-56 (1937).

335. Druce, J., Rhenium, p 47, University Press, Cambridge, 1948.

336. Scharnow, B., "Mesoperrhenates", Z. anorg. allgem. Chem., 215, 185-89 (1933).

337. Ruff, O., "New Developments in the Chemistry of Fluorine", Angew. Chem., 46, 739-42 (1933).

338. Aynsley, E., Peacock, R., and Robinson, P., "The Reaction of Fluorine With the Oxides and Oxycompounds of Manganese and Rhenium", J. Chem. Soc., 1950, 1622-24.

339. Emeléus, H., and Gutmann, V., "The Fluorides of Niobium, Tantalum, Tungsten, and Rhenium", J. Chem. Soc., 1950, 2115-18.

340. Druce, J., Rhenium, pp 49-52, University Press, Cambridge, 1948.

341. Rulfs, C., and Elving, P., "Rhenium Iodide and Chloride", J. Am. Chem. Soc., 72, 3304 (1950).

342. Wrigge, F., and Biltz, W., "The Molecular State of Red Rhenium Chloride in Solution", Z. anorg. allgem. Chem., 228, 372-82 (1936).

343. Geilmann, W., and Wrigge, F., "Some Reactions of Rhenium Chloride", Z. anorg. allgem. Chem., 214, 248-60 (1933).

344. Geilmann, W., Wrigge, F., and Biltz, W., "Rhenium Trichloride", Nachr. Ges. Wiss. Göttingen, Math-physik. Klasse, No. 5, pp 579-87 (1932).

345. Klemm, W., and Frischmuth, G., "Ammoniates of Rhenium Trihalides", Z. anorg. allgem. Chem., 230, 209-14 (1937).

346. Yost, D., and Shull, G., "Density and Molecular State of Rhenium Tetrachloride and Rhenium Hexachloride in the Gaseous State", J. Am. Chem. Soc., 54, 4657-61 (1932).

347. Geilmann, W., Wrigge, F., and Biltz, W., "Rhenium Pentachloride", Z. anorg. allgem. Chem., 214, 244-47 (19[illegible]).

348. Schröter, W., Das Rhenium, p 39, Verlag von Ferdinand Enke, Stuttgart, 1932.

349. Jezowska-Trzebiatowska, B., and Jodko, C., "Complex Chlorides of Quadrivalent Rhenium", Roczniki Chem., 19, 187-98 (1939).

350. Krauss, F., and Dählmann, H., "Chemistry of Rhenium: IV. Halogen Compounds of Rhenium", Ber., 65B, 877-80 (1932).

351. Druce, J., Rhenium, p 56-9, The University Press, Cambridge, 1948.

352. Schmid, H., "Studies in the Chemistry of Rhenium: I. Potassium Rhenium (IV) Chloride, and Organic Derivatives of Tetravalent Rhenium", Z. anorg. allgem. Chem., 212, 157-97 (1933).

353. Krauss, F., and Steinfeld, H., "Chemistry of Rhenium: III. Compounds of Tervalent and Tetravalent Rhenium", Ber., 64B, 2552-56 (1931).

354. Geilmann, W., and Wrigge, F., "Double Salts of Rhenium Trichloride With Rubidium and Cesium Chlorides", Z. anorg. allgem. Chem., 223, 144-48 (1935).

355. Biltz, W., Wrigge, F., Prange, E., and Lange, G., "Rhenium Hydropentaiodic Acid", Z. anorg. allgem. Chem., 234, 142-49 (1937).

356. Briscoe, H., Robinson, P., and Rudge, A., "Potassium Rheni-Iodide", J. Chem. Soc., 1931, 3218-20.

357. Wiechert, K., "Preparation of Oxyfluorides With Anhydrous Hydrogen Fluoride", Z. anorg. allgem. Chem., 261, 310-23 (1950).

358. Briscoe, H., Robinson, P., and Rudge, A. J., "Rhenium Oxychloride", J. Chem. Soc., 1932, 1104-1107.

359. Brukl, A., and Plettinger, E., "Rhenium Oxytetrachloride", Ber., 66B, 971-73 (1933).

[illegible] [illegible] A., and Ziegler, K., "Rhenium Oxybromides", Monatsh., 63, 329-34 (1933).

361. Jakob, W., and Jezowska, B., "The Electroreduction of Perrhenic Acid", Ber., 66B, 461-62 (1933).

362. Jakob, W., and Jezowska, B., "The Electroreduction of Acid Perrhenate Solutions. The Complex Chloride of Quinquevalent Rhenium", Z. anorg. allgem. Chem., 214, [illegible]37-53 (1933).

363. Schulten, H., "Metal Carbonyls: XXX. Compounds of Rhenium With Carbon Monoxide", Z. anorg. allgem. Chem., 243, 164-73 (1939).

364. Hieber, W., Schuh, R., and Fuchs, H., "Metal Carbonyls: XXXVII. Rhenium Halopentacarbonyls, Their Tendency of Formation and Properties", Z. anorg. allgem. Chem., 248, 243-55 (1941).

365. Feit, W., "Monothioperrhenic Acid", Z. anorg. allgem. Chem., 199, 262-70 (1931).

366. Biltz, W., and Weibke, F., "The Systemic Doctrine of Affinity: LVI. The Affinity of Rhenium for Sulfur. 2. Rhenium Heptasulfide", Z. anorg. allgem. Chem. 203, 3-8 (1931).

367. Haraldsen, H., "The Systemic Doctrine of Affinity: LXIII. The System Rhenium-Phosphorus, Z. anorg. allgem. Chem., 221, 397-417 (1935).

368. Wallbaum, H., "Disilicides of Columbium, Tantalum, Vanadium, and Rhenium", Z. Metallkunde, 33, 378-81 (1941); Chem. Zentr. 1942 II, 9.

369. Weichmann, F., Heimberg, M., and Biltz, W., "Systemic Study of Affinity: LXXXV. The Affinity of Rhenium for Arsenic", Z. anorg. allgem. Chem., 240, 129-38 (1939).

370. Weichmann, F., Heimberg, M., and Biltz, W., "Systemic Study of Affinity: LXXXV. The Affinity of Rhenium for Arsenic; A Correction", Z. anorg. allgem. Chem., 240, 368 (1939).

371. Rulfs, C., and Elving, P., "Solubility of Thallous Rhenide", J. Am. Chem. Soc., 72, 3304 (1950).

372. Druce, J., Rhenium, p 68, University Press, Cambridge, 1948.

373. Gilman, H., Jones, R., Moore, F., and Kolbezen, M., "Reaction of Rhenium Trichloride With Methyl Magnesium Iodide", J. Am. Chem. Soc., 63, 2525-26 (1941).

374. Morgan, G., "Recent Researches in Certain of the Rarer Elements", J. Chem. Soc., 1935, 554-70.

375. Druce, J., "Ethoxides and Isopropoxides of Manganese and Rhenium", J. Chem. Soc., 1937, 1407-1408.

376. Lebedinskii, V., and Ivanov - Emin, B., "Complex Rhenium Compounds", J. Gen. Chem. (USSR), 13, 253-65 (1943) (English Summary p 265-66).

377. Hieber, W., and Fuchs, H., "Metal Carbonyls: XXXIX. Amino - Substituted Rhenium Carbonyls", Z. anorg. allgem. Chem., 248, 269-75 (1941).

378. Hölemann, H., "Chemistry and Electrochemistry of Rhenium: V. Investigations on Complex Thiocyanates of Rhenium and Rhenium Oxychloride", Z. anorg. allgem. Chem., 235, 1-24 (1937).

379. Tribalat, S., "The Complex Thiocyanates of Rhenium", Compt. rend., 223, 34-36 (1946).

380. Druce, J., "Rhenium Oxythiocyanate", Rec. trav. chim., 54, 334-35 (1935).

381. Miller, C., "The Behavior of Rhenium and of the Complex Thiocyanates of Rhenium and Molybdenum With Toluene - 3, 4-Dithol", J. Chem. Soc., 1941, 792.

382. Geilmann, W., and Brünger, K., "Analytical Chemistry of Rhenium: IV. Some Microchemical Tests for Rhenium", Z. anorg. allgem. Chem., 199, 77-90 (1931).

383. Kronman, E., and Bibikova, A., "Microchemical Detection of Rhenium", Mikrochemie, 12, 187-88 (1932).

384. Kronman, E., and Berkman, N., "New Microchemical Test for Rhenium", Z. anorg. allgem. Chem., 211, 277-80 (1933).

385. Druce, J., Rhenium, p 19, University Press, Cambridge, 1948.

386. Yagoda, H., "Detection of Rhenium in the Sodium Carbonate Bead", Ind. Eng. Chem., Anal. Ed., 8, 133-34 (1936).

387. Poluektov, N., "Sensitive Catalytic Spot Test for Rhenium", J. Applied Chem. (USSR), 9, 2312-14 (1936) (in German, p 2315).

388. Poluektov, N., "Detection of Rhenium by a Spot Test", J. Applied Chem. (USSR), 11, 534-38 (1938) (in German, p 538).

389. Anisimov, B., "Identification of Rhenium by the Drop Method", J. Applied Chem. (USSR), 17, 658-59 (1944).

390. [illegible], J., "Microchemical Reactions of Rhenium Compounds", Publ. inst. invest. microquim., Univ. nacl. litoral (Rosario, Arg.), 11, 35-38 (1947).

391. Duval, C., "Critical Study of the Reactions of the Cations: III. Rhenium", Anal. Chim. Acta, 2, 311-12 (1948).

392. Wenger, P., and Duckert, R., "Critical Study of Qualitative Reagents for Cations: V. Regents for Detecting Rhenium Cations and Perrhenate Anions", Helv. Chim. Acta, 25, 599-604 (1942).

393. Kao, C., and Chang. T., "Detection of Rhenium in Noyes' and Bray's System of Qualitative Analysis", J. Chinese Chem. Soc., 2, 6-12 (1934).

394. Geilmann, W., and Wrigge, F., "Analytical Chemistry of Rhenium: XII. Some Crystal Tests for Rhenium Trichloride and for Chlororhenic Acid", Z. anorg. allgem. Chem., 231, 66-77 (1937).

395. Hurd, L., Scott's Standard Methods of Chemical Analysis, 5th Ed, p 768-71, D. Van Nostrand Co., New York, 1939.

396. Geilmann, W., and Wrigge, F., "Analytical Chemistry of Rhenium: III. Reactions in the Dry Way", Z. anorg. allgem. Chem., 199, 65-76 (1931).

397. Yoe, J., "Some Observations on Reactions Between Certain Metallic Ions and the Ammonium Salt of Aurintricarboxylic Acid", J. Am. Chem. Soc., 54, 1022-23 (1932).

398. Geilmann, W., Wrigge, F., and Weibke, F., "The Analytical Chemistry of Rhenium: VII. Detection and Determination of Small Quantities of Rhenium With the Aid of Potassium Thiocyanate and Stannous Chloride", Z. anorg. allgem. Chem., 208, 217-24 (1932).

399. Hurd, L., and Babler, B., "Determination of Rhenium: II. The Geilmann Reaction", Ind. Eng. Chem., Anal. Ed., 8, 112-14 (1936).

400. Hurd, L., "Determination of Rhenium: I. Qualatative", Ind. Eng. Chem., Anal. Ed., 8, 11-15 (1936).

401. Wenger, P., Duckert, R., and Ankajdi, E., "New Method of General Analysis for Cations Based on the Use of Potassium Ethyl Xanthate: II", Helv. Chim. Acta, 28, 1592-1609 (1945).

402. McAlpine, R., and Soule, B., Qualitative Chemical Analysis (Based on the Text by Prescott and Johnson), pp 293-96, D. Van Nostrand, Co., New York, 1933.

403. Wada, I., and Ishii, R., "Detection and Separation of Rhenium", Sci. Papers Inst. Phys. Chem. Research (Tokyo), 31, 55-84 (1937).

404. Miller, C., "Qualitative Semimicroanalysis With Reference to Noyes and Bray's System: The Copper and the Tellurium Group", J. Chem. Soc., 1941, 786-92.

405. Geilmann, W., and Bode, H., "Analytical Chemistry of Rhenium: XXI. Separation of Rhenium From the Elements of the Hydrogen Sulfide Group; I. Separation From Silver, Mercury, Lead, Bismuth, Copper, and Cadmium", Z. anal. Chem., 132, 250-74 (1951).

406. Geilmann, W., and Bode, H., "Analytical Chemistry of Rhenium: XXII. Separation of Rhenium From Arsenic, Antimony, Tin, Gold, Germanium, Selenium, and Tellurium", Z. anal. Chem., 133, 177-92 (1951).

407. Heyrovský, J., "The Catalytic Deposition of Hydrogen on the Dropping Mercury Cathode", Přívoda, 28, 212-19 (1935).

408. Schleicher, A., "Qualitative Microanalysis by Electrolysis and Spectrography", Z. anal. Chem., 101, 241-54 (1935).

409. Tougarinoff, B., "Two Color Tests for Rhenium", Bull. soc. chim. Belg., 43, 111-14 (1934).

410. Prévot, A., "Detection and Determination of Rhenium by Means of X-Ray Emission Spectrum", J. chim. phys., 45, 251-57 (1948).

411. Tribalat, S., "Determination of Rhenium With α-Benzildioxime", Compt. rend., 224, 469-71 (1947).

412. Geilmann, W., and Weibke, F., "Analytical Chemistry of Rhenium: II. Determination of Rhenium as Nitron Perrhenate After Previous Precipitation as Sulfide", Z. anorg. allgem. Chem., 195, 289-308 (1931).

413. Geilmann, W., and Weibke, F., "The Analytical Chemistry of Rhenium: VI. Simple Method for Separating Molybdenum and Rhenium", Z. anorg. allgem. Chem., 199, 347-52 (1931).

414. Bibikova, I., "A New Method for Separating Molybdenum From Rhenium in the Colorimetric Determination of the Latter", Redkie Metal. (Rare Metals), 1935, No. 6, 24-26.

415. Michailova, O., Pevsner, S., and Archipova, N., "Microchemical Methods in the Determination of One Milligram of Rhenium After Preliminary Separation of Molybdenum", Z. anal. Chim., 91, 25-28 (1932).

416. Young, R., and Bernays, [illegible], "Possible Source of [illegible] Gravimetric Determinations Involving the Use of Hydrogen Peroxide Followed by Nitron", Ind. Eng. Chem., Anal. Ed., 12, 90 (1940).

417. Muller, J., and LaLande, W., "The Precipitation of Rhenium Sulfide From Ammoniacal Solution. A Separation of Rhenium and Molybdenum", J. Am. Chem. Soc., 55, 2376-78 (1933).

418. Geilmann, W., and Bode, H., "Analytical Chemistry of Rhenium: XIX. Solubility of Rhenium Heptoxide in Alkali Sulfide and Polysulfide Solutions", Z. anal. Chem., 130, 320-23 (1950).

419. Geilmann, W., and Lange, G., "Precipitation and Determination of Rhenium as a Sulfide", Z. anal. Chem., 126, 321-34 (1944).

420. Geilmann, W., Wiechmann, F., Wrigge, F., et al., "The Analytical Chemistry of Rhenium. Precipitation of Rhenium of Different Valences as Sulfide", Z. anal. Chem., 126, 418-26 (1944).

421. Geilmann, W., and Bode, H., "Analytical Chemistry of Rhenium: XVIII. Precipitation of Rhenium as Sulfide by Sodium Thiosulfate", Z. anal. Chem., 130, 222-32 (1950).

422. Pushin, N., "Rhenium and Its Compounds", Bull. soc. chim. roy. Yougoslav, 2, 111-28 (1931).

423. Krauss, F., and Steinfeld, H., "Chemistry of Rhenium: II. Determination of Rhenium as Thallium Perrhenate", Z. anorg. allgem. Chem., 197, 52-56 (1931).

424. Geilmann, W., and Weibke, F., "Analytical Chemistry of Rhenium: V. Separation of Rhenium by Distillation With Hydrogen Chloride", Z. anorg. allgem. Chem., 199, 120-28 (1931).

425. Kronman, E., "The Analytical Chemistry of Rhenium", Z. anal. Chem., 90, 31-34 (1932).

426. Hoffman, J., and Lundell, G., "Volatilization of Metallic Compounds From Solutions in Perchloric or Sulfuric Acid", J. Research Natl. Bur. Standards, 22, 465-70 (1939).

427. Hiskey, C., and Melochs, V., "Determination of Rhenium in Molybdenite Minerals", Ind. Eng. Chem., Anal. Ed., 12, 503-506 (1940).

428. Geilmann, W., and Bode, H., "Analytical Chemistry of Rhenium: XX. Separation of Rhenium by Distillation", Z. anal. Chem., 130, [illegible].

429. Hoffman, J., and Lundell, G., "Separation and Colorimetric Determination of Rhenium and Molybdenum", J. Research Natl. Bur. Standards, 23, 497-508 (1939).

430. Hurd, L., and Hiskey, C., "Determination of Rhenium. Estimation in Pyrolusite", Ind. Eng. Chem., Anal. Ed., 10, 623-26 (1938).

431. Geilmann, W., and Bode, H., "Analytical Chemistry of Rhenium: XVI. Colorimetric Determination of Small Quantities of Rhenium", Z. anal. Chem., 128, 489-95 (1948).

432. Geilmann, W., and Bode, H., "Analytical Chemistry of Rhenium: XVII. Separation and Determination of Small Quantities of Rhenium in Technical Products", Z. anal. Chem., 128, 495-507 (1948).

433. Malouf, E., and White, M., "Colorimetric Determination of Rhenium", Anal. Chem., 23, 497-9 (1951).

434. Melaven, A., and Whelsel, K., "Colorimetric Determination of Rhenium", Anal. Chem., 20, 1209 (1948).

435. Willard, H., and Smith G., "Tetraphenylarsonium Chloride as an Analytical Reagent. Determination of Rhenium", Ind. Eng. Chem., Anal. Ed., 11, 305-306 (1939).

436. Tribalat, S., "Extraction and Determination of Traces of Rhenium, Especially in The Molybdenites", Anal. Chim. Acta, 3, 113-25 (1949).

437. Tribalat, S., "Extraction of the Chloride and Perrhenate of Tetraphenylphosphonium by Chloroform", Anal. Chim. Acta 4, 228-34 (1950).

438. Tribalat, S., "Extraction and Determination of Rhenium by Triphenylbenzylphosphonium Chloride", Anal. Chim. Acta, 5, 115 (1951).

439. LaCoste, R., Earing, M., and Wilberley, S., "Colorimetric Estimation of Various Metal Derivatives of Sodium Diethyldithiocarbamate", Anal. Chem., 23, 871-74 (1951).

440. Geilmann, W., and Hurd, L., "Analytical Chemistry of Rhenium: VIII. Volumetric Determination of Rhenium Oxides", Z. anorg. allgem. Chem., 211, 277-80 (1933).

441. Geilmann, W., and Hurd, L., "Analytical Chemistry of Rhenium: X. Determination of Rhenium as the Dioxide", Z. anorg. allgem. Chem., 214, 260-68 (1933).

442. Geilmann, W., and Wrigge, F., "Analytical Chemistry of Rhenium: XI. Volumetric Determination of the Valence of Rhenium Compounds", Z. anorg. allgem. Chem., 222, 56-64 (1935).

443. Druce, J., "Volumetric Estimation of Potassium Perrhenate", Chem. News, 145, 186-87 (1932).

444. Geilmann, W., and Hurd, L., "Analytical Chemistry of Rhenium: IX. Determination of Chlororhenic Acid in the Presence of Perrhenic Acid", Z. anorg. allgem. Chem., 213, 336-42 (1933).

445. Tomíček, O. and F., "An Electro-Analytical Estimation of Rhenium", Tran. Electrochem. Soc., 76, 105-111 (1939).

446. Voigt, A., "Analytical Chemistry of Rhenium", Z. anorg. allgem. Chem., 249, 225-28 (1942).

447. Furman, N., Bricker, C., and McDuffie, B., "Method for the Determination of Certain Metals Present in Minor Concentration in Various Substances", J. Wash. Acad. Sci., 38, 159-66 (1948).

448. Lingane, J., "Polarographic Investigation of Rhenium Compounds: I. Reduction of Perrhenate Ion at the Dropping-Mercury Electrode", J. Am. Chem. Soc., 64, 1001-1007 (1942).

449. Geyer, R., "The Polarographic Reduction of Rhenium", Z. anorg. allgem. Chem., 263, 47-62 (1950).

450. Rulfs, C., and Elving, P., "Oxidation Levels of Rhenium: I. Polarographic and Coulometric Reduction of Perrhenate", J. Am. Chem. Soc., 73, 3284-86 (1951).

451. Poluektov, N., "Colorimetric Determination of Rhenium by a Catalytic Reaction", J. Applied Chem. (USSR), 14, 695-702 (1941).

452. Young, C., "Plating Rhenium and Rhenium-Nickel Alloys", Metal Ind., N. Y., 34, 176-77 (1936).

453. Hurd, L., Colehour, J., and Cohen, P., "Toxicity Tests With Potassium Perrhenate", Proc. Soc. Exptl. Biol., N. Y., 30, 926-28 (1933).

454. Maresh, F., Lustock, M., and Cohen, P., "Physiological Studies of Rhenium Compounds", Proc. Soc. Exptl. Biol. Med., 45, 576-79 (1940).

455. Druce, J., Rhenium, p 71, University Press, Cambridge, 1948.

456. Noddack, W. and I. (to Siemens and Halske A.-G.), "Catalyst for Oxidation Processes", Brit. Pat. 346, 652 (October 8, 1929).

457. "Catalyst" (to Siemens and Halske A.-G.), Fr. Pat. 682,446 (September 30, 1929).

458. "Catalytic Reactions and (Rhenium) Catalyst for Use Therein (Oxidation of Ammonia)" (to Siebert Ges. m.b.H.), Brit. Pat. 385, 859 (June 8, 1932).

459. "Use of Rhenium as a Catalyst" (to N. - V. de Bataafsche Petroleum Maatschappij), Brit. Pat. 358,180 (July 29, 1930).

460. "Hydrogenating Carbonacious Materials" (to International Hydrogenation Patents Co., Ltd.), Fr. Pat. 761,632 (March 23, 1934).

461. Tropsch, H., and Kassler, R., "Catalytic Properties of Rhenium", Ber., 63B, 2149-51 (1930).

462. Anisimov, S., Krasheninnikova, V., and Platonov, M., "Catalytic Properties of Rhenium and of Some of Its Compounds", J. Gen. Chem. (USSR), 5, 1059-65 (1935).

463. Platonov, M., Anisimov, S., and Krasheninnikova, V., "The Catalytic Properties of Rhenium", Ber., 68B, 761-75 (1935).

464. Platonov, M., Anisimov, S., and Krasheninnikova, V., "Catalytic Properties of Rhenium: II. Dehydrogenation of Propyl Alcohols", Ber., 69B, 1050-53 (1936).

465. Tyler, P., "Depression Period Well Past for the Rare Metals and Minerals", Mining Met., 17, 17-22 (1936).

466. Platonov, M., and Tomilov, V., "Catalytic Properties of Rhenium: III. Methods of Obtaining Rhenium Catalysts", J. Gen. Chem. (USSR), 7, 776-77 (1937).

467. Platonov, M., and Anisimov, S., "The Catalytic Properties of Rhenium: V. Dehydrogenation of Butyl Alcohols", J. Gen. Chem. (USSR), 7, 1360-63 (1937).

468. Platonov, M., and Tomilov, V., "Catalytic Properties of Rhenium: IV. Catalytic Decomposition of Formic Acid and Ethyl Alcohol", J. Gen. Chem. (USSR), 7, 778-81 (1937).

469. Platonov, M., Tomilov, V., and Tur, E., "The Catalytic Properties of Rhenium: VI. The Decomposition of Methanol Over Rhenium", J. Gen. Chem. (USSR), 7, 1803-1804 (1937).

470. [illegible], Anisimov, S., and Platonov, M., "Catalytic Properties of Rhenium: VII. Dehydration of Cyclohexanol Over [illegible]", J. Gen. Chem. (USSR), 7, 2895-98 (1937) (In English, p 2898).

471. Platonov, M., "The Catalytic Properties of Rhenium: IX. The Dehydrogenation of Alcohols Over Rhenium Disulfide", J. Gen. Chem. (USSR), 11, 683-85 (1941).

472. Platonov, M., "The [illegible] Properties [illegible]: VIII. Dehydrogenation of Isoamyl Alcohol", J. Gen. Chem. (USSR), 11, 590-91 (1941).

473. Platonov, M., and Anisimov, S., "Catalyst for the Dehydrogenation of Alcohol", Russ. Pat. 52,780 (March 31, 1938).

474. Kleese, W., "Possible Applications of Rhenium Metal and Its Alloys", Metall., 5, 155-56 (1951).

475. Zenghelis, C., and Stathis, K., "Preparation of Rhenium in a Colloidal State and Its Catalytic Properties", Atti X° congr. intern. chim., 2, 821-24 (1938).

476. Zenghelis, C., and Stathis, K., "Preparation of Colloidal Rhenium and Its Catalytic Properties", Compt. rend. 209, 797-99 (1939).

477. Zenghelis, C., and Stathis, K., "Synthesis of Ammonia Catalyzed With Metallic Rhenium", Österr. Chem. Ztg., 40, 80-81 (1937).

478. McGeer, J., and Taylor, H., "Ammonia Decomposition and Related Phenomena on Rhenium Catalysts", J. Am. Chem. Soc., 73, 2743-51 (1951).

479. Deutsche Gold-und Silber-Scheideanstalt vorm. Roessler, "Catalyst for Carrying Out Catalytic Reactions in Gaseous Phase", Bel. Pat. 445,998 (July 31, 1942).

480. N.-V. de Bataafsche Petroleum Maatschappij, "Catalyst for the Hydrogenation of Coal, Tar, and Mineral Oil", Ger. Pat. 693,707 (June 20, 1940).

481. Tribalat, S., "The Catalytic Action of Rhenium on the Reduction of Nitrogen at Different Degrees of Oxidation", Bull. soc. chim. France, 1951, 131-34.

482. Schulze, A., "Thermo-Elements at High Temperatures", Z. Ver. deut. Ing., 77, 1241-42 (1933).

483. Goedecke, W., "Thermocouples and the Reproducibility of Their Data. Criteria for Their Usefulness in Measuring High Temperatures", Siebert Festschrift, pp 72-99 (1931).

484. Laise, C., "Refractory Alloy Composition", Brit. Pat. 520,025 (April 12, 1940).

485. Weiger, J. (to P. R. Mallory and Co.), "[illegible] of Rhenium or Its Alloys for Electrical Make-and-Break Cont[illegible]", U. S. Pat. 1,877, 261 (September 13, 1933).

486. Noddack, I. and W., (to Siemens and Halske A. G.), "[illegible]ting Lamp Filaments, etc. With Rhenium", Ger. Pat. 527,105 (June 5, 1929).

487. Siemens and Halske A. G., "Incandescent Electric Lamps With Filaments of Rhenium", Brit. Pat. 350,204.

488. Noddack, W. and I., (to Siemens and Halske A. G.), "Use of Metallic Rhenium as an Electric Glower for Incandescent Lamps, Etc., U. S. Pat. 1,829,756 (November 3, 1931).

489. Stauffer, R., and Smith, Wm. (to Eastman Kodak Co.) "Photographic Emulsion", U. S. Pat. 2,458,442 (January 4, 1949).

490. Esperson, G., "Thermionic Emitting Properties of Thoria-Rhenium", J. Applied Physics, 21, 261 (1950).

491. Druce, J., Rhenium, p 73, University Press, Cambridge, 1948.

492. Arend, A., "Rhenium", Indust. Chemist, 21, No. 245, 293-296 (1945).

References to Rhenium Not Cited in This Survey

In the course of this survey, approximately 125 references were encountered containing information on or pertaining to rhenium which were not adjudged sufficiently pertinant to be included in the text, or which were not available in either the original or the abstract form in Columbus. Since these references might contain material of importance, particularly to a worker in some specialized field, they are catalogued below. They are presented in a chronological order by years and alphabetically by author within the year.

1925

Berg, O., "Roentgenspectroscopy and the Detection of Eka-Manganese", Z. Techn. Phys., 6, 597-603 (1925).

Noddack, W., and Tacke, I., "The Separation of the Elements Rhenium and Masurium", Metallborse, 15, 1597-99 (1925).

1926

Loring, F., "On the Synthesis of Elements", Chem. News, 133, 356-58 (1926).

Meggers, W., and Kiess, C., "Spectral Structures for Elements of the Second Long Period", J. Am. Opt. Soc., 12, 417 (1926).

Noddack, I. and W., "On the Elements Masurium and Rhenium. Critical Considerations of Some Recent Researches", Metallbörse, 16, 2633-34 (1926).

Noddack, W., and I., "New Researches on the Elements Masurium and Rhenium", Metallbörse, 16, 2129-30 (1926).

Patton, I., and Waldbauer, L., "Radioactivity of Alkali Metals", Chem. Rev., 3, 81-93 (1926).

1927

Druce, J., "The Interaction of Manganese Salts and Permanganates, Parts I and II", Chem. News, 134, 145-47, 161-63 (1927).

Druce, J., "Elements Whose Existence Has Been Announced, but Which are Not Recognized", Sci. Prog., 21, 479-91 (1927).

Noddack, I. and W., "Rhenium", Ergeb. exakt. Naturw., 6, 333-73 (1927).

1928

Hahn, O., "New Advancements in Element and Isotope Research", Z. angew. Chem., 41, 516 (1928).

1929

Loring, F., "Mass Numbers of the Chemical Elements and Observations on Element Formation", Chem. News, 139, 231 (1929).

Noddack, I. and W., "New Research on the Properties of Rhenium", Forsch. U. Fortchr. 5, 3 (1929).

St. John, C., "Elements Unidentified or Doubtful in the Sun", Astrophys. J., 70, 160-74 (1929).

1930

Anon., "Rhenium Metal and Its Compounds; Some Recent German Research", Chem. Age, (Lond.) 22, Supp. pp 22-3, (April 5, 1930).

Friederich, E., "Using Rhenium and Its Alloys for Making Electric Heating Devices", Ger. Pat. 536,471 (June 7, 1930).

Siemens and Halske A. G., "Coating Tungsten Filaments With Rhenium", Brit. Pat. 351,216 (June 4, 1930).

Sonder, R., "The Abundance of Elements and the Existence of Nuclear Periodicity", Naturwissenschaften, 18, 939-40 (1930).

Tollert, H., "Potassium Determination as Potassium Perrhenate", Naturwissenschaften, 18, 849 (1930).

1931

Agte, C., and Becker, K., "Rhenium", Umschau, 35, 520-22 (1931).

Anon., "Tungsten-Rhenium Alloys", Engineer, 151, Supp. (Metallurgist), 96 (June 26, 1931).

Briscoe, H., Robinson, P., and Stoddart, E., "The Alleged Thallous Thioperrhenate", J. Chem., Soc., 1931, 2976-77.

Collenberg, O., "The Discovery and Properties of Rhenium", Svensk., Kem. Tids., 43, 265-81 (1931).

Druce, J., "Atomic Weight of Rhenium", Sci. Progress, 25, 499-500 (1931).

Geay, E., "The Elements Hafnium, Rhenium, Indium, and Their Applications", Rev. chim. ind., 40, 98-101 (1931).

Heyne, G., "Physical and Chemical Properties of Rhenium", Z. anorg. Chem., 197, 224 (1931).

Huppert, O., "Researches on Rhenium", Technique moderne, 23, 596 (1931).

Kronman, E., "Distribution of Rhenium in Nature and Its Industrial Production". Mineral Suir'e, 6, No. 10-11, 945-55 (1931).

LeBlanc, M., and Sachse, H., "The Electron Conductivity of Solid Oxides With Different Valences", Physik Z., 32, 887-89 (1931).

Loring, F., "Resistivities of the Metals at 18 C, and the Problem of Their Relative Abundance in the Universe", Chem. News, 142, 403-407 (1931).

Loring, F., "The Optical Spectrum of Rhenium and Attempts to Identify This Element in the Stars", Chem. News, 142, 3212 (1931).

Meggers, W., "The Spectrum of Rhenium", J. Franklin Inst., 211, 373-74 (1931).

1932

Briscoe, H., Robinson, P., and Stoddart, E., "Thioperrhenates", J. Chem. Soc., 1932, 2811-12.

Doligue, R., "Rhenium, Element Number Seventy-Five", Bull. sci. pharmacol., 39, 677-86 (1932).

Druce, J., "Chemistry of Dvi-Manganese (Rhenium)", Chem. Weekblad, 29, 57-59 (1932).

Druce, J., "Perrhenic Acid and Its Salts", Chem. and Ind., pp 632-33 (1932).

Egyesült Izzólámpa és Villamossági, R. T., "Obtaining Coherent Masses From Powdered Metals, e.g. Tungsten, Rhenium, and Molybdenum", Brit. Pat. 384,309 (November 22, 1932).

Einecke, E., "The Analytical Chemistry and Physics of Rhenium", Z. anorg. allgem. Chem., 90, 127-29 (1932).

Enrique Saurez del Real, "The Elements 43 and 75, - Masurium and Rhenium", Mem. rev. acad. nacl. cienc. Antonio Alzata, 53, 231-38 (1932).

Kronman, E. "The Element Rhenium", J. Chem. Ind. (Moscow), 1932, No. 5, 23-28.

Kronman, E., "Rhenium", J. Chem. Ind. Russia, 145, 186-87 (1932).

Schober, H., "The Spectra of Rhenium; III. The Arc Spectrum in the Visible Region Between 5400 and 4000 Å from Copper Electrodes", Sitzber. Akad. Wiss. Wien., Math - naturw. Klasse, Abt. IIa, 141, 631-16 (1932).

Tollert, H., "The Determination of Potassium With Perrhenate Salts", Z. anorg. allgem. Chem., 204, 140-42 (1932).

Tropsch, H., and Kassler, R., "Rhenium as a Catalyst", Zpravy Ustavu Vedecky Vyskum Uhli Praze, 2, 13 (1932).

Zeeman, P., Gisolf, J., and de Bruin, T., "Magnetic Resolution and the Nuclear Moment of Rhenium", Proc. Acad. Sci. Amsterdam, 35, 2-9 (1932).

1933

Brandes, W., and Geller, A., "Rare Elements", Z. prakt. Geol., 41, [illegible] (1933).

Druce, J., "Some Properties of Rhenium (Dvi-Manganese)", Ind. Chemist, 9, 244 (1933).

Prettre, M., "Le Rhenium", Bull. Soc. Chim. France, 53, 669-81 (1933).

Samuel, R., and Despande, A., "Absorption Spectra of Complex Salts of the Metals Chromium, Manganese, Rubidium, Palladium, Rhenium, Osmium, Iridium, and Platinum", Z. Physik, 80, 395-401 (1933).

1934

Ivernova, V., "Precision Methods for the Measurement of the Parameters of Crystal Lattices", J. Tech. Phys. (USSR), 4, 459-[illegible]5 (1934).

Kronman, E., Bibikova, V., and Axenova, M., "Extraction of Rhenium From Molybdenites", J. Appl. Chem. Russia, 7, 47-50 (1934).

1935

An[illegible]ssen, H., "Plating With Rhodium and Rhenium", Chem. Ztg., 59, [illegible]76, 449 (1935).

Freitag, B., "Uncommon Metals and Their Practical Uses", Warme 58, 662-63 (1935).

Hahn, O., and Meitner, L., "The Artificial Transformation of Uranium by Neutrons", Naturwissenschaften, 23, 37-38 (1935).

Lange, H., "Optical Constants of Rhenium and Gallium for the Wave Lengths 589 and 436 mμ", Z. physik, 94, 650-54 (1935).

Morgan, G., "Report of the Director of Chemical Research: X. General Research", Dept. Sci. Ind. Research (Brit.), Chem. Research Board, Triennial Rept. 1935-1937, 7-8.

Pitzer, K., "The Crystal Structure of Tetramminocadmium Perrhenate", Z. Krist., 92, 131-35 (1935).

Shtsherbakov, D., "Problems of Super-Rare and Dispersal Elements, Redkie Metal. (Rare Metals), 1935, No. 3, 28-38.

Silina, F., "Rare Elements are Obtaining Wide Industrial Application", Redkie Metal. (Rare Metals), 1935, No. 5, 51-55.

Wardlaw, W., "Some Rarer Metals (Germanium, Gallium, Indium, Rhenium)", Ann. Rep. Prog. Chem., 31, 1[illegible]-126 (1935).

1936

Druce, J., "Precursors of Rhenium and Masurium", Chemistry and Industry, 55, 577-78 (1936).

Fink, C., and Deren, P., "Electrodeposition of Rhenium", Vereinigte Chem. Fab. zu Leopoldshall Zweigstelle du Kaliwerke Aschersleben, Ger. Pat. 626,322, (February 24, 1936).

Kimura, K., and Koyama, Y., "Chemical Investigations of Japanese Minerals Containing Rarer Elements: XXII. Spectrographic Detection of Gallium, Germanium, Indium, Rhenium, and Thallium in Various Japanese Minerals", J. Chem. Soc. Japan, 57, 1190-94 (1936).

Schlintlmeister, J., "Study of the Origin of the α-rays of 2 cm. Range", Sitzber. Akad. Wiss. Wien, Math. - naturw. Klasse, Abt IIa, 145, 449-60 (1936).

Simonds, H., and Young, C., "Colouring of Metals: III. White Metals", Iron Age, 137, 30-33 (1936).

Šmída, J., "Recent Contributions to the Completion of the Atomic System of Elements", Příroda, 29, 298-302 (1936); Chem. Obzor, 13, Abstracts p 129 (1938).

1937

Bogomolov, Y., "Rare Metals in the Smelting of Iron", Teoriya Prakt. Met., 9, No. 2, 84-88 (1937).

Geilmann, W., and Lange, G., "Analytical Chemistry of Rhenium: XIII. Determination of Chlorine in Rhenium Compounds", Z. anorg. allgem. Chem., 234, 289-97 (1937).

Nischk, K., "Developments in the Electroplating Art During 1936 Based on the German Patent Literature", Oberflächentech., 14, 203-205, 213-15 (1937).

Schüler, H., and Korsching, H., "The Alterations of the Magnetic Moments of Atomic Nuclei by the Introduction of Pairs of Particles", Z. Physik, 105, 495-500 (1937).

1938

Druce, J., "Recent Work on Rhenium", Sci. Progress, 32, 132-34 (1938).

Hulubei, H., and Cauchois, Y., "Probable Existence of Element 93 in a Natural State", Compt. rend. 207, 333-35 (1938).

1939

Fink, C., and Deren, P., "Electroplating With Rhenium", Vereinigte chemishe Fabriken zu Leopoldshall, U. S. Pat. 2,138,573 (November 29, 1939).

Loring, F., "Some Physico-Chemical Numerics", Chem. Prod. and Chem. News, 2, 24-29 (1939).

Van Arkel, A., Reine Metalle, Verlag von Julius Springer, Berlin, 1939.

1940

Fröhlich, K., "Pen Points of Rhenium", Umschau, 44, 652-53 (1940).

Noddack, I. and W., and Bohnstedt, U., "The Distribution Coefficients of the Heavy Metals Between Iron (II) Sulfide and Iron", Z. anorg. allgem. Chem., 244, 252-80 (1940).

Zenghelis, C., and Stathis, C., "Preparation of Rhenium in a Colloidal State and Its Catalytic Properties", Kolloid - Z., 90, 129-31 (1940).

Zingg, E., "The Isobaric Paris Cd-In, In-Sn, Sb-Te, Re-Os", Helv. Phys. Acta, 13, 219-58 (1940).

1941

Schuh, R., "Metal Carbonyls: XL. The Absorption Spectra of the Carbon Monoxide Compounds of Rhenium", Z. anorg. allgem. Chem., 248, 276-82 (1941).

1942

Cooper, J., "The Auger Effect in Relative Intensities and Widths of X-Ray Lines", Phys. Rev., 61, 234-42 (1942).

Voigt, A., "Metallic Rhenium", Gebr. Borchers A. G., Ger. Pat. 723, 303 (June 18, 1942).

1943

Druce, J., "Recent Progress With Rhenium", Ind. Chemist, 19, 343-44 (1943).

Lund, H., "Rare Metals and Their Uses", Ingeniøren, 52, No. 18, 20-21, No. 24, 29-30 (1943).

Tyler. Minerals Yearbook - 1943, U. S. Gov't. Printing Office.

1944

Duke, F., "Salicylamines as Organic Precipitants. Quantitative Precipitation of Nickel and Copper and Determination of Copper in Brass and Bronze", Ind. Eng. Chem., Anal. Ed., 16, 750-[illegible] (1944).

Mathieu, J., "The Magnetic Properties of the Transition Elements", Cahiers phys. 22, 33-36 (1944).

Miller, C., "Toluene - 3,4 - Dithol as a Selective Reagent for W: The Detection of W, Especially in Mo and Re Compounds, and in Fe Alloys", Analyst, 61, 109-112 (1944).

1945

Blokhin, M., "X-Ray Spectral Analysis and Its Possibilities", Zavodskaya Lab., 11, 1069-74 (1945).

Bolz, H., "The Rare Metals Go to Work and to War II", Modern Machine Shop, 18, 140-52 (1945).

1946

Iskol'dskiĭ, I., and Skokhor, T., "Metallothermy in the Light of the Electrochemical Series", J. Applied Chem. (USSR), 19, 693-704 (1946).

Stirling, J., "Some Miscellaneous Metal Platings", Pract. Eng., 14, 208-209 (1946).

1947

Barber, W., "Search for Positron-Electron Branching in Certain β-Emitting Iostopes", Phys. Rev., 72, 1156-59 (1947).

Carobbi, G., "Suggestions for a Crystallo-Chemical System of Ions", Atti e mem. accad. sci., Modena, 7, 3-25 (1947).

Iandelli, A., "Intermetallic Compounds of the More Electropositive Elements", Gazz. Chim. ital., 77, 24-25 (1947).

Klinkenberg, P., "The Spectrum of the Rhenium Atom, Re I", Physica, 13, 581-604 (1947).

Tribalat, S., "Reduction and Determination of Arsenates in the Presence of Catalysts, Especially Rhenium", Anal. Chim. Acte, 1, 149-52 (1947).

1948

Jacobi, E., "The Chemistry of Element 43", Helv. Chim. Acta, 31, 2118-23 (1948).

O'Conner, P., and Seaborg, G., "High-Energy Spollation and Fission Products of Uranium", Phys. Rev., 74, 1189-90 (1948).

Org, S., "The Inhibitory Action of Metals on the Growth of Bacillus Tuberculosis: VII. Manganese and Rhenium", Proc. Koninkl. Nederland, Akad. Wetenschap, 51, 910-18 (1948).

Penner, S. S., "Free Volumes of the Metallic Elements at Their Boiling Points", J. Chem. Phys., 16, 745-46 (1948).

Vanossi, R., "Identification of Rhenium", Anales soc. cient. argentina, Sección Santa Fe, 145, 207-41 (1948).

Vanossi, R., "Separation and Identification of Elements Which are Distilled by Acids. Osmium, Ruthenium, Germanium, Rhenium, Selenium, Mercury, Arsenic, Antimony, Tin", Anales asoc. quim. argentina, 36, 155 (1948).

1949

Baumann, E., Zizmer, N., Oshry, E., and Seidlin, S., "Behavior of the Thyroid Towards Elements of the Seventh Periodic Group: II. Rhenium", Proc. Soc. Exptl. Biol. Med., 72, 502-506 (1949).

Beach, L., Peacock, C., and Wilkinson, R., "The Radiations of Rhenium^{186} and Rhenium^{188}", Phys. Rev., 76, 187 (1949).

Druce, J., "Element Rhenium and Some of Its Compounds", Chem. Products, 12, 326-27 (149).

Kemp, L., (To Texas Co.), "Motor Fuel", U. S. Pat. 2,461,064, (Feburary 8, 1949).

Pospekhov, D., "Pyrophoric Metals", J. Appl. Chem. (Russia), 22, 5-12 (1949).

Rogers, L., "Electroseparation of Technetium From Rhenium and Molybdenum", J. Am. Chem. Soc., 71, 1507-1508 (1949).

Sullivan, W., "Artifically Produced Radioisotopes of Tungsten and Rhenium", Univ. Microfilms (Ann Arbor, Mich.) Pub. No. 1262, 128 pp, Microfilm Abstracts, 9, No. 2, 47-48 (1949).

1950

Bane, R., and Rodder, C., "Manganese, Technetium, and Rhenium", Natl. Nuclear Energy Ser., Div. VIII, 1, Anal. Chem, Manhatten Project, pp 438-44 (1950).

Gatterer, A., Junkes, J., et al., "Atlas of Persistent Spectra: III. Spectra of Rare Metals and Semi Metalloids", [illegible] From Astrophys. Lab. of the Vatican Observatory, Vatican City, [illegible]

Gehlhoff, P., Justi, E., and Kohler, M., "Hall Effect for Iridium, - Relation Between the Hall Effect and Electronic Arrangement of The Noble Metals", Z. Naturforsch., 5a, 16-18 (1950).

Kornilov, I., "Solubilities of Elements of the Periodic System in Nickel", Izvest. Akad. Nauk S.S.S.R., Otdel, Khim. Nauk., 1950, 475-84.

Pecherskaya, A., and Stender, V., "Potentials of the Evolution of Hydrogen in Acid Solutions", Zhur. Fiz. Khim., 24, 856-59 (1950).

Pospekhov, D., "Color of Metal Carbonyls and Related Compounds", Zhur, Obshcĭ Khim., 20, 1737-46 (1950).

Shipitsin, S., "Spectral Analysis of Biologic Materials", Izvest. Akad. Nauk S.S.S.R., Ser. Fiz., 14, 677-82 (1950).

Taylor, H., "Effect of the Heterogeniety of Catalysts on Chemisorption and Chemical Kinetics", J. Chim. Phys. 47, 1225 (1950).

1951

Butement, F., "New Radioactive Isotopes Produced by Nuclear Photo-disintegration", Proc. Phys. Soc. (London), 64A, 395-403 (1951).

Healy, J., and Andrews, A., "Elements of the Third, Fourth, and Fifth Series as Possible Adherence-Producing Materials for Sheet-Iron Enamels", J. Am. Ceram. Soc., 34, 214-19 (1951).

Melaven, A., "Rhenium, A Rare Metal", Mine's Magazine, 41, 24 (September, 1951).

Smolenskii, G., and Kozhevnikova, N., "The Problem of the Origin of Seignettoelectricity", Doklady Akad. Nauk S.S.S.R., 76, 519-22 (1951).

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