

Cambridge University Press

978-1-107-69324-1 - Rhenium: Dvi-Manganese, the Element of Atomic Number 75

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Excerpt

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CHAPTER I

INTRODUCTION

SEARCH FOR THE CONGENERS OF MANGANESE

AFTER Mendeléef had enunciated the periodic law in 1869, attention was directed towards a search for missing elements which the Russian savant confidently predicted would ultimately be discovered to fill the blank spaces that he had left when drawing up his Table of the Elements. The fulfilment of his predictions to the minutest details, by the discovery of

Eka-boron	Scandium	(Nilson, 1875)
Eka-aluminium	Gallium	(Lecoq de Boisbaudran, 1879)
Eka-silicon	Germanium	(Winkler, 1886)

convinced men of science that the periodic law was a useful generalization, accounting for the relationships of the elements. It stimulated further investigations, but whereas Mendeléef had given full details concerning properties to be expected of the three elements cited above, his other prognostications were less specific. To the missing elements in group VII he gave the provisional names eka-manganese and dvi-manganese, but no detailed predictions of the properties to be expected of these elements. He merely assumed that they would resemble manganese in general properties.

Among the claims to the discovery of alleged elements that might conceivably have corresponded with eka-manganese are

Davyum	at.wt. 100	(Kern, 1877)
Ilmenium	at.wt. 104.6	(Hermann, 1846)
Lucium	at.wt. 100	(Barrière, 1896)
Nipponium	at.wt. 100	(Ogawa, 1908)

whilst possible precursors of dvi-manganese (rhenium) are

Uralium	at.wt. 187	(Guyard, 1869)
Pluranium	—	(Osann, 1828)
'Ruthenium'	—	(Osann, 1828)

It is interesting to note the davyum showed a thiocyanate (sulphocyanide) reaction identical with the one now used for rhenium. Rang(1), in a Periodic Table issued in 1895, placed davyum in the space for eka-manganese and uralium in that for dvi-manganese.

No new element appears to have been suspected or detected in manganese minerals prior to 1925, but both platinum ores and columbite (Noddacks's original sources of rhenium and masurium) have been fertile fields for alleged discoveries of new elements. In platinum ores Osann(2) claimed to have found three new ones, pluranium, polinium and ruthenium (not identical with the recognized ruthenium discovered by Claus in 1845). Osann later admitted that polinium was impure iridium and that 'pluranium oxide' was probably a mixture of the oxides of titanium, zirconium and silicon. His ruthenium, however, gave volatile reddish prisms which Berzelius pronounced to be new. Such a red body might have been impure rhenium trioxide, although in 1926 Zvjaginstsev(3) and other Russian workers recently re-examined platinum minerals and concluded that there could be no new element there, contrary to the claim of the Noddacks. It was Claus who, in the middle of last century, established the existence of the six recognized platinum metals, and since then no discovery of any new element in platinum ores has been substantiated. Several chemists have, however, found what they believed to be evidence of the presence of new bodies in platinum minerals. The most significant of these are uralium, announced by Guyard(4) in 1869, and davyum, claimed by Kern(5) from platinum residues. The stated density (20.25) and atomic weight (187) of uralium (or ouralium as it was sometimes transcribed from Russian) are almost identical with those of rhenium, but its malleability, ductility and its general resemblance to platinum in chemical properties indicate that it could not have been rhenium. Rose's pelopium(6) from Bavarian tantalite might likewise have been one of the congeners of manganese, but the so-called pelopic acid was subsequently regarded as impure niobic acid, and the claim that a new element had been found was dropped.

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Of more significance was ilmenium, an element said to occur in ilmenite by Hermann(7). It was stated to have an atomic weight of 104.6. The density of the red-brown oxide, to which the formula TiO_2 was assigned, was 3.95–4.20, and it gave a characteristic red colour with potassium ferrocyanide. Salts of ilmenous and ilmenic acids, a white chloride and some double chlorides were also described. In the *Bulletin* of the Société Impériale de Moscou for 1872 Hermann gave a further account of the isolation of tantalum, niobium and ilmenium from columbite by fractional crystallization of the double potassium fluorides and sodium salts. He claimed to have isolated the metal by heating its double fluoride with metallic potassium. The black powder so obtained readily ignited in air, on warming, to give a pentoxide. Five years later(8) he brought forward a mass of evidence (dry tests, analyses, preparations, etc.) to show the elementary nature of ilmenium and to refute the criticisms of Marignac and others. Its isolation as a black powder that readily ignited in air would be consistent with the behaviour of rhenium. Little attention appears to have been given to Hermann's claims which he probably weakened by announcing another new element, neptunium (not to be confused with the artificially prepared element of atomic number 93), which he said was present in a columbite from Haddam, Connecticut.

The alleged rare earth element, lucium, patented by Barrière(9) might have corresponded with eka-manganese, but it was shown by Crookes(10) and by Shapleigh(11) to be impure yttrium, although it was accepted as a distinct element by several contemporary French savants.

The announcement in 1908 by Ogawa(12) that he had found a new body, nipponium, in thorianite, molybdenite and reinite, with an atomic weight of 100, again suggested that the eka-manganese gap had been at last filled. The reported chemical properties of nipponium accorded with those expected for a congener of manganese. Thus, it formed both acidic and basic oxides and an anhydrous chloride which gave a green solution and a green body on fusion with alkalis. About the same time Miss Evans(13) obtained what were thought to be indications of a new

element in thorianite, and it was thought that this one was identical with nipponium. The claims for a new element did not, however, commend themselves to contemporary men of science, although Skrobal and Artmann concluded (14) from its reactions that it must be a new substance. The suggestion was also made that Boucher's 'new element' in cast iron (15) and one claimed by Ruddock in certain steels (16) might also be identical with Ogawa's nipponium. The reactions given by Boucher correspond in part with those for rhenium, but at the time it was considered (17) that they could largely be accounted for by the presence of molybdenum.

From the foregoing it will be observed that among the unrecognized elements there are several possible precursors of masurium, but only the very doubtful uralium and the still more improbable pluranium are possible precursors of rhenium. Renewed impetus was given to the search for the missing elements after Moseley had discovered that each element could be assigned an atomic number calculated from the frequency of the main X-ray spectral lines, since the square root of the frequency of vibration of the X-rays is proportional to the nuclear charge and therefore to the atomic number (18).

HISTORY OF RHENIUM

The discovery of dvi-manganese was first claimed by Noddack, Tacke and Berg in June 1925 (19). This was followed a few months later by the announcements of Druce and Loring (20) and of Heyrovský and Dolejšek (21).

From theoretical reasoning the German investigators argued that platinum ores and also certain minerals, notably columbite, should contain the missing congeners of manganese. They estimated that these elements would be present in native platinum to the extent of 10^{-3} to 10^{-4} and in columbite to the extent of 10^{-5} to 10^{-6} . From these sources they obtained a 'residue' containing 0.5% of eka-manganese and 5% of dvi-manganese. They named the new elements masurium and rhenium after the east and west German provinces of Masurenland and Rheinland, and

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supposed that there was about 10^{-13} part of eka-manganese and 10^{-12} part of dvi-manganese in the earth's crust, compared with 7×10^{-12} part of manganese and 10^{-2} part of iron.

Their claims to the discovery of these elements did not pass unchallenged, and for some time other investigators retained Mendeléeef's provisional names. Whether the early criticisms of the work of I. and W. Noddack (Fräulein Ida Tacke married Dr Walter Noddack in 1926) are eventually substantiated or not, quantities of the element of atomic number 75 have since been isolated and the name rhenium has become the recognized one for this element.

Simultaneously, Loring and Druce were examining pyrolusite and crude manganese compounds for indications of the existence of an element beyond uranium and having an atomic number 93. In the course of this work (22) it was found that these sources contained traces of a new element which was identified as dvi-manganese. It was characterized by some chemical tests (formation of a sodium salt, precipitates with ferro- and ferricyanides, green spectral lines on a platinum wire flame test and a fugitive higher chloride) and by X-ray analysis (23). The results of the X-ray analysis were confirmed later by Prof. Manne Siegbahn (24) who made a spectroscopical examination of the original preparations and found lines characteristic for an element of atomic number 75 as Loring had previously announced (20).

The line $\lambda = 1.43$ (1.4298) corresponded with L_{α_1} of element 75			
= 1.4408	„	„ L_{α_2}	„
= 1.2358	„	„ L_{β_1}	„
= 1.204	„	„ L_{β_2}	„

Heyrovský and Dolejšek also showed the presence of dvi-manganese in commercial (and even 'pure') manganese salts. They detected the new element during investigations on the electrolytic deposition potentials of manganese salt solutions using Heyrovský's newly introduced polarographic dropping mercury cathode method. The presence of one part of the new element in 20,000 parts of the preparations was corroborated spectroscopically and a re-examination of both sets of prepara-

tions from manganese sources confirmed previous announcements(25). Later, however, Heyrovský has stated(26) that his polarographic results with bivalent manganese compounds may not have been conclusive.

In 1926, W. Prandtl(27) criticized all claims to the discovery of a new element. In particular he denied the occurrence of dvi-manganese in columbite, a mineral with which he had had considerable experience. Again, as stated above, some Russian men of science (Zvjaginstsev and Seljakov and Korsunski) were also unable to detect the presence of dvi-manganese in native platinum, and they estimated that it could not be present in amounts exceeding 0.0003 % (3). Since they made this announcement no reference has been made to the occurrence of rhenium in platinum minerals. Both columbite and platinum ores have been abandoned by the German investigators as sources of rhenium, which is now extracted from molybdenum glance, a source indicated by Loring(28), and was obtained in considerable quantity from an unspecified industrial sulphide residue by a process introduced by Feit(29). Should a great demand for columbite in making certain stainless steels again arise there might be an accumulation of residues that could be examined further to ascertain the presence (or absence) of rhenium in this mineral.

Whilst defending themselves against the criticisms of their own work, W. and I. Noddack(30) joined with Prandtl in his criticisms of other work. They cited that of Hartley and Ramage(31) and of Bosanquet and Keeley(32), in which these investigators stated that they were unable to find any congener of manganese in pyrolusite by spectroscopic methods. They considered that manganese minerals are among the poorest sources of rhenium. Loring(33), however, directed attention to the weakness of their own spectroscopic evidence and indicated the precautions taken in his work. Actually he obtained the X-ray spectral lines of rhenium with a sample (Kahlbaum's) of commercial manganese phosphate(34).

The original method of I. and W. Noddack for isolating crude eka- and dvi-manganese from platinum ores consisted in treating the mineral with *aqua regia*, evaporating the solution and igniting

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the residue, which was then reduced in hydrogen. The part insoluble in *aqua regia* was heated in a stream of chlorine and the chloride reduced with zinc. The two products were together heated alternately in hydrogen and oxygen and gave sublimes of the oxides of osmium, ruthenium and arsenic, together with a new body, darkened by hydrogen sulphide. In the case of columbite this was first fused with sodium hydroxide and nitrate to remove the bulk of the iron, niobium and tantalum, and the filtrate was treated repeatedly with hydrogen sulphide in both alkaline and acid solution. The redissolved sulphide solutions were concentrated to small bulk and precipitated with mercurous nitrate. The combined precipitates were reduced and the final product, on X-ray examination, was stated to show the presence of both congeners of manganese.

In the process outlined by their patent (35) I. and W. Noddack simplified the procedure somewhat. In this patent it is stated that molybdenum minerals form suitable raw materials for the extraction of rhenium. The mineral containing this element is dissolved as far as possible in nitric acid and molybdenum removed by addition of phosphoric acid and ammonium nitrate. The rhenium (together with other elements) is then precipitated with hydrogen sulphide. The sulphide precipitate is converted into crude oxide, and by repeating the process and finally by fractional sublimation, a product rich in rhenium was obtained.

In directing attention to the difficulties met with in preparing pure manganese chloride from residues left after making chlorine from pyrolusite, W. Smith (36) stated in 1924 that, in quantitative experiments, some 0.04 % of material was unaccounted for. This suggested a possible source for the manganese congeners. The first method adopted for extracting dvi-manganese (rhenium) from the manganese salts of commerce was as follows:

Quantities of 100 g. of crude manganese sulphate or chloride were dissolved in about 600 c.c. of water together with 50 g. of ammonium chloride and 25 c.c. of 0.880 ammonia. Hydrogen sulphide was passed through the solution until it was saturated with the gas. After standing, the precipitate was filtered off. It should have contained any iron sulphide and aluminium and

chromium hydroxides if these metals were present in the original salt, together with manganese sulphide. The filtrate was re-treated with hydrogen sulphide until no further precipitation occurred. Filtrate and washings were allowed to stand for several days whilst still alkaline and saturated with hydrogen sulphide to make sure that as much manganese as possible had been removed. The final filtrate was afterwards boiled for some minutes to expel excess of hydrogen sulphide and some ammonia. It was neutralized with hydrochloric acid and evaporated to dryness and the residue was heated to drive off ammonium compounds and to remove any sulphur set free during the treatment. The residue was dissolved in dilute acetic acid, and a slight excess of ammonium oxalate was added to precipitate the calcium present. The filtrate from the calcium oxalate precipitate was evaporated to dryness and again heated to drive off ammonium salts. The 75 mg. of residue so obtained from 400 g. of manganese sulphate contained about 1% of dvi-manganese according to estimates made at the time. No further enrichment could be achieved by repeating the process with accumulated preparations.

The extraction and concentration of the new element from pyrolusite (which contains very little of element of atomic number 75) by these methods proved slow and unsatisfactory. It was ascertained that the dvi-manganese formed a volatile compound which was evolved in the excess of chlorine when pyrolusite was acted upon by hydrochloric acid alone(37). The chlorine containing traces of dvi-manganese compounds was either (a) absorbed by alkalis, (b) precipitated with barium hydroxide, or (c) acted upon by metallic zinc which readily converted it into crude hydrated rhenium hydroxide. The products from (c) and (b) were readily converted into rhenium heptoxide by heating in a stream of oxygen. From solutions of (a) it was possible to crystallize out some potassium perrhenate.

Still another method consisted in heating the pyrolusite or other source of dvi-manganese with concentrated nitric acid and then working up the solution which contained perrhenic acid. By the last two methods sufficient quantities of the new element

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were obtained to enable some of its properties and reactions to be investigated and some of its compounds to be prepared and studied.

After Heyrovský had detected rhenium in 'pure' manganese sulphate by means of his dropping mercury cathode, he separated a product rich in the new element by dipping strips of platinum and zinc into concentrated manganese sulphate solutions. The X-ray spectrum of this product gave at least three clear lines characteristic of the element of atomic number 75. The lines Dolejšek observed were

$$L_{\alpha_1}, 1.430; \quad L_{\beta_1}, 1.233; \quad L_{\beta_2}, 1.2043; \quad \text{and} \quad L_{\gamma_1}, 1.059.$$

Later Heyrovský and Dolejšek showed (38) that the new element accumulated in manganese amalgam when this and platinum foil were placed in concentrated manganese sulphate solution. They have also had what might be indications of the presence of ekamanganese in some of the enrichment products.

The technical preparation of rhenium from waste sulphide slime in an unspecified metallurgical process was worked out by Feit (29) in 1930. The weathered slime was extracted with water to give a brown-green solution containing chiefly copper and nickel. By regulated addition of amounts of ammonia most of the copper and nickel and some zinc were separated as double sulphates. Further additions of ammonia to the thick black mother liquor yielded dark crystals of the ammonium salts of molybdic, vanadic and phosphoric acids and their complexes. The pale yellow filtrate yielded crystals of crude potassium perrhenate on addition of potassium chloride in excess.

The impure grey product was washed with cold water, dissolved in hot dilute sodium hydroxide, filtered and cooled to deposit purer potassium perrhenate, and two more recrystallizations gave a pure product.

Prof. E. S. Kronman (39) and his colleagues at the Moscow Rare Metals Institute have extracted rhenium compounds (equivalent to about 5 mg. of rhenium per kg. of material) from Russian and Japanese molybdenum glance. With this product they were able to make several important researches, especially on the microchemical reactions of rhenium.

In extracting rhenium from molybdenum glance the mineral was treated with nitric acid and then with sulphuric acid. The rhenium was distilled off in the volatile fraction either with a current of air at 300° C. for 3 hr. or equally well in a stream of hydrochloric acid gas at 200° C.

According to Driggs(40) when ores or concentrates containing rhenium are strongly heated with sodium bisulphate and nitrate, rhenium heptoxide volatilizes. It is purified by conversion into the sulphide (with arsenic sulphide). This, on reduction with hydrogen and heated to about 1000° C. to drive off arsenic, leaves rhenium alone.

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