THE ISOLATION OF ELEMENT 43 AND SOME OBSERVATIONS ON ITS CHEMICAL BEHAVIOR

G. E. Boyd, Q. V. Larson and E. B. Motta
Oak Ridge National Laboratory
Oak Ridge, Tenn.

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Introduction

Interest in the chemistry of the apparently missing elements in Nature has been renewed during the past decade as a consequence of the recent striking development of nuclear transmutation techniques. This has been the case particularly for element 43, or eka-manganese, whose discovery was heralded in 1925, but whose chemical properties remained unreported until the radiochemical investigations of Perrier and Segre.

The importance of element 43 to systematic inorganic chemistry is revealed by even a casual examination of the Mendeleff periodic arrangement of the elements. Until recently the chemistry of only two members, namely manganese and rhenium, of Group VII A was known. Further, since element 43 is a member of the transition group starting with Y and proceeding through Pd, the relation of its chemistry to Mo and Ru is of relevance. In fact, a continuing source of interest in the conduct of this work was in the testing of the predictions of chemical behavior of element 43 based on the generalizations of the periodic table. A practical value of the added chemical information was also its value to the initiation and conduct of an exhaustive search for the element in Nature.

As is well known, the occurrence of 43 in Nature has been reported by the Noddacks who have claimed the discovery of the element. In view of the incontestable discovery of element 75, rhenium, by these workers, and of the significant lack of published data on its chemistry one can only speculate as to the validity of their assertions. The characteristic X-ray emission spectrum as observed by Berg and I. Noddack is in substantial agreement with the recently reported measurements of Burkhardt, Reed and Saunders,
although Prandtl has criticized the earlier work on the basis that the presence of higher order spectrallines from heavy element impurities were not excluded.

As a matter of fact, however, nothing of the chemistry of the element was known until the researches of Perrier and Segre about ten years ago in which extremely small amounts of the element isolated from deuteron bombarded molybdenum were employed. In a number of interesting qualitative experiments it was shown that the chemistry of the element at these low concentrations resembled that of rhenium more closely than that of Mn, a result to be expected on the basis of the periodic table. As was recognized by these workers, the chemical behavior at very low concentrations might well be different than for weighable amounts and the experience of recent years has given support to this view. It is now appreciated that interferences due to adsorption, hydrolysis, complex ion formation with impurities, etc., frequently do occur. Further, owing to the extreme dilution, reaction rates may be slowed and further the oxidation potentials may be shifted appreciably.

Production of 43 by Neutron Irradiation of Ruthenium and Molybdenum

In early 1946 the possibility of producing tangible quantities of element 43 by means of nuclear transmutation reactions using neutrons from the chain reacting pile seemed to offer an opportunity for the production of small, yet weighable quantities of the element. Our first bombardments were made with Ru hydroxide. This work, although it did not lead to a satisfactory nuclear chemical synthesis of the element owing to the surprisingly low neutron capture cross-section of the light Ru isotope, did result in our being able to confirm that the 90 day 43 radioactivity of Perrier, Caccioquotti and Segre was indeed correctly ascribed to element 43 and further we were able to assign this radio-isotope to mass 97. In addition to the low
nuclear chemical yield obtained in the neutron irradiation of Mo, the use of this element gave another equally serious advantage owing to the simultaneous formation of a long lived 12 d ruthenium isotope which on decay emitted intensely penetrating gamma radiation. Owing to this, it was necessary to carry out isolation procedures with extensive shielding and by means of cumbersome remote control manipulators.

A second possible target material for the synthesis of 43 was molybdenum metal. The possibility of using this element was based upon the observation of Seaborg and Segre in 1939 that the six hour activity produced in the deuteron bombardment of Mo was the excited (isomeric) state of 43\(^{99}\), and that the ground state possessed a half-life of at least 15 y. Subsequently, Glendenin in an unsuccessful search for this isotope amongst the uranium fission products was able to conclude that the decay period was at least 3000 y. Reference to a section of the chart of the nuclides will make clearer the possibility of the production of element 43 by the pile irradiation of molybdenum metal. (Figure 1: Chart of Nuclides in Rh to Zr region)

Neutron capture by the Mo isotope of mass 98, present in naturally occurring molybdenum to the extent of 28.4\%, gives rise to the 67 h Mo\(^{99}\) which in turn decays partly (10\%) to the 6.0 h excited isomeric state of 43\(^{99}\) and partly (90\%) to the long-lived ground state.

At radioactive equilibrium, the rate of production of element 43 activity may be computed from the following equation:

\[
d\frac{dN_{43}}{dt} = \bar{\nu} \sigma_{act} N_{Mo99} - \lambda N_{43}^{99}
\]

where \(\bar{\nu}\) is the thermal flux of neutrons \((a/cm^2/sec)\); \(\sigma_{act}\), the activation cross-section \((cm^2/atom)\) for Mo\(^{99}\); \(N_{Mo99}\), the number of target Mo\(^{99}\) atoms; and, \(t\), the time in seconds.
Since the second term on the right hand side of Equation (1) is negligible relative to the first (i.e. the rate of decay of the Te^{99} is negligible relative to its rate of formation), the number of Te^{99} atoms formed after a total radiation time, t, is given by:

$$N_{Te^{99}} = \frac{\nu \sigma_{ac} N_{Mo} t}{4}$$  \hspace{1cm} (2)

To illustrate the quantities produced, let us consider our most recent "production" irradiation: In this instance, 5700 g. of the purest Mo metal powder obtainable was irradiated for one year by an average neutron flux of $1.2 \times 10^{12}$ n/cm$^2$/sec. The value of $\sigma_{ac}$ of 0.42 x $10^{-24}$ cm$^2$/atom may be used. Substituting these quantities into Equation (2), a value of $1.06 \times 10^{20}$ atoms is obtained for $N_{Te^{99}}$. This number corresponds then to 17.5 mg. of Te^{99} which has been formed in 5.7 kg. of Mo.

Thus, the problem of the isolation is the problem of separating 2.5 p.p.m. of element 43 from Mo metal.

Analytical Procedures

In order to monitor the steps in the extraction and isolation of 43 from its molybdenum matrix it was first necessary to develop analytical procedures which would allow a determination of the efficiency of each step in the operation as well as supply information as to the losses being suffered. For this purpose it is useful to have a variety of carrying agents which will bring down this element when they are precipitated from aqueous solutions. In addition, it is desirable to know at what acidities the co-precipitation is quantitative as well as how much of the carrying agent should be precipitated to effectively collect the 43. Since certain studies to be described shortly had indicated that the separation of element 43 from Mo could be accomplished by distillation with concentrated $\text{H}_2\text{SO}_4$, the co-precipi-
tation, experiments were done mainly with H$_2$SO$_4$ solutions of the element. The $^{60}$Co was used as tracer.

Co-precipitation studies with Re$_2$O$_7$ showed 100% carrying from 3.5 up to 11.5 M solutions of H$_2$SO$_4$. Further, quantitative collection of the 43 could be obtained with as little as 1 mg per 100 ml.

Studies with PtS$_2$ similarly showed 100% carrying over the even wider range of 0.25 to 11.0 M H$_2$SO$_4$. Quantitative collection of the 43 could be obtained with as little as 1 mg per 100 ml.

Studies with other acid insoluble sulfides have shown good co-precipitation, viz: As$_2$S$_3$, CdS, CuS, etc.

Co-precipitation by means of two additional rhenium insoluble compounds, tetraphenyl arsonium perrhenate and nitron perrhenate (diphenyl-endu-anilo-hydro-triazole) was studied. The former worked best at pH = 7 and with 1 mg per 10 ml at 25° and 1 mg per 200 ml at 0°C. The use of nitron perrhenate was limited owing to the formation of insoluble nitron sulfate compounds. Precipitation was possible only from neutral or faintly acid solutions of low anion content.

The analytical procedure devised from these studies accordingly consisted in the precipitation of 2 mg of Pt (as PtS$_2$) from 4 M H$_2$SO$_4$ solution after a preliminary treatment with a few drops of Br-water to remove any reducing substances present in the acid as well as to insure the oxidation of the 43 to an oxidation state yielding an acid insoluble sulfide. After 30 min. digestion at 90°C, the precipitate was filtered, mounted and counted at 30% geometry with a bell-type mica end-window G.M. tube.

The Isolation of Element 43

Separation of 43 from Mo. The earlier work of Perrier and Segre described one separation procedure based on the dissolution of the molybdenum in aqua regia, or in alkaline peroxide, followed by its precipitation with
8-hydroxy-quinoline and then, after acidification, precipitation of the
43 with rhenium sulfide. Alternatively, a separation based on ether ex-
traction of the 43 from HCl and KSCN solutions after oxidizing the 43
with Cl₂ was suggested.

Neither of these methods seemed appropriate, however, for the
problem of processing kilogram amounts of molybdenum metal powder for it
appeared that large volumes of liquid would be involved thereby requiring
time consuming filtration and/or batch extraction and evaporation procedures.
Fortunately, in connection with our earlier work on the production of 43 in
ruthenium, an efficient wet volatility method had been tested. Here, follow-
ing the pioneering general studies of Hoffman and Lundell and some pre-
liminary experiments of Glendenin, it was demonstrated that a quantitative
separation and recovery of very small amounts of 43 formed by neutron
irradiation in ruthenium could be effected by distillation of the ruthenium
with concentrated H₂SO₄. Accordingly, preliminary experiments were performed
in which an amount of H₂SO₄ was added to a 15 g. quantity of irradiated No
powder sufficient to dissolve it completely and to give a clear solution.
The excess acid was then distilled away to almost dryness, and upon cooling
a second fresh volume of acid was added and the distillation repeated. Sub-
sequently, a third volume of concentrated acid was added and distilled until
dry molybdc anhydride remained as a residue in the still-pot. The data
presented in Table I shows that over 90% recovery may be achieved by two dis-
tillations:
Table I  
Separation of Element 43 from Molybdenum by Distillation with Concentrated Sulfuric Acid

<table>
<thead>
<tr>
<th>Distillation Number</th>
<th>Volume of 18M H₂SO₄ Distilled</th>
<th>c/a in Analysis</th>
<th>c/a in Duplicate Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>190</td>
<td>2440</td>
<td>2320</td>
</tr>
<tr>
<td>2</td>
<td>195</td>
<td>240</td>
<td>235</td>
</tr>
<tr>
<td>3</td>
<td>180</td>
<td>30</td>
<td>33</td>
</tr>
</tbody>
</table>

It would seem that two distillations will remove almost all the 43 under these conditions. Evidently, about 90% comes over in the first distillation.

The 5.7 kg. of neutron irradiated W metal powder was worked up in approximately 190 g aliquots giving two approximately 1600 ml volumes of H₂SO₄ distillate containing roughly 0.3 mg. of element 43.

Subsequent steps required a concentration and purification to effect the isolation of 43 in pure state.

An excellent volume reduction was affected by dilution of the concentrated H₂SO₄ distillate to 4 M followed by Br₂ oxidation and precipitation of PtS₂ (1 mg per 200 ml), which, after dissolution in ammonia and 30% H₂O₂ resulted in the 43 being present in a 50 ml volume compared a starting volume of 1600 ml. The ammoniacal 43-containing solution was carefully evaporated to dryness taking care that it remained alkaline by the repeated addition of ammonia. The residue was then taken up in 25 ml of concentrated H₂SO₄, placed in a distilling flask and the 43 separated from the bulk Pt and (NH₄)₂SO₄ by distillation.

Separation of 43 and Re. Throughout the foregoing steps the Re impurity originally present in the W to the extent of a few p.p.m. was also
carried along so that the next step in the isolation (before the formation of a pure compound of 43) required its removal. In many respects, the separation of Re and 43 constituted the most difficult task in the isolation. Already Perrier and Segre had reported that a separation could be made with moist HCl at 100°C when both Re and 43 were contained in concentrated H2SO4. In this case, the Re was completely volatilized along with a small amount of 43. This experiment was considered sufficiently important that it was repeated using radioactive Re and 43 with the results given in Table II.

Table II

<table>
<thead>
<tr>
<th>Element</th>
<th>Activity Contained Initially in 50 ml of 18 M H2SO4 c/m</th>
<th>Fraction in 16 M H2SO4 after Distillation of 100 ml of 12 M HCl</th>
<th>Fraction in HCl Distillate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re</td>
<td>10,671</td>
<td>6%</td>
<td>76%</td>
</tr>
<tr>
<td>Tc</td>
<td>10,520</td>
<td>81</td>
<td>3</td>
</tr>
</tbody>
</table>

Although these data substantiated the earlier findings, and showed that Tc in contrast to Re does not form a volatile chloride, for various reasons the method was not considered suitable for the purification.

Alternatively, a separation of 43 and Re by fractional precipitation from concentrated HCl solutions was investigated. The data from this study are presented by Figure 2 from which it may be seen that above 8M HCl virtually no 43 is carried by PtS2 whereas the Re is removed quantitatively even up to nearly 12M. These observations have proved most useful in the purification.

Yet another purification method based on exchange adsorption has proved of value. In this, columns of anion exchanger were employed and 1M HCl was used as an eluting agent with the results given in Figure 3 which
show that the Re moves down the bed at a velocity greater than does the 43 and that an extremely good separation can be realised.

After purification, the preparation of the element was accomplished by means of electrodeposition. It was not possible to check Segre's observation that the element could be deposited on platinum, although firmly adherent layers were formed on polished Cu cathodes. The data brought together in Tables III and IV summarise the studies made in connection with the electrodeposition studies.

Table III
Factors in the Electrodeposition of Element 43

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Time (min)</th>
<th>pH</th>
<th>HEPF 2 (M)</th>
<th>Fraction Electrodeposited (%)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>120</td>
<td>1.2</td>
<td>0</td>
<td>30.6</td>
<td>Bright Re deposit</td>
</tr>
<tr>
<td>2</td>
<td>120</td>
<td>1.2</td>
<td>0</td>
<td>45.9</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>120</td>
<td>1.2</td>
<td>2x10^-3</td>
<td>76.6</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>120</td>
<td>5.5</td>
<td>0</td>
<td>84.7</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>120</td>
<td>5.5</td>
<td>2x10^-3</td>
<td>91.3</td>
<td>Black Re deposit</td>
</tr>
<tr>
<td>6</td>
<td>120</td>
<td>10.5</td>
<td>0</td>
<td>~3.1</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>120</td>
<td>10.5</td>
<td>2x10^-3</td>
<td>21.1</td>
<td></td>
</tr>
</tbody>
</table>

Table IV
The Electrodeposition of Element 43

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Fraction Electrodeposited (%)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>91.3</td>
<td>One ag Re present</td>
</tr>
<tr>
<td>6</td>
<td>87.5</td>
<td>One ag Re present</td>
</tr>
<tr>
<td>9</td>
<td>89.8</td>
<td>No Re present (except as impurity)</td>
</tr>
<tr>
<td>10</td>
<td>20.0</td>
<td>No Re present (Pt cathode)</td>
</tr>
<tr>
<td>11</td>
<td>87.3</td>
<td>No Re present</td>
</tr>
</tbody>
</table>
Characterization of the Element

Half-life, Radiations and Isotopic Mass. To characterize the radio-active isotope of element 43 which made possible the isolation of the element, three items of information were needed: the half-life, the nature of the radiations emitted, and the isotopic mass. The half-life was determined in a specific activity measurement in which a 100 µg sample of 43, exhaustively freed of Re by fraction on an ion-exchange column, was electrodeposited on a weighed Cu disc which was then counted. A direct comparison with a Co sample of known disintegration rate similarly electrodeposited on a Cu backing and counted identically to the 43 allowed the disintegration rate to be determined by the equation:

\[-dN_e/dt = \lambda N_e\]

the values of the transformation const. \(\lambda\) and hence the half-life may be computed. A half-life of \(9.4 \times 10^5\) y was thus determined. The nature of the radiations emitted may be illustrated by the data plotted in Figure 4, which shows the reduction in counting rate caused by increasing thickness of Al absorbers. This curve reveals a 7.2 mg half-thickness and gave a Feuett range of 85 mg corresponding to 320 KeV beta rays. No gamma radiation was detectable.

A sample of 43 electrodeposited on Cu served for the mass identification in a 60° Micr type mass spectrograph. The expected mass of 99 was found.

Optical Line Spectrum. Further characterization of the element was accomplished by a determination of its optical spark spectrum, a region of which is shown in Figure 5. The spectrographer at the Oak Ridge National Laboratory has reported that the line at 4031.3A is sensitive to \(<1.0 \mu g\) whereas the lines at 4271.2, 4261.9, 4095.3, 4088.4 and 3237.0A are sensitive...
to 1.0 μg. These lines are free from Re interference and can be used in the identification of 43. Spectrochemical analyses have been employed frequently in our studies to determine the purity of our 43 preparations in various phases of the isolation procedure.

**Absorption Spectrum.** An optical absorption spectrum taken with a Beckman spectrophotometer of a 10⁻⁴ M solution of the element in concentrated H₂SO₄ is shown in Figure 6. This solution was characterised by a bright purple coloration. Addition of concentrated H₂O₂ to this mixture produced a bright yellow-orange coloration whose spectrum is shown in Figure 6 also.

**Chemical Studies**

**Net Volatility.** As was evident in the isolation of the element, the volatile compounds of element 43 play an important part in its chemistry. Accordingly, a number of separate studies in which a comparison of the volatility of 43 and Re was made were performed. These experiments, as well as those to be described later, were deliberatively comparative. The working principle was always to compare the element with Re since there was already ample evidence of a close similarity between the two. One advantage in thus using Re as a 'stand-in' was that an internal monitor of each experiment was thus always present.

First, a series of distillations with concentrated H₂SO₄ were performed, the results from which are shown in Figure 7. Good indication that 43 is not readily oxidised to its volatile state by hot, concentrated H₂SO₄ may be seen in the delay in its appearance in the distillate relative to Re. The presence of a small amount of H₂O₂ to the acid, however, oxidises the element, and the inherently greater volatility of the higher oxide of 43 than Re is evidenced.
A comparative distillation of Re and 43 with concentrated HClO₄ is shown likewise in Figure 7, where it is seen that the 43 comes over in the first fraction, whereas the Re does not appear until the very end. Evidently, two factors are involved: oxidation potential and temperature.

A co-distillation of 43 and Re from concentrated HCl caused less than 1% of the To to appear in the distillate whereas a total of 15% of the Re appeared in the last three fractions of HCl condensed. Since as we have seen the Re may be completely volatilised by HCl from concentrated H₂SO₄ at 200°C, the apparent reason for the failure of the Re to distill in this experiment must be the lower temperature employed.

Solvent Extraction. Two types of solvent extractions were conducted. First, extractions were attempted using hexane together with small amounts of diphenyl thiourea. If 43 behaved analogously to Ru(III), a good partition into the organic phase from 1 M H₂SO₄ solution should have been observed. In actuality, only 15% of the 43 was found in the hexane, independently of whether or not the diphenyl thiourea was present. Rhenium gave a slightly better transfer to the organic phase - approximately 40% was observed to go into the hexane, whereas with diphenyl thiourea this was increased to 60%.

It has been known for some time that Re may be extracted into ether from 3 M HCl solutions containing KSCN after reduction of the upper oxidation state by Sn(II). Table V shows the results taken in a series of extractions with several reducing agents.

Table V

<table>
<thead>
<tr>
<th>Element</th>
<th>Fraction in Ether Phase (1:1 Volume ratio)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No Reducing Agent</td>
</tr>
<tr>
<td>43</td>
<td>23%</td>
</tr>
<tr>
<td>Re</td>
<td>0.5%</td>
</tr>
</tbody>
</table>
These experiments reveal that an ether extractable hexavalent state exists, and further that it was more readily formed by mild reducing agents than was Re(VI). Interestingly, a similar yellow-brown coloration to that characteristic of ReO(6CH)₄ was observed also for the 43.

It was observed that a re-extraction of the 43 from the ether phase could be accomplished by shaking with ammoniacal hydrogen peroxide solutions.

Oxidation–Reduction. Several additional experiments were conducted which gave information about the various oxidation states of 43 in addition to the above described studies on volatility and solvent extraction. In agreement with Perrier and Segre, it was found when Ru was reduced by alcohol or formaldeyde, no 43 was carried down, showing the element to be more electronegative than the noble metals. On the other hand, treatment of acid solutions with amalgamated zinc powder caused the 43 to be separated from solution. Reduction of MnO₄⁻ to MnO₂ either in acid or in alkaline solution in the presence of 43 did not cause any losses of 43 upon the separation of MnO₂.

Exchange Adsorption. First indication that the ionic forms of element 43 present in acid aqueous solutions were probably variable was obtained in preliminary determinations of the exchange adsorption using both cationic and anionic exchange types. As was expected, the 43 showed a good anion exchange adsorption, as is revealed in Table VI where a distinct difference from perhenate may be seen.
Experiments were conducted next with a cation-exchanger to see if cationic forms were present. Actually, an uptake of Tc was found, suggesting this to be true for acid solutions. An attempt to prove the exchange reversible, however, was unsuccessful and required the postulation of non-ionic (or colloidal) Tc to be present as well. Thus, 1-2M H$_2$SO$_4$ solutions appeared to have not only anionic and cationic $^{43}$ ions, but radiocolloidal $^{43}$ as well.

**Migration Experiments.** A series of migration studies were undertaken in order to obtain further information concerning the nature of the ionic species of element $^{43}$ in aqueous solutions of varying composition. Colloidal membranes were employed in an experimental arrangement shown in Figure 8. In the first experiments, Re and $^{43}$ were present in 2 M NH$_4$OH, and, after the electrodialysis had been allowed to proceed for 17 h, it was found that both elements had passed completely from the middle compartment into the anode (+) cell compartment indicating the existence of only anionic species, as was anticipated.

Subsequently a series of migration experiments were carried out in which the two elements were present in the 4 M H$_2$SO$_4$ solutions with the results indicated by Table VII.

### Table VI

Exchange Adsorption of $^{43}$ and Re from 0.1 N HCl Acid Solutions by Amberlite IR-1

<table>
<thead>
<tr>
<th>Weight of Exchanger (gm)</th>
<th>V/m</th>
<th>$^{43}$ Adsorbed</th>
<th>$^{87}$ Re Adsorbed</th>
<th>$K_d$ for $^{87}$ Re</th>
<th>$K_d$ for $^{43}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>10$^4$</td>
<td>25</td>
<td>5</td>
<td>(3300)</td>
<td>590</td>
</tr>
<tr>
<td>0.05</td>
<td>2x10$^3$</td>
<td>41.4</td>
<td>25</td>
<td>1400</td>
<td>660</td>
</tr>
<tr>
<td>0.10</td>
<td>10$^3$</td>
<td>54.5</td>
<td>35</td>
<td>1200</td>
<td>540</td>
</tr>
<tr>
<td>0.30</td>
<td>3.3x10$^2$</td>
<td>75</td>
<td>65</td>
<td>1300</td>
<td>650</td>
</tr>
<tr>
<td>Av. = 1300 ± 100</td>
<td></td>
<td></td>
<td></td>
<td>590 ± 50</td>
<td></td>
</tr>
</tbody>
</table>
Table VII

Migration Studies with Re and 43 Ions in 4 N HgSO₄

<table>
<thead>
<tr>
<th>Element</th>
<th>Electro Dialysis Time</th>
<th>Fraction in Cathode (-) Compartment</th>
<th>Fraction in Center Compartment</th>
<th>Fraction in Anode (+) Compartment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re</td>
<td>17 h</td>
<td>23%</td>
<td>37%</td>
<td>30%</td>
</tr>
<tr>
<td>43</td>
<td>17 h</td>
<td>12%</td>
<td>64%</td>
<td>16%</td>
</tr>
<tr>
<td>Re</td>
<td>65 h</td>
<td>38%</td>
<td>38%</td>
<td>19%</td>
</tr>
<tr>
<td>43</td>
<td>65 h</td>
<td>38%</td>
<td>38%</td>
<td>19%</td>
</tr>
</tbody>
</table>

To exclude the possibility that electrode processes were responsible for this somewhat unexpected indication of both cationic and anionic species, another experiment was devised in which a continuous removal of liquid in the anode (+) compartment was effected. Electro dialysis for 64 h then gave 23% of the 43 in the cathode (-) compartment and 34% in the center. This result appears to confirm the presence of cationic species in strongly acid solutions, although the possibility of some formation at the anode cannot be rigorously excluded.

Summary

Evidence for Re(VII). The various co-precipitation reactions of 43 with Re afford good evidence for the formation of a fairly stable heptavalent state. Thus, 43 is carried down by Re₂S₇ and particularly by 6₄As₂Re₄, nitropon perhenate as well as by H₄ReO₄, Cs₂ReO₄ and Ti₂ReO₄. The observation that 43 concentrates in crystals of KReO₄ formed from aqueous solution shows that its compound is correspondingly less soluble.

A conclusive demonstration of the VII state of 43 has been given by S. Fried and W. H. Zachariasen who prepared the compound Ni₄TeO₄ and identified it by X-ray diffraction.
Evidence for Te(VI). The quantitative extraction of 43 into ether after reduction with Sn(II) and complex ion formation may be taken as an indication that the hexavalent compound, TeO(SCN)$_4$, was formed. The analogous rhenium compound ReO(SCN)$_4$ is well known.

Evidence for Te(V). The radiocolloidal behavior of 43 in acid solution may be analogous to the behavior of MnO$_2$. An X-ray diffraction of an electrodeposited of 43 indicates the phase TeO$_2$.

Compounds of Te. Te$_2$S$_7$: The brown, heptasulfide of 43 precipitates readily from 4 M H$_2$SO$_4$ solutions. As little as 3 mg/l can be precipitated by means of HgS.

NH$_4$TeO$_4$: a white crystalline compound.