

Some Chemical Properties of Element 43

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solution originally having the composition sodium chloride, 4 molal, and zinc sulfate, 2 molal. Finally curve 5 is for a 2 molal sodium chloride and $\frac{1}{2}$ molal zinc chloride solution. From

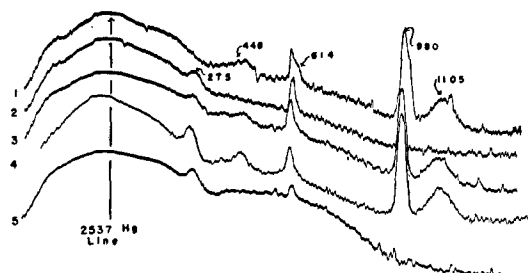


FIG. 2. Microphotometer tracings of the Raman spectra from zinc chloride and zinc sulfate solutions of the following compositions: curve 1, 1 molal zinc sulfate; curve 2, 1 molal zinc chloride; curve 3, 1 molal zinc sulfate 1 molal zinc chloride; curve 4, 4 molal sodium chloride 2 molal zinc sulfate; curve 5, $\frac{1}{2}$ molal zinc chloride 2 molal sodium chloride.

these last two curves it is apparent first that the sodium chloride reacts with some of the zinc sulfate to form zinc chloride but not with all of it. In other words, if the equilibrium were entirely in the direction of formation of zinc chloride and production of sodium sulfate, the line at $\Delta\bar{\nu}$ 275 in curve 4 should have at least twice the intensity it has in curve 3 if the degree of ionization in a 1 molal and 2 molal solution does not differ greatly. This is not quite realized. On the other hand, if there were equal interchange of all ions so as to produce a 2 molal sodium chloride and

1 molal zinc chloride solution, omitting the sulfates from consideration, the $\Delta\bar{\nu}$ 275 line in curve 4 should have approximately twice the intensity it has in curve 5. This also is not realized. Consequently one is led to the conclusion that the equilibrium in such mixtures is slightly in the direction toward the formation of excess zinc chloride. However, in view of the amount of experimental error involved in treating these curves from a strictly quantitative point of view, such a deduction can be considered as only tentative. From curve 3 can be drawn the conclusion that the effect of the zinc ion is not to repress noticeably the ionization of zinc chloride, but to leave the equilibrium relatively undisturbed. This is possibly due to the equal homopolarity of the bonds in either case.

The spectrograph used in these experiments was designed by the author. The optical system consists of two quartz lenses, focal length 24 centimeters, effective aperture F 6.5, each fully corrected for spherical aberration, and one right-hand and one left-hand 60° quartz prism. The dispersion on the photographic plates at $\lambda 2537$ is 16.5A per millimeter. The microphotometer used to trace the plates is a two-speed Kipp and Zonen type A Moll instrument. The wavelengths of the Raman lines were determined by interpolation from the nearest iron arc lines. The source of excitation was a special model of the Hanovia Sc 2537 silica lamp.

Some Chemical Properties of Element 43

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1. INTRODUCTION

PROFESSOR E. O. LAWRENCE gave us a piece of molybdenum plate which had been bombarded for some months by a strong deuteron beam in the Berkeley cyclotron. The molybdenum has been also irradiated with secondary neutrons which are always generated by the cyclotron. The molybdenum plate shows a strong activity, chiefly due to very slow electrons. The

radioactivity is due to more than one substance of a half-value period of some months and to the radioactive phosphorus isotope P^{32} .¹ The substance was sent from Berkeley on December 17, 1936 and we started our chemical investigation on January 30, 1937; all short period substances have decayed in these 6 weeks and we could

¹ We will give more details on the radioactive side of this investigation in a later paper to appear in the *Physical Review*.

investigate only substances with a comparatively long period.

According to usual nuclear reactions one would expect to find in molybdenum irradiated with neutrons or deuterons the formation of isotopes of zirconium, columbium, molybdenum, and element 43, of which zirconium can be produced only by fast neutrons and element 43 by deuterons, whereas molybdenum and columbium could be formed by deuterons and by neutrons.

There is always, of course, the possibility that the activity is due to some impurity of molybdenum, but we will show that this cannot play any important part in the formation of our radioactive isotopes. However, we found also a strong activity of P^{32} , possibly due to some surface contamination. Initially we did not eliminate this impurity which interfered considerably with the beginning of the analysis. Later on, some precipitates showed the decay period and the absorption coefficient for β -rays characteristic of P^{32} and we checked this result chemically, eliminating any P^{32} . For some reason, which we do not know, it seems that every substance which has been bombarded in the Berkeley cyclotron is strongly contaminated with P^{32} . We have employed the P^{32} extracted from molybdenum and from other metals of the cyclotron's walls as an indicator for some biological experiments.² The two faces of the molybdenum plate showed very different activities hence the transmutation is chiefly due to particles which are efficiently stopped by the molybdenum plate i.e. to charged particles (deuterons).

2. ANALYSIS

In a first analysis we tested whether the activity was due to columbium. About 200 mg of molybdenum with an activity of some thousands of our radioactive units (R.U.)³ were dissolved in aqua regia, and after adding 5 mg of rhenium, evaporated to dryness. The residue was dissolved with potassium hydroxide containing a small amount of potassium columbate. The addition of rhenium and the subsequent addition of manganese were made in order to protect any 43 in the later precipitations. We had no stable isotope of

43 and as very little is known about its chemical properties, we added the elements having presumably the closest resemblance to it. These are manganese and rhenium which lie in the same column of the periodic system above and beneath 43. We will see however that the resemblance with rhenium is much closer than the resemblance with manganese; a result which was expected.⁴

Manganese was added as manganese columbate prepared separately adding a slight excess of potassium columbate to a solution of manganous sulfate and ammonium sulfate. Manganese columbate being little soluble remains suspended in the mixture. Adding this mixture to the molybdenum solution the precipitate showed a tendency to blacken immediately on account of the evident formation of manganese dioxide; a few drops of hydrogen peroxide were added in order to ensure a complete precipitation of manganese; afterwards we passed a current of carbon dioxide through the solution in order to secure a precipitate of columbium pentoxide possibly free from molybdenum.

This precipitate was very active; we fused it with potassium carbonate and nitrate. The fused mass was extracted with water and the solution reduced with alcohol. Repeating this treatment a few times we got a perfectly inactive residue of manganese dioxide.

To the alkaline solution containing columbium we added sulfuric acid and precipitated columbium pentoxide. We added 7 mg of ammonium sodium phosphate and 20 mg of zirconium nitrate to the acid solution. The precipitate contains columbium, phosphorus and zirconium; it is very active (more than 1000 R.U.). We fused it repeatedly with potassium carbonate and potassium hydrate; each time we extracted the fused mass with water and acidified the solution with sulfuric acid in order to isolate columbium. However, we obtained always precipitates showing a definite activity, though the activity did not follow quantitatively columbium and had the radioactive characters of P^{32} . Finally we took a rather large quantity of columbium pentoxide which showed an activity of 56 R.U. and starting from it we prepared crystalline sodium metacolumbate. The identity of this salt was checked also by its optical and crystalline

² Nature (London) **139**, 836 (1937); *ibid.* in press.

³ The β -activity of 1 gram of uranium corresponds to about 300 R.U.

⁴ See e.g. I. and W. Noddack, *Naturwiss.* **6**, 333 (1927).

characters; it showed no activity and we could precipitate quantitatively the activity from the solution as magnesium ammonium phosphate whose identity was also checked crystallographically. We may conclude from these tests that columbium does not have any activity.

Subsequently we found that also fractions containing zirconium were inactive. We dissolved some active molybdenum in aqua regia, added 7.5 mg of rhenium, 10 mg of zirconium nitrate and evaporated over the water bath. We transformed the molybdic acid into ammonium molybdate by adding a little ammonia; and we added afterwards an excess of nitric acid. We obtained a precipitate of ammonium phosphomolybdate and zirconium phosphate which showed a strong activity. We treated this precipitate with ammonia but the activity did not change appreciably, indicating that only a small fraction of phosphorus had been converted into ammonium phosphomolybdate; however, this fraction was recovered as magnesium ammonium phosphate. The residue of the first ammonia treatment contained the bulk of phosphorus and zirconium and had an activity of about 1500 R.U. We fused it with sodium carbonate, extracted the fused mass with water, fused again the residue containing zirconium with sodium pyrosulphate and precipitated zirconium hydroxide with ammonia. The precipitate of zirconium hydrate is inactive whereas we recovered quantitatively the activity in this filtrate by precipitating phosphorus as magnesium ammonium phosphate. This test rules out the presence of a radioactive isotope of zirconium.

We were able to show that molybdenum also cannot be responsible for the activity. Of several tests we mention only the following. Rhenium and phosphorus and ammonium nitrate were added to the molybdenum solution. Ammonium phosphomolybdate precipitated; we dissolved it with ammonia and separate phosphorus as magnesium ammonium phosphate and molybdenum as sulphide. The former carries every activity, whereas molybdenum sulphide is inactive.

We have thus shown that the activity is not due to columbium, zirconium, or molybdenum. On the other hand the radioactivity of the irradiated molybdenum has radioactive characters quite different from P^{32} which was the only

radioactive substance found until this point of the research. We had to investigate, as already pointed out, the possible presence of a radioactive isotope of the element 43 (masurium of I. and W. Noddack).⁵ This should be found in the fraction containing rhenium since we did not find any trace of activity together with manganese.

Since from the first analysis we had an indication that the activity could be contained in a rather volatile substance as one would expect the higher oxides of 43 to be. We had precipitated the sulphides in an acid solution after separation of columbium. The precipitate showed an activity which was reduced to less than one-half of its former value by a very moderate ignition.

However, due to the absence of a stable isotope of element 43 and to the extreme scarcity and uncertainty of information about its chemical properties, it seemed worth while to investigate further the chemical properties of the activity in order to obtain some chemical information about element 43 and to obtain the chemical characteristics of the carrier of the activity.

A considerable difficulty in this investigation comes from the extreme softness of the emitted radiation, whose half-value thickness is about 1.5 mg/cm²; moreover, the absorption curve is far from exponential and it is practically impossible to correct properly the measured activity values in order to take into account the absorption of the β -rays from the precipitates. This difficulty is even increased for some fine precipitates (e.g., sulphides) which penetrate into the pores of filter paper, and show, for this reason, a smaller activity than they really have. Until now we have not secured a better filtering device.

3. CHEMICAL PROPERTIES OF ELEMENT 43

The first step for any chemical study of the activity is its concentration with the smallest possible amount of inactive substance. The best method for this concentration we have found, is to dissolve about 200 mg of irradiated molybdenum in aqua regia, add from 2 to 5 mg of rhenium and evaporate over the water bath. The residue is then dissolved with ammonia, and hydrogen sulfide passed through the solution.

⁵ W. Noddack, I. Tacke, O. Berg, Sitzber. preuss. Akad. Wiss. Physikmath. Klasse, 19, 400 (1925).

We then add a few milligrams of a manganous salt and after standing 12 hours filter.

The precipitate of manganous sulphide carries a small amount of a black substance, possibly rhenium sulphide or some sulphoperrhenate.⁶ This precipitate contains the bulk of the activity. It can be freed completely from manganese with dilute hydrochloric acid and, if necessary, with sulfur dioxide without any loss of activity. To check this last point we precipitated the solution containing the dissolved manganese again with hydrogen sulfide and collected manganese sulphide of the normal pink color, and found it inactive.

The black substance carrying the activity is easily dissolved in cold hydrogen peroxide, as does rhenium sulphide and shows also some other rhenium reactions. However, in order to have a better knowledge of its chemical nature, we repeated the precipitation of manganese with hydrogen sulphide, both from a molybdenum solution without rhenium and from a rhenium solution without molybdenum. The former gave a pink manganese sulphide, and the precipitate was easily and completely dissolved in dilute hydrochloric acid, the latter on the other hand gave a black precipitate with the properties stated above.

Further rhenium additions and manganese precipitations from the same molybdenum solution give the usual black precipitate, but its activity decreases rapidly in successive separations, e.g. Three separations with the method described above, from the same active molybdenum solution yield activities of 1000.20 and 0 R.U. Similar results, but not so clear cut and with a lower yield were obtained also by substituting zinc for manganese.

Another way of concentrating the activity is to heat the active molybdic anhydride, to which some rhenium has been added, in an oxygen current at about 550°. Rhenium volatilizes and carries the activity which may be collected together with rhenium in an alkaline solution and precipitated as sulphide according to Noddack.⁴

The active rhenium sulphide produced by one of the above described methods is dissolved in hydrogen peroxide and the activity measured by

evaporating 1 cc of the solution over the water bath on a crucible cover. Solutions standardized in this way contained of an order of magnitude 0.05 mg of rhenium and had an activity of about 20 R.U. per cc. Due to the preparation method it is probable that the elements were in their highest normal oxidation state.

With the titrated solutions mentioned above we have performed the following reactions:

Sulphides

We added hydrochloric acid to the solution and passed hydrogen sulfide through it. The activity was transferred practically quantitatively along with rhenium, copper, and cadmium. The hydrochloric acid concentrations were, respectively, 12 percent, 4 percent and 1 percent of hydrochloric acid.

Rhenium sulphide was treated with yellow ammonium sulphide without any loss of activity. The active product on the other hand is easily dissolved, as stated above, with hydrogen peroxide together with rhenium sulphide.

Oxidation and reduction

According to the position of element 43 in the periodic table, one would expect oxidation and reduction reactions to have a considerable importance for the chemistry of this element. The only data we could collect until now are the following: we add to the active solution a manganese salt and precipitate manganese dioxide with nitric acid and potassium chlorate. The precipitate is not active. We add potassium permanganate to an alkaline active solution and we reduce manganese with alcohol; no activity is found in the manganese dioxide precipitate. We add potassium ruthenate to the active solution, and precipitate ruthenium by reduction with formaldehyde. No activity is found in the precipitate. On the other hand metallic zinc precipitates the activity from a hydrochloric acid solution with a good yield.

Volatility

According to the position of element 43 in the periodic table one expects the higher oxides to be rather volatile. A first indication of this point was given, as we said, by the first analysis. Since volatility is analytically important, we have investigated it more carefully. It depends of course upon the valency of the investigated

⁶ W. Feit, quoted by I. and W. Noddack, *Das Rhenium* (Leipzig 1933), p. 57.

compounds. We have tried to reach the highest oxidation.

In a series of tests we have evaporated a few cc of the active solution on porcelain crucible covers over the water bath and measured the activity of the residue. Evaporation over the water bath, even if repeated, does not diminish the activity. Heating the covers to 400° causes the activity to begin to decrease and at 500° it disappears rapidly. In these experiments we have tried to evaporate acid anhydrides without alkali. However, we do not know whether we have done this since the residue contains a small fraction of a milligram of rhenium and even a trace of a base would be sufficient to neutralize the anhydride. As a check we have volatilized the same solution after alkali addition. The volatilization temperature was only slightly higher.

As it is well known⁷ rhenium may be separated quantitatively from molybdenum by passing moist hydrochloric acid through a strong (80 percent sulphuric acid) sulphuric solution at about 200°. We tried whether under these conditions the activity followed the rhenium or remained in the residue and found that it remains in the residue, e.g., in an experiment we distilled a sulphuric solution containing 200 R.U. of our activity, 5 mg rhenium and traces of impurities, possibly molybdenum, at 180° for one and one-half hours passing moist hydrochloric acid through the solution; 125 cc of the liquid distilled over. We precipitated all the rhenium and a trace of the activity from the distillate with hydrogen sulfide. The greater part of the activity is precipitated from the residue together with a small quantity of impurities by hydrogen sulfide. The activity is then completely recovered by adding a few mg of rhenium to the residue after the first precipitation and precipitating again with hydrogen sulfide. This separation from rhenium is especially important since it is the only method available for separating the activity from rhenium.

We have also separated the activity from a potassium ruthenate solution with a distillation in a chlorine current according to Debray and Joly.⁸ Ruthenium distills and the activity re-

mains in the residue. This separation from ruthenium gives information about the volatility in a chlorine current of element 43 and rules out the possibility that the activity is due to ruthenium confirming thus the test referred under "oxidation and reduction."

We have already pointed out that ignition in an oxygen current may be used for separating the activity from molybdenum, though the sulphide method seems to us to be preferred.

Organic reagents

Among the various organic reagents which we have tested, we have had good results in separating the activity from molybdenum with 8-hydroxyquinoline and nitron as Geilmann and Weibke⁹ did for the separation of rhenium from molybdenum. Moreover we could also precipitate the bulk of molybdenum with benzidine in presence of rhenium and extract the activity from the filtrate as a sulphide. However, this method of separation is less reliable than the former.

Precipitation of thallium perrhenate according to Krauss and Steinfeld¹⁰ from an active solution carries the largest part of the activity.

SUMMARY

Deuteron irradiated molybdenum shows an activity which has to be ascribed to element 43 according to its chemical characters, since, as is easily seen, all other possible elements are ruled out.

Element 43 in its chemical behavior bears a close resemblance to rhenium showing the same reactions but for the volatilization in a hydrochloric acid current. However, it must be borne in mind that having used rhenium as a "carrier" for extremely small quantities of element 43, some reactions could be different for "weighable" quantities of this element.

Our warmest thanks are due to Professor E. O. Lawrence and to the Radiation Laboratory of the University of California whose most generous gift of radioactive substance made this investigation possible. We hope also that this research carried on months after the end of the irradiation and many thousands of miles away from the cyclotron may help to show the tremendous possibilities of this instrument.

⁷ Geilmann and Weibke, *Zeits. f. allgem. anorg. Chemie* **199**, 120 (1931).

⁸ Debray and Joly, *Comptes rendus, Paris* **106**, 328 (1888).

⁹ Geilmann and Weibke, *Zeits. f. anorg. allgem. Chemie* **199**, 347 (1931).

¹⁰ Krauss and Steinfeld, *Zeits. f. anorg. allgem. Chemie* **197**, 52 (1931).