[CONTRIBUTION FROM THE ARGONNE NATIONAL LABORATORY]

The Preparation of Solid Neptunium Compounds[1]

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Neptunium, element number 93, was first synthesized by McMillan and Abelson who studied its chemistry on a tracer scale.[3] The particular isotope of neptunium used in this work, the long-lived, alpha-emitting Np^{237}, was first identified by Wahl and Seaborg.[4] The first isolation of this isotope in weighable quantities was accomplished by Magnusson and LaChapelle and will be the subject of a separate paper.[5] The chemistry of neptunium in aqueous solution has been intensively studied and the results will be published later by the workers in that field.

The object of this work was to make a study of the preparation and properties of several of the simpler solid neptunium compounds and compare them with the corresponding uranium and plutonium compounds.

Since only microgram quantities of neptunium were available at the time this work was carried out it was necessary to develop special techniques for working on this scale. It has been found that identification of solid reaction products by means of an analysis of their X-ray diffraction patterns can be carried out rapidly and in favorable cases with less than 10 micrograms of material. This is particularly true when the compound produced is isomorphous with similar compounds of other elements. Accordingly, the identification of the compounds of neptunium was made by Dr. W. H. Zachariasen by a consideration of the X-ray diffraction data obtained by him and of the method of chemical preparation used.

No X-ray crystal structure data will be given in this paper since it is expected that they will be published separately by Zachariasen and coworkers in the near future.

Neptunium dioxide, NpO_2, and sodium neptunyl acetate, $NaNpO_2(C_2H_3O_2)_3$, were the first compounds of neptunium identified. They were both prepared by Magnusson and LaChapelle,[5,6] the oxide by ignition of a hydroxide precipitate and the sodium neptunyl acetate by a method similar to that used for the preparation of the analogous uranyl and plutonyl salts. Neptunium dioxide is a brownish solid, isomorphous with thorium dioxide, uranium dioxide and plutonium dioxide. Sodium neptunyl acetate is pink under 30 × magnification (transmitted light) and pale green by reflected light. It is isomorphous with the corresponding plutonium and uranium compounds.

Neptunium hexafluoride was reported by Florin,[7] who used the reaction

$$2NpF_3 + 3F_2 \longrightarrow 2NpF_6$$

The reaction was carried out by heating a sample of neptunium trifluoride on a nickel filament in a stream of fluorine and condensing the volatile neptunium hexafluoride in a thin-walled glass capillary "U" tube. The neptunium hexafluoride as prepared by this method consisted of a mass of brownish-white crystals which were shown to be isomorphous with uranium hexafluoride. The melting point was determined as 53° under its own pressure at that temperature. The compound was reported to be quite volatile and could be sublimed from one end of the capillary to the other by slight warming.

Techniques

It is appropriate at this point to describe some of the more common techniques used in the handling of solids on the ultra-micro scale. Some of the techniques described were developed by Dr. P. L. Kirk and co-workers at the Metallurgical Laboratory in 1943 and 1944, while others were developed by various members of the staff in the course of their own investigations. No attempt will be made to assign credit for the development of many of these techniques since they were frequently the product of conferences of many individuals.

Preparation of Capillaries for X-Ray Samples.—A great deal of effort was expended in developing methods for the preparation of samples for X-ray diffraction analysis since, as mentioned above, many of the analyses were accomplished by this method. This involved the preparation and mounting in very thin-walled glass capillaries of samples of the order of 10 micrograms. In order to obtain satisfactory X-ray diffraction patterns of microgram quantities of a solid in a glass capillary, the wall thickness must not be greater than 0.030 mm. One of the most satisfactory methods of obtaining capillaries with this specification is as follows. A four-inch length of well-cleaned 10-12 mm. diameter Pyrex tubing is drawn down to approximately one third of its diameter by means of a sharp *oxygen-gas* flame. The constricted

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[1] The work reported here, which was done in 1945, summarizes the investigations of a number of neptunium compounds which were amenable to preparation and study by a specialized technique. The relationship of this to the general program of investigation on neptunium and the other transuranium elements, which began in 1940 and extended to the various laboratories connected with the Plutonium Project by 1942–1943, will become clear in the near future upon publication of the volumes on the Transuranium Elements of the Plutonium Project Record of the National Nuclear Energy Series. The neptunium (Np^{237}) used in the investigations described in this paper was a by-product in the operation of the uranium-graphite chain-reacting piles and was made available as the result of the efforts of a number of participants in this over-all program. In particular, the first small amounts of neptunium from this source were made available as the result of the work of J. J. Katz and co-workers, and the development of a process for the extraction of the subsequent larger amounts was due to the work of F. W. Albaugh and R. C. Thompson and co-workers.

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[3] E. M. McMillan and P. H. Abelson, *Phys. Rev.*, **57**, 1185 (1940).

[4] A. C. Wahl and G. T. Seaborg, *Chem. Eng. News*, 2190 (1945).

[5] L. B. Magnusson and T. J. LaChapelle, CN-1764 (A-2471), July, 1944, p. 9; THIS JOURNAL, **70**, 3534 (1948).

[6] L. B. Magnusson and T. J. LaChapelle, CN-2159, Sept., 1944, p. 16.

[7] A. E. Florin, MUC-GTS-2165, Jan. 23, 1946, p. 1.

tube is heated with an *air-gas* flame at its narrowest point until sufficiently soft and is then rapidly drawn out to a thin capillary. Capillaries of 0.100 mm. inside diameter and a wall thickness as low as 0.010 mm. may be readily produced by this means. The cutting of capillaries of these dimensions may be accomplished by gently rubbing the capillary at the desired point with a small fragment of unglazed porcelain. Light pressure will cause the capillary to break cleanly at the point scratched by the chip. The end of the capillary may be satisfactorily sealed by using a very small flame. Care should be taken to prevent over-thickening of the glass at the bottom of the capillary, since an increase in wall thickness enhances the diffuse scattering of the X-ray beam and thus intensifies background darkening on the film.

Quartz capillaries are much more difficult to make. Ten-millimeter quartz tubing with a 1 mm. wall may be drawn into satisfactory X-ray capillaries by means of a sharp *oxy-hydrogen* flame in the same manner as described above except that a "soft" *oxy-hydrogen* flame is used for the final drawing instead of an *air-gas* flame as in the case of Pyrex. These capillaries are generally not circular in cross-section, nor are they of uniform wall thickness.

Filling X-Ray Capillaries.—Since these tubes are very fragile, and of small diameter, it is generally preferable to leave the stem attached rather than try to fill the narrow tube directly, although this may be done under the microscope. These tubes may be held for observation on the stage of a dissecting microscope by means of a lump of modeling clay. Particles of the solid may be introduced into a larger tube in any convenient way but care should be taken not to put in too much material at one time nor to add particles too large to fall to the bottom of the capillary. In general, powders may be persuaded to fall to the bottom of a fine capillary by holding it in a vertical position and tapping the stem sharply. Sometimes light rubbing at the throat of the tube with a knurled edge or file will shake the powder loose from the walls into the capillary. Rubbing should not be attempted at points lower than the throat because of the danger of breaking the capillary.

After the particles have been satisfactorily packed into the end of the capillary, it may be sealed. If necessary, the stem of the capillary may end in a ground joint so that it may be evacuated before sealing.

Emptying Capillaries.—It is frequently necessary to reuse material submitted for X-ray analysis. In such cases, the capillary (usually one-half to three-quarters inch long) is held lightly in the fingers and opened by scratching with a chip of unglazed porcelain. The opened capillary is then attached to a stout wire with a bit of clay and inverted over a suitable container. The wire is then tapped sharply, causing the contents of the capillary to fall out into the container.

Preparation of Solids from Solution.—The preparation of solids from solutions involves either evaporation of the solvent or precipitation from solution by a chemical reagent. Evaporation may be done from small platinum boats. These boats are usually rectangular in shape, 6 by 3 mm. by about 3 mm. deep. For example, a nitrate solution can be placed in a boat such as this, the solution evaporated to dryness and, if necessary, the nitrate ignited to an oxide. Samples of the oxide or nitrate can be removed from the boat by means of a needle and introduced into an X-ray capillary for examination. Alternatively, the oxide can be treated with other reagents to produce new compounds. These operations can very easily be carried out on the 50-microgram scale.

In precipitation of solids from solution, the following technique was found very satisfactory in the case of substances precipitating in a bulky gelatinous form (such as certain hydroxides). These hydroxides can be precipitated, washed, and centrifuged in a microcone. This leaves the desired product tightly packed at the bottom of the cone. The supernatant liquid is removed and the cone and contents are dried slowly at about 70°. It is found that the precipitate has a tendency to shrink away from the walls of the cone under these conditions so that it forms a loose single piece, or at most a few pieces. Various operations can now be performed on these small amounts of material *in situ*, or the material may be transferred to another reaction vessel, such as an X-ray capillary made from a ground joint which can then be connected to a vacuum apparatus. This type of manipulation lends itself to the preparation of halides which later may be sublimed on the walls of the capillary, after which the capillary may be sealed off to the proper length and the contents (both the sublimate and residue) studied by X-ray diffraction methods.

Experimental

Preparation and Properties of Neptunium Trifluoride and Neptunium Tetrafluoride.—Neptunium trifluoride and tetrafluoride were prepared by the reactions

$$NpO_2 + {}^1/_2H_2 + 3HF \longrightarrow NpF_3 + 2H_2O \quad (1)$$

$$NpF_3 + {}^1/_4O_2 + HF \longrightarrow NpF_4 + {}^1/_2H_2O \quad (2)$$

For the preparation of neptunium trifluoride, Np(IV) hydroxide was precipitated in a microcone with gaseous ammonia from a solution containing 50 micrograms of Np(IV) at a concentration of 1 g. per liter in dilute sulfuric acid. The gelatinous precipitate was washed and then dried in an oven at 70° to a pellet, which was transferred to a platinum vessel (made from the cover of a one-milliliter J. Lawrence Smith crucible, with a platinum holder spot-welded to it). The platinum vessel was placed in an all-platinum hydrofluorination apparatus and treated with a hydrogen–hydrogen fluoride mixture (*ca.* 1:1) for one and one-half hours at 500°.[8] The system was cooled in the gas mixture which was then pumped out and replaced with nitrogen. The reaction product was crushed and transferred to an X-ray capillary for analysis. The product was reported to be neptunium trifluoride, isomorphous with uranium trifluoride and plutonium trifluoride.

The sample of neptunium trifluoride was transferred back to the platinum crucible and treated in the hydrofluorination apparatus with an oxygen–hydrogen fluoride mixture for one hour at 500°. The light green reaction product was shown by X-ray diffraction methods to be neptunium tetrafluoride, isomorphous with thorium tetrafluoride, uranium tetrafluoride and plutonium tetrafluoride.

The neptunium trifluoride, as observed with about 50 micrograms of material, was black. Preparations on the 250-microgram scale appeared dark purple, darker than the purple plutonium trifluoride. The neptunium tetrafluoride was light green.

The reactions for the preparation of the neptunium fluorides are analogous to the reactions for the preparation of plutonium trifluoride and plutonium tetrafluoride from plutonium dioxide and plutonium trifluoride, respectively.[9] It may be inferred that the direct synthesis of neptunium tetrafluoride from neptunium dioxide will take

$$NpO_2 + 4HF \longrightarrow NpF_4 + 2H_2O \quad (3)$$

place with hydrogen fluoride free of hydrogen. Reaction (1) does not take place for uranium dioxide; at 500°, the action of a hydrogen–hydrogen fluoride mixture gives rise to uranium tetrafluoride. Neptunium tetrafluoride has also been synthesized directly from the oxide by the action of an oxygen–hydrogen fluoride mixture at 500°.

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(8) The authors wish to acknowledge the valuable assistance of Mr. A. E. Florin at this stage of the preparation.

(9) A. E. Florin and R. Heath, CK-1372 (A-2015), March, 1944, p. 7.

Preparation of Neptunium Trichloride and Neptunium Tetrachloride.—Uranium dioxide or oxalate reacts with carbon tetrachloride vapor at 450–500° according to an equation of the type

$$UO_2 + 2CCl_4 \longrightarrow UCl_4 + 2COCl_2 \qquad (4)$$

The uranium tetrachloride slowly sublimes out of the reactor. Plutonium dioxide, on the other hand, reacts with carbon tetrachloride vapor according to the equation

$$PuO_2 + 2CCl_4 \longrightarrow PuCl_3 + 2COCl_2 + {}^1/_2Cl_2 \qquad (5)$$

and at 750–800° the plutonium trichloride is obtained as a green sublimate.

It has been found that Np(IV) oxalate (or the dioxide) reacts with carbon tetrachloride vapor at 500° to give a yellow sublimate of neptunium tetrachloride. In this respect, therefore, neptunium is more like uranium than like plutonium in its chemical behavior. Just as uranium tetrachloride may be reduced by hydrogen to form uranium trichloride, so neptunium tetrachloride may be reduced to neptunium trichloride.

Many anhydrous chlorides are extremely hygroscopic and it was believed that transferring 50-microgram samples of neptunium chlorides even in the relatively anhydrous atmosphere of a "dry box" would result in hydration. Therefore, their preparations were carried out directly in an X-ray capillary. The apparatus used is diagrammed in Fig. 1. By manipulation of stopcocks B and C it is possible alternately to admit carbon tetrachloride vapor onto the neptunium compound at the bottom of the capillary, and to pump it out along with the volatile reaction products. During the time the capillary is evacuated, any volatile neptunium chloride formed has an opportunity to sublime up to the cold portion of the tube. The heating block was wound with resistance wire and the temperature determined by means of a thermocouple.

The reaction and apparatus were tested with a sample of about 50 micrograms of uranium dioxide. The temperature of reaction was 530° and the carbon tetrachloride was alternately admitted and pumped off every few minutes. During the period of one-half hour some dark material was observed to collect in the capillary just outside the hot nickel block. The capillary was sealed off in two parts; one contained the residue and the other the sublimate. X-Ray analysis showed that the sublimate was uranium tetrachloride and the residue primarily uranium dioxide. The reaction system was evidently rather inefficient, since only a small fraction of the uranium dioxide was converted to sublimed uranium tetrachloride. Fortunately, the few micrograms of material synthesized were disposed as a thin layer on the walls of the X-ray capillary, in such a manner as to be maximally effective in producing diffraction. Hence, an interpretable, although weak, pattern was produced.

In the experiment with neptunium, approximately 20 micrograms of oven-dried (70°) oxalate[10] was treated in the same manner described above. After a short time, a yellow sublimate was formed in the capillary above the hot zone. The capillary was sealed off in two portions and submitted for X-ray analysis. The sublimate was neptunium tetrachloride, isomorphous with uranium tetrachloride and thorium tetrachloride, and the residue was neptunium dioxide.

In later syntheses, on approximately the same scale, a larger fraction of the neptunium dioxide was converted to sublimed neptunium tetrachloride by prolonged treatment with carbon tetrachloride vapor at 530°.

The mode of synthesis and the volatilization of neptunium tetrachloride also indicate its close similarity to uranium tetrachloride and suggest similar physical characteristics. It may be remarked here that comparison of the vapor pressures and melting points of the isomorphous thorium tetrachloride and uranium tetrachloride[11,12,13,14] indicate that neptunium tetrachloride will be found to be more volatile and lower melting than uranium tetrachloride.

The reduction of neptunium tetrachloride to neptunium trichloride was carried out directly in the X-ray capillary in which the neptunium tetrachloride had been formed. Several micrograms of yellow sublimed neptunium tetrachloride was obtained as previously described. The nickel furnace was moved up to surround the neptunium tetrachloride and maintained at 450°. Hydrogen, purified by passage over hot copper and through a liquid air-cooled charcoal trap, was admitted to one atmosphere pressure into the reaction system through the stopcock B (Fig. 1). The hydrogen was allowed to react for ten minutes and was then pumped out to remove the hydrogen chloride formed as a reaction product. Hydrogen was admitted two times more with subsequent evacuation. Calculations indicated that these three treatments should provide a more than adequate supply of hydrogen to reduce several micrograms of neptunium tetrachloride to neptunium trichloride, provided the equilibria involved are similar to those in uranium tetrachloride to uranium trichloride reduction.[15] The material in the capillary had diminished in quantity, suggesting that some sublimation of neptunium tetrachloride had occurred. The residue was identified by X-ray methods as neptunium trichloride,

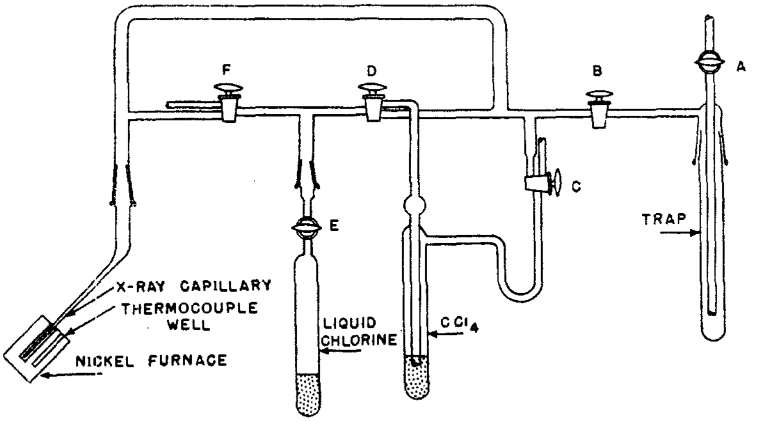

Fig. 1.—Apparatus for the preparation of neptunium halides.

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[10] The oxalate was precipitated from a solution that was 0.8 *M* nitric acid, 0.1 *M* oxalic acid, containing *ca.* one gram of neptunium per liter. The neptunium was probably in the (IV) state because it was obtained from a neptunium sulfate solution that had been saturated with sulfur dioxide for a period of twelve hours. The neptunium was precipitated with gaseous ammonia and redissolved in nitric acid for the oxalate precipitation. The oxalate precipitated slowly as a crystalline material when an ammonium oxalate solution was added. The observed solubility (assay by Dr. J. C. Hindman) was 200 mg./l.

(11) Fisher, *et al.*, *Z. anorg. allgem. Chem.*, **242**, 161 (1939).

(12) T. Butler and A. Newton, CC-1500 (A-2083), May, 1944, p. 7.

(13) A. Schelberg and R. W. Thompson, A-809, p. 5.

(14) M. Mueller, R. L.-4.6.257, May, 1944, p. 24.

(15) G. E. MacWood and D. Altman, RL-4.7.600, p. A-4.

isomorphous with uranium trichloride and plutonium trichloride.

The yellow color of the material had disappeared and the solid appeared white, but somewhat iridescent. It is possible that neptunium trichloride may be more highly colored since observations on such minute quantities of material are unreliable.

In later preparations of this compound the difficulty due to volatilization of the neptunium tetrachloride during the treatment with hydrogen was circumvented by treating the oxide with a mixture of hydrogen and carbon tetrachloride at relatively low temperatures (350–400°). When the reaction was completed, the neptunium trichloride was sublimed out at 750–800°. For this reaction it is, of course, necessary to use quartz capillaries.

Neptunium Oxychloride, $NpOCl_2$.—This compound resulted when a sample of neptunium tetrachloride was heated to 450° *in vacuo* in a sealed capillary. Apparently, residual oxygen (or water) adsorbed on the walls was present in sufficient quantity to oxidize (or hydrolyze) the neptunium tetrachloride to neptunium oxychloride. The compound appeared as clusters of light yellow needles which could be sublimed at 550°. An X-ray diffraction pattern of this compound showed it to be isomorphous with uranium oxychloride. Attempts to reduce this compound to neptunium (III) oxychloride, NpOCl, with hydrogen at 450° failed, probably because of an impurity (water) in the hydrogen, and the product was neptunium dioxide. Therefore, the experiments cannot be regarded as providing information as to the existence or stability of neptunium (III) oxychloride.

Attempted Preparation of a Higher Chloride of Neptunium.—Since neptunium, in aqueous solution, forms ions of oxidation numbers five and six as well as three and four, it was of interest to attempt the preparation of the higher chloride in the solid state, especially as uranium pentachloride and uranium hexachloride[16,17] are known to exist, whereas plutonium tetrachloride has not been prepared. The experiment described here was an unsuccessful attempt to prepare these higher chlorides of neptunium by the action of chlorine gas on neptunium tetrachloride at elevated temperatures. A sketch of the apparatus is given in Fig. 1.

The chlorine used in this and the following experiments was tank chlorine which was passed through a sulfuric acid bead tower, condensed in liquid nitrogen, distilled into a −120° bath (solid ethyl bromide) with pumping to remove oxygen, and finally distilled into the receiver.

The apparatus was tested with uranium dioxide. A small quantity of uranium dioxide was placed in the X-ray capillary and the system evacuated. Carbon tetrachloride vapor was admitted onto the heated uranium dioxide and then pumped off. It was found that the optimum temperature for the formation of uranium tetrachloride in this apparatus was 510–530°. After sufficient uranium tetrachloride was formed, the furnace was moved up on the capillary so that the uranium tetrachloride could be heated. The stopcocks were then manipulated to saturate the carbon tetrachloride with chlorine gas, and this mixture passed over the uranium tetrachloride heated to 390–400°. It was observed that in the cool portion of the capillary a red zone formed, beyond which was a black zone. When sufficient material had been collected, the reaction was stopped, and the capillary sealed off.

The zones of condensation were about 1 mm. wide and were separated from each other by about 0.5 mm. The boundaries were quite sharp and it was possible to obtain X-ray diffraction patterns of the individual zones. The compounds in order of their increasing volatility were uranium tetrachloride, uranium pentachloride and uranium hexachloride.

When this experiment was repeated with neptunium tetrachloride, the vaporized material failed to condense in distinct zones. Examination of the condensed material under the microscope showed it to consist of transparent yellow bipyramids. In thicker layers or in reflected light the crystals appeared reddish. This compound was shown by X-ray diffraction methods to be neptunium tetrachloride.

Neptunium Tribromide, Tetrabromide and Triiodide.—Uranium dioxide reacts with aluminum chloride at 250–500° to form uranium tetrachloride according to the equation

$$3UO_2 + 4AlCl_3 \longrightarrow 3UCl_4 + 2Al_2O_3 \qquad (6)$$

A modification of this method in which neptunium dioxide was treated with aluminum metal and the appropriate halogen or with aluminum halide resulted in the formation of the corresponding tribromide, triiodide and tetrabromide, respectively

Ninety micrograms of neptunium dioxide, prepared by the precipitation of the hydroxide with gaseous ammonia from an acid sulfate solution, was dried at 70° for twelve hours so that it formed a small pellet at the bottom of a microcone. A quartz 19/38 joint was drawn into a capillary *ca.* 0.1 mm. in diameter with a wall thickness of 0.015 mm. The capillary was sealed at the end and the pellet of neptunium dioxide was introduced. A small amount of aluminum metal (*ca.* 50 micrograms) was added on top of the oxide and the system connected to the apparatus shown in Fig. 1, where the contents were dried by heating the tip of the capillary to 400° for fifteen minutes *in vacuo*.

At this point bromine vapor which was free of chlorine and iodine was admitted to the mixture of the oxide and aluminum metal. The aluminum slowly reacted with the bromine at slightly elevated temperatures to form aluminum bromide which condensed as a crystalline solid just beyond the warm zone of the tube. When the lumen of the capillary was almost closed by the slug of aluminum bromide, the excess bromine was pumped out and the capillary was sealed off so that its length was about four inches.

The capillary was then placed inside a heavy-walled glass tube which was sealed at both ends and contained air at atmospheric pressure. This system was inserted in a steel jacket which was heated in a furnace to 350–400° for twelve hours. The air inside the heavy-walled tube tended to equalize the strain on the thin-walled quartz capillary as the pressure of the aluminum bromide developed.

At the end of the heating period the heavy glass tube was opened and the capillary was found to contain a greenish melt. The excess aluminum bromide was separated by heating to 250° and driving it to the cool end of the capillary where it condensed as a solid mass of crystals. The portion of the capillary containing the aluminum bromide was sealed off from the end containing the relatively non-volatile residue.

When the residue was heated to 600°, a silvery material which was shown by X-ray analysis to be aluminum metal sublimed out. Further heating to 800° volatilized a green compound which was shown to be neptunium tribromide, isomorphous with uranium tribromide.

Neptunium triiodide was prepared in an analogous manner from the neptunium dioxide, aluminum and iodine. After removal of the excess aluminum iodide the triiodide was sublimed at 800°. It proved to be a brownish compound (probably slightly contaminated with iodine) which was shown to be isomorphous with plutonium triiodide and uranium triiodide.

It was found that neptunium dioxide reacts with aluminum bromide in the absence of excess aluminum metal to give neptunium tetrabromide. Fifty micrograms of neptunium dioxide was placed in a thin-walled quartz capillary and dried *in vacuo* at 400° for one hour. Approximately 250 micrograms of anhydrous aluminum bromide was added on top of the oxide (this operation was carried out in a dry box) and the system evacuated and sealed off so that the length of the capillary was about

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[16] C. H. Prescott, Jr., ANL-JJK-14B-102.

[17] H. G. Rieber and H. A. Young, ANL-JJK-14B-103.

four inches. The capillary was placed inside a heavy-walled glass tube as described above and heated to 350° for twelve hours.

At the end of the heating period the capillary was removed from the tube and the excess aluminum bromide was removed by sublimation at 250° whereupon the portion of the capillary containing it was sealed off. When the remainder of the capillary was heated to 500°, a reddish-brown compound sublimed out whose X-ray diffraction pattern showed it to be neptunium tetrabromide, isomorphous with uranium tetrabromide. On further heating to 800°, green neptunium tribromide sublimed. The amount of neptunium tetrabromide obtained was approximately 20% of the total volatile material.

The experiments do not settle the questions of whether or not neptunium tetrabromide thermally decomposes according to the equation

$$NpBr_4 \longrightarrow NpBr_3 + {}^1/_2Br_2 \qquad (7)$$

at temperatures of 500° or so, and whether neptunium tetraiodide can exist.

The fact that when neptunium tetrabromide, prepared by the action of aluminum bromide containing no excess aluminum, was sublimed in a *sealed* tube it partially decomposed to neptunium tribromide suggests that the reaction (7) does indeed take place at 500° or less, and that if neptunium tetrabromide were sublimed in a tube being continuously evacuated, reaction (7) would proceed more extensively. In the experiment in which excess aluminum was present, neptunium tribromide could be formed either by the direct reduction of neptunium tetrabromide by aluminum metal or *via* a mechanism involving reaction (7) and removal of bromine vapor by the aluminum.

In the synthesis of neptunium triiodide, there was no evidence for excess aluminum and some evidence for the presence of excess iodine. Probably therefore neptunium tetraiodide very readily decomposes to neptunium triiodide and iodine or does not exist at all. In a subsequent section, it is pointed out that the thermal instability of uranium tetraiodide implies a still greater thermal instability of neptunium tetraiodide.

Preparation and Properties of Neptunium Metal.—Neptunium metal was prepared by the reaction of barium vapor with neptunium trifluoride at 1200° in a beryllia "double crucible" system which is shown in Fig. 2.

Because only a limited amount of neptunium was available for this purpose (*ca.* 250 micrograms), many practice reductions using uranium tetrafluoride and plutonium tetrafluoride as stand-ins were carried out in an attempt to determine conditions favorable for the production of neptunium metal. The apparatus was similar to that developed by Westrum for the production of plutonium on the microgram scale.[18,19]

The inner crucibles were "vitrified" by heating *in vacuo* at 1500–1800° for an hour in order to minimize the chances of metal soaking into the otherwise porous crucible material. Before making a run the system was thoroughly outgassed at about 1400° for one hour or until the pressure was reduced to 10^{-6} mm.

Attempts to prepare uranium and plutonium metal on the 50-microgram scale by reduction of the tetrafluorides

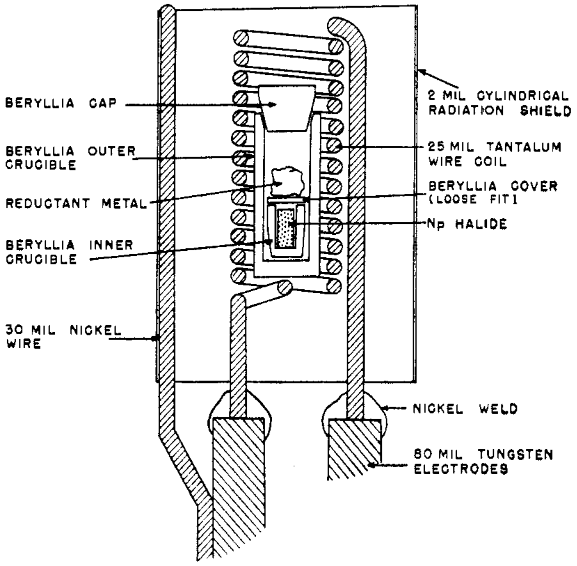

Fig. 2.

with barium metal at *ca.* 1200° were uniformly successful, but two attempts to prepare neptunium metal from neptunium tetrafluoride under similar conditions failed completely. When the crucibles were opened they were found to be empty but somewhat alpha-active, suggesting that either the fluoride or metal had soaked into the crucible. These results led to the possibility of two choices: the use of a more volatile reductant such as magnesium which would minimize the tendency for the metal or fluoride to soak in by permitting the reaction to take place at a lower temperature, or the use of neptunium trifluoride instead of neptunium tetrafluoride as the starting compound. Neptunium trifluoride would be expected to have a higher melting point than the tetrafluoride and thus would be less likely to soak into the crucible.

Tests of magnesium as a reducing agent for uranium and plutonium fluorides under these conditions were not encouraging in that the appearance of metal produced was not as good as that obtained in the barium reductions. Therefore, it was decided to use neptunium trifluoride as the starting material.

Accordingly, the remainder of the neptunium tetrafluoride (*ca.* 150 micrograms) was converted to neptunium trifluoride by the action of hydrogen fluoride and hydrogen at 500° and this material was used in the preparation of neptunium metal.

Three runs of 50 micrograms each were made, using barium as the reductant at a maximum temperature of about 1200° for one and one-half to two minutes. Each of these reductions was successful, yielding several pieces of metal weighing from 10 to 40 micrograms each. The metal is silvery in color and about as malleable as uranium prepared under the same conditions. The metal is not particularly affected by air during the intervals necessary for manipulations (one-half hour).

The method used for the determination of the density of neptunium metal was the same as that devised by Kirk for the earlier work on plutonium.[20] This displacement of a piece of metal, weighing 40.32 micrograms[20a] was measured in two different capillary pycnometers whose diameters were 0.231 and 0.333 mm. The measured densities were 17.9 and 17.6 g./cc., respectively. The apparatus is shown in Fig. 3.

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[18] E. F. Westrum, Jr., CK-1586 (A-2251), May, 1944, p. 20.

[19] E. F. Westrum, Jr., CN-2495, Jan., 1945, p. 12.

[20] P. L. Kirk, R. S. Rosenfels, S. Fried and H. L. Baumbach, CK-1145 (A-1631), Dec., 1943, p. 15.

[20a] The metal was weighed on the Kirk, Craig, Boyer quartz fiber microbalance which is described in *Chem. Eng. News*, **24**, 1196 (1946).

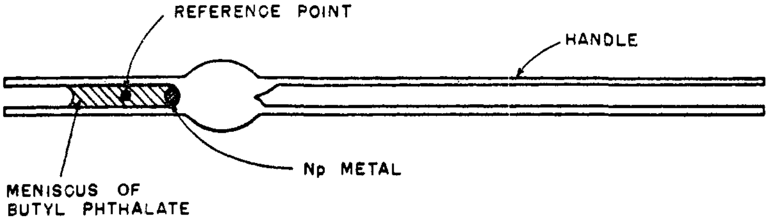

Fig. 3.—Displacement of meniscus measured from reference point before and after introduction of metal globule.

The X-ray diffraction pattern obtained from some flattened pieces of metal was complex and has not been interpreted.

The observation that the neptunium apparently soaked into the crucible during the attempted reduction of neptunium tetrafluoride whereas the reductions of uranium tetrafluoride were successful suggests that the melting point of neptunium tetrafluoride is less than that of uranium tetrafluoride (960°) and that the neptunium tetrafluoride melted and soaked into the crucible before the reductant vapor attacked it. By extrapolation, the melting point of plutonium tetrafluoride should be even lower. Since, however, plutonium tetrafluoride readily decomposes *in vacuo* to plutonium trifluoride,[21] the melting and soaking into the crucible of the plutonium tetrafluoride during a reduction may be prevented by the formation of a trifluoride skin around the tetrafluoride.

The Preparation of Neptunium Hydride.—Neptunium hydride was prepared by the action of hydrogen on the metal. The apparatus was that developed by Baumbach for the preparation of plutonium hydride on the microgram scale,[22] and is shown in Fig. 4.

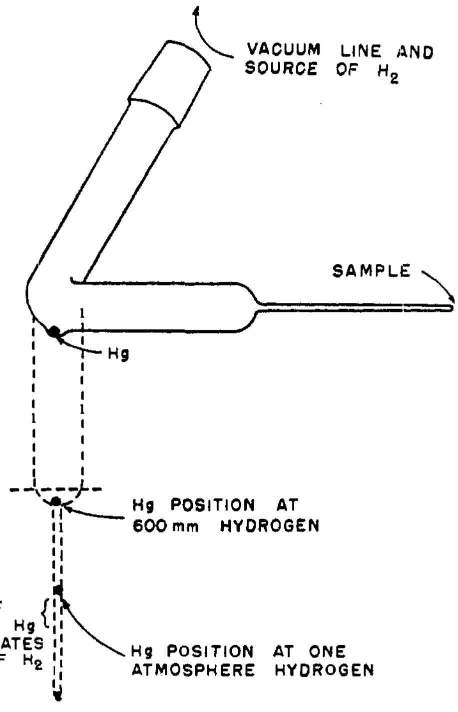

Fig. 4.

The metal weighed 20.88 micrograms and did not react with hydrogen when this gas was admitted at a pressure of one atmosphere but after a few minutes of heating to 50° rapidly absorbed gas. Examination of the hydride under a microscope showed that the metal had broken up into a black flaky material very similar in appearance to uranium or plutonium hydride. The volume of hydrogen absorbed corresponded to the formula $NpH_{3.6-3.8}$.

X-Ray diffraction patterns of this compound exhibited lines which could not be assigned to any neptunium hydride but according to Zachariasen are very probably due to the lower oxide, NpO. A small amount of oxygen adsorbed on the walls of the capillary could easily account for the appearance of this compound.

Preparation of Neptunium Oxysulfide and Sesquisulfide.—These compounds were prepared by reaction of neptunium dioxide with a hydrogen sulfide–carbon disulfide mixture at 1000°, since the results obtained at Berkeley on the preparation of thorium and uranium sulfides indicate that this mixture is a more potent "sulfiding" agent than hydrogen sulfide itself.[23]

A quartz microcone containing 50 micrograms of neptunium dioxide was placed in a quartz tube and treated at 1000° for two hours with the mixture of hydrogen sulfide and carbon disulfide obtained by bubbling dry hydrogen sulfide through carbon disulfide at room temperature. The black, brittle reaction product was shown by X-ray analysis to be neptunium oxysulfide.

The neptunium oxysulfide was treated again at 1000° with the hydrogen sulfide–carbon disulfide mixture, but this time for twelve hours. The product had not changed visibly in appearance but was shown to be neptunium sesquisulfide, isomorphous with uranium sesquisulfide and thorium sesquisulfide.

The chemistry of the neptunium–sulfur system seems to be intermediate in a rather interesting way between that of the uranium sulfides and that of the plutonium sulfides. The oxysulfide of neptunium is NpOS like UOS, and differs from the oxysulfide of plutonium, Pu_2O_2S. In the fully sulfided product, however, the oxidation number of the neptunium is reduced to three.

When U_3O_8 is converted to a sulfide by hydrogen sulfide at 1300–1400° in a graphite system, the product is US_2, with some decomposition to U_2S_3. The U_2S_3 reverts to US_2 as the reaction product is cooled in hydrogen sulfide.[24] When treated similarly, PuO_2 is converted to Pu_2S_3.[25] While Pu_2S_3 is presumably like cerium sulfide, Ce_2S_3, which is a "normal-valent" sulfide that does not show metallic conductivity, U_2S_3 is a "reduced" sulfide showing semi-metallic conductivity, and US_2 is a normal-valent sulfide.

Since neptunium sesquisulfide was prepared under conditions that in general lead to the production of normal-valent sulfides, it is presumably also a normal-valent sulfide. However, its crystal structure is isomorphous with that of the reduced sulfide, U_2S_3, rather than that of the normal sulfide, Pu_2S_3.

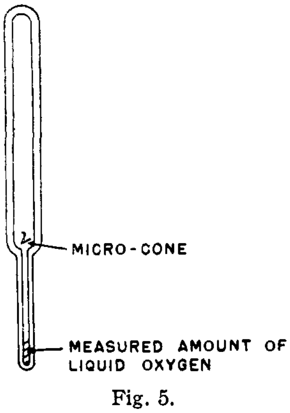

Fig. 5.

It would be of great interest to synthesize a neptunium sulfide at 1400° in a graphite system and determine whether neptunium sesquisulfide with the plutonium

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[21] S. Fried and N. Davidson, ANL-4055, Oct., 1947, p. 5.

[22] H. L. Baumbach and S. Fried, CK-1145 (A-1631), Dec., 1943, p. 17.

[23] N. Lofgren, CK-941, p. 7.

[24] L. Brewer, L. A. Bromley, P. W. Gilles and N. Lofgren, CT-2290, Nov., 1944, p. 3.

[25] N. Davidson, CN-2431, Dec., 1944, p. 2.

sesquisulfide structure would be obtained. It would also be of interest to treat neptunium sesquisulfide with sulfur at a relatively low temperature in an attempt to prepare neptunium disulfide.

Attempted Preparation of a Higher Oxide of Neptunium.—On the basis of the similarity of neptunium to uranium it was decided to attempt the preparation of a crystalline higher oxide (higher than neptunium dioxide) of this element by ignition of a neptunium salt in a high pressure of oxygen. The apparatus used in this experiment is shown in Fig. 5. The inside diameter of the heavy-walled bomb tubing was 4 mm. and the inside diameter of the capillary was 1 mm. The neptunium salt was contained in the cone. The tube was connected by means of a stopcock to a line filled with oxygen. Oxygen was condensed in the small capillary by means of a liquid nitrogen bath. The amount condensed was measured as the length in the capillary and was chosen to give a pressure of *ca.* 28 atmospheres at 400° after sealing off at the proper point. These capillary bombs were annealed in an oven before use and if carefully sealed off were found to withstand 30 atmospheres. They were enclosed in steel jackets when heated in a furnace. The application of this apparatus to a synthesis of UO_3 from U_3O_8 is described elsewhere.[26]

The neptunium as Np(IV) in hydrochloric acid was evaporated to dryness at 70°, taken up in 6 M nitric acid and evaporated to dryness again. From previous observations by L. B. Magnusson it was probably Np(IV) nitrate at this stage. The cone containing the neptunium was placed in the bomb which was filled with oxygen to give a pressure of 28 atmospheres at 400°, and the system sealed off. When heated to 400°, the bomb burst at the top "seal off." The sample was intact and was placed in another bomb where it was maintained at 350° for five hours, 250° for twelve hours and 125° for four hours. The sample gave the X-ray diffraction pattern of neptunium dioxide plus a few other weak unidentifiable lines.

Survey of the Chemistry of Neptunium Compounds.—The electropositive elements uranium, neptunium and plutonium have oxidation states 3, 4, 5 and 6 in aqueous solution. Anhydrous compounds in which these elements exhibit the 3, 4 and 6 oxidation states are known, and, as discussed later, there may be +5 anhydrous compounds of these elements.

These three elements therefore form an interesting series in which to study trends in the stability of anhydrous compounds of the different oxidation states as a function of the electropositive (U, Np, Pu) and electronegative (O, F, Cl, Br, I, S) components of the compounds. One may seek to correlate these trends with the trends in the stability of the different oxidation states in solution.

The simple principles stated below were of value in the present research in anticipating what neptunium compounds might be formed in a particular reaction. We may consider that in the anhydrous compounds of these elements, the small positively charged ions of the various oxidation states are stabilized by coördination to the anions of the electronegative atoms. The small and difficultly polarizable anions $O^=$ and F^- in general form compounds of higher oxidation number than do the more readily polarizable and oxidizable anions, Cl^-, Br^-, $S^=$ and I^-. In aqueous solution, the positive ions of the different oxidation states are stabilized by solvation and complex formation. It is interesting to observe that in general it is easier to obtain the higher oxidation states of the elements under discussion in aqueous solution than among dry compounds. Thus, the free energies of solution of uranium hexafluoride and uranium hexachloride are more negative than the free energies of solution of uranium tetrafluoride and uranium tetrachloride, respectively. Similarly, Pu(III) may be oxidized to Pu(IV) in aqueous solutions by chlorine or bromine, but evidently anhydrous plutonium tetrachloride and plutonium tetrabromide do not exist.

A detailed discussion of the correlation between the trends in the stabilities of the solid compounds of these three elements and the trends in the stabilities of the different oxidation states in aqueous solution is deferred until the authors who have determined the potentials between the different oxidation states in aqueous solution publish their results. It may be said here that both the III–IV and the IV–VI potentials become more negative in a regular manner in the series (uranium, neptunium and plutonium) in accordance with the general increase in the stability of anhydrous compounds of the lower oxidation states in this series.

In Table I an attempt has been made to summarize the available information as to the existence and stability of compounds of uranium, neptunium and plutonium. Predictions as to possibility of existence of certain compounds are indicated by enclosing the compound and prediction in parentheses. The question marks signify those cases where from the observed trends one cannot predict whether the compounds will be stable or unstable because they are borderline cases. The reasons underlying these predictions are generally rather obvious when account is taken of the principles stated above.

Our knowledge of the properties of +5 compounds of these elements is meager. It is not known with certainty whether uranium pentachloride and uranium pentafluoride contain U(V) atoms in their structures or non-equivalent U(IV) and U(VI) atoms. In solution, the +5 oxidation state of neptunium is more stable with respect to decomposition into the +4 and +6 states than is the case for either uranium or plutonium and it may be that neptunium pentafluoride will be a true +5 compound of neptunium.

Acknowledgment.—We cannot adequately acknowledge our indebtedness to many colleagues at Chicago and at other Manhattan District sites who contributed to the background of techniques and ideas underlying the research described here. We have profited from our association with Dr. J. C. Hindman, Mr. T. LaChapelle and Mr. L. B. Magnusson, who were simultaneously investigating the solution chemistry of neptunium. The essential contribution of Dr. W. H. Zachariasen is in part evident from the text. We are indebted to him for his unstinting coöperation and for many helpful discussions. In addition, we wish to express our deep appreciation

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(26) S. Fried and N. Davidson, CN-3053, July 1945, p. 9.

TABLE I

SURVEY OF THE ANHYDROUS COMPOUNDS OF URANIUM, NEPTUNIUM AND PLUTONIUM

Coördinating anion	Uranium	Neptunium	Plutonium
$O^{=}$	UO_3 decomposes to U_3O_8 on ignition above *ca.* 700°		
	Uranyl salts, uranates	Neptunyl salts: $NaNpO_2Ac_3$	Plutonyl salts: $NaPuO_2Ac_3$
	U_3O_8: a mixture of U(IV) and U(VI)[a]		
	UO_2: by H_2 on U_3O_8	Only NpO_2 and PuO_2 obtained by ignition of Np, Pu salts in high pressure O_2 or in air, respectively[b]	
	No U_2O_3	(Np_2O_3: probably very unstable in view of the difficulty in reducing PuO_2 to Pu_2O_3)	Pu_2O_3: by C or Ba reduction of PuO_2 not by H_2 at 1000°[c]
F^-	UF_6: very stable relative to decomposition into UF_4 or UF_5 and F_2	NpF_6	PuF_6: experiments indicate that it exists but is quite unstable[d]
	UF_5: exists only in solid state	(NpF_5: probable)	(PuF_5: ??)
	UF_4: reduced by H_2 (1000°) to:	NpF_4: reduced by H_2 in presence of HF to:	PuF_4: very readily reduced by H_2 or apparently thermally decomposes to:[f]
	UF_3[e]	NpF_3	PuF_3
Cl^-	UCl_6, UCl_5: readily thermally decompose to:	($NpCl_5$ not formed when $NpCl_4$ sublimed in Cl_2)	
	UCl_4: reduced by H_2 to:	$NpCl_4$: reduced by H_2 to:	Evidently no solid $PuCl_4$. May exist in gas phase in presence of Cl_2[g]
	UCl_3	$NpCl_3$	$PuCl_3$
Br^-	No UBr_5		
	UBr_4: reduced by H_2 to:	$NpBr_4$: reduced by Al, and certainly by H_2, and probably also by thermal decomposition to:	No $PuBr_4$
	UBr_3	$NpBr_3$	$PuBr_3$
I^-	UI_4: can be thermally decomposed to:[h]	Probably no NpI_4	
	UI_3	NpI_3	PuI_3
Oxyhalides	UO_2Cl_2, $UOCl_2$	$NpOCl_2$	($PuOCl_2$?)
	Attempts to make UOCl in this laboratory not successful[i]	(NpOCl, NpOBr, NpOI??)	PuOCl, PuOBr, PuOI
$S^{=}$	US_2: U_2S_3 is an electrical conductor and may contain U(IV) and free electrons. US_2 is said to be unstable in presence of H_2 + CS at 1400°C., decomposes to U_2S_3[j]	(NpS_2 ??) Np_2S_3	Pu_2S_3
	UOS	NpOS (Np_2O_2S ??)	Pu_2O_2S

[a] W. H. Zachariasen, CK-2267, Jan., 1945, p. 11. [b] G. H. Moulton, LA-172, Nov., 1944, p. 2. [c] E. F. Westrum, Jr., CN-2159, Oct., 1944, p. 2. [d] A. E. Florin, CN-2159, Oct., 1944, p. 5. [e] British Report (422) CT, J. H. Spencer Palmer, p. 10. [f] Fried, Davidson, ANL-4055, Oct., 1947, p. 5. [g] N. Davidson, CN-3001, May, 1945, p. 4. [h] G. E. MacWood and D. Altman, RL-4.7.600, p. A-7. [i] B. M. Abraham, private communication. [j] L. Brewer, L. A. Bromley, P. W. Gilles and N. Lofgren, CT-2290, Nov., 1944, p. 3.

to Dr. G. T. Seaborg and to Dr. W. M. Manning for encouragement and advice in all phases of this work.

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Summary

A description of the micro-techniques used in the preparation of neptunium compounds is given.

Neptunium trifluoride, tetrafluoride and hexafluoride have been prepared by the following reactions, respectively.

$$NpO_2 + {}^1/_2H_2 + 3HF \longrightarrow NpF_3 + 2H_2O$$
$$NpF_3 + {}^1/_4O_2 + HF \longrightarrow NpF_4 + {}^1/_2H_2O$$
$$2NpF_4 + 3F_2 \longrightarrow 2NpF_6$$

Neptunium tetrachloride was prepared by the action of carbon tetrachloride vapor upon Np(IV) oxalate or neptunium dioxide at 500° in a pyrex X-ray capillary. Reduction of neptunium tetrachloride by hydrogen at 450° yielded neptunium trichloride.

The action of chlorine gas on neptunium tetrachloride at elevated temperatures failed to yield any higher chlorides of neptunium.

Neptunium tetrabromide was prepared by the action of aluminum bromide on neptunium dioxide, and the tribromide by the same reaction in the presence of excess aluminum.

Neptunium triiodide was prepared by the action of aluminum iodide on neptunium dioxide.

Neptunium metal was prepared by action of barium vapor on neptunium trifluoride at 1200°. The density of the metal was determined.

Neptunium metal was found to react with hydrogen to form a hydride.

The reaction of a hydrogen sulfide–carbon disulfide mixture on neptunium dioxide at 1000° for two hours gave rise to neptunium oxysulfide. Prolonged treatment under the same conditions yielded neptunium sesquisulfide.

Ignition of Np(IV) nitrate in 28 atmospheres of oxygen at 400° did not produce a higher oxide of neptunium. Under the same conditions U_3O_8 is converted to UO_3.

Some regularities in the stabilities of compounds of uranium, neptunium and plutonium in their different oxidation states are pointed out.

CHICAGO, ILL. RECEIVED APRIL 12, 1948

[CONTRIBUTION FROM THE LOS ALAMOS SCIENTIFIC LABORATORY, UNIVERSITY OF CALIFORNIA]

The Extraction of Ferric Chloride by Isopropyl Ether. I

BY NORMAN H. NACHTRIEB[1] AND JOHN G. CONWAY[2]

This is the first of several papers in which an account is given of experiments on the extraction of ferric chloride from aqueous hydrochloric acid solutions by diisopropyl ether. Although the extraction has received considerable attention since its discovery by Rothe over fifty years ago[3] a complete explanation of the phenomenon has not yet been given. A considerable number of papers have described applications of the extraction to the separation of iron from other elements in chemical analysis.[4,5,6,7] The extraction is of interest for its own sake, however, for as pointed out by Dodson, Forney and Swift[8] the partition coefficient is a function of the total iron concentration. Sandell[9] also calls attention to this anomaly, in which the efficiency of extraction of ferric chloride by diethyl ether increases with increasing total iron concentration. Kato and Ishii[10] reported the empirical formula of the ether-extracted compound to be $2[FeCl_3 \cdot HCl] \cdot 9H_2O \cdot 15(C_2H_5)_2O$ and proposed a structure for a dimeric molecule in which chlorine was considered to occupy positions corresponding to the apices of tetrahedra around central iron atoms; water molecules were considered to lie along the edges of the tetrahedra with such an orientation as to minimize the dipole moment of the molecule. Axelrod and Swift[11] reported the empirical formula of the iron salt extracted by β,β'-dichlorodiethyl ether as $HFeCl_4 \cdot 4.5H_2O$ and also suggested that the ethereal iron complex was a dimer.

In this first paper general observations are reported on the rate of attainment of equilibrium, the analysis of the ether phase for iron, chloride, ionizable hydrogen and water, the variation of the distribution coefficient with aqueous hydrochloric acid concentration, the temperature dependence of the distribution coefficient, and the absorption spectrum of the ether phase in the visual region.

Experimental

By and large, the analytical procedures of Dodson, Forney and Swift[8] were used. Technical grade isopropyl ether was shaken with alkaline potassium permanganate to destroy peroxides, dried over calcium chloride, and distilled. The fraction boiling between 60.0 and 60.1° at 587.9 mm. was reserved for use. Stock solutions of ferric chloride were prepared from reagent grade $FeCl_3 \cdot 6H_2O$ and standardized by the Zimmerman–Reinhardt and Volhard procedures.[12]

Free acid was calculated from titrations with standard sodium hydroxide by allowing for the quantity of base consumed in the precipitation of iron as hydrated ferric oxide. All extractions were carried out in 100-ml. glass-stoppered cylinders with 50.0 ml. of isopropyl ether and 50.0 ml. of aqueous solution of known ferric chloride and hydrochloric acid concentrations, except as noted. Unless otherwise indicated the extractions were carried out at 25.0 ± 0.1°.

Ether phase aliquots were shaken with distilled water and the determinations of iron and acidity performed on the solutions so derived; this obviated the necessity of removing the ether by distillation and simplified analysis. Macro concentrations of iron were determined by the Zimmerman–Reinhardt procedure, as stated; trace concentrations of iron were determined spectrophotometrically with ortho-phenanthroline.[13] Hydrogen chloride concentrations were calculated by subtracting three times

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[3] J. W. Rothe, *Stahl u. Eisen*, **12**, 1052 (1892).

[4] Langmuir, THIS JOURNAL, **22**, 102 (1900).

[5] Speller, *Chem. News*, **83**, 124 (1901).

[6] R. A. Wolfe and R. G. Fowler, *J. Opt. Soc. Am.*, **35**, 86 (1945).

[7] S. E. Ashley and W. M. Murray, *Ind. Eng. Chem., Anal. Ed.*, **10**, 367 (1938).

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[9] E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience Publishers, New York, N. Y., 1944, p. 28.

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[12] W. C. Pierce and E. L. Haenisch, "Quantitative Analysis," 2nd ed., John Wiley & Sons, Inc., New York, N. Y., 1940, p. 189.

[13] G. F. Smith and F. P. Richter, "Phenanthroline and Substituted Phenanthroline Indicators," The G. Frederick Smith Chemical Co., Columbus, Ohio, 1944, p. 67.