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The Electrolysis of Uranium Halides

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Abstract

The electrolysis of tetra- and tri-halides of uranium in fused salt systems at temperatures from 700° - 900°C has been investigated. Serious losses are caused by reaction with atmospheric oxygen, refractories and electrode materials. The tetra-halides are particularly active as oxidizing agents, even apart from the electrolytic process. The electrolytic behavior of trivalent uranium salts indicates the existence at high temperatures of an oxidation state of uranium lower than U(III).

The Electrolysis of Uranium Halides

Introduction

The general behavior of uranium halides in electrolysis of fused salt electrolytes was investigated. The ultimate purpose of this investigation was to provide information of both practical and theoretical nature which might be applied to the production and refinement of uranium or similar metals in relatively small quantities.

Loss of uranium because of reaction with oxide and silicate refractories or with atmospheric oxygen proved to be very serious. Satisfactory electrode materials are scarce; generally speaking, tungsten is perhaps the best of all.

Electrochemical evidence was found for the existence, at high temperatures, of divalent uranium, or at least for very high solubility of uranium metal in the molten uranium trihalides. Because of this, the trihalides of uranium, preferably dissolved in other fused salts, provide the best electrolyte for the electrolytic preparation of uranium metal.

Experimental

The uranium salts used in this work were the tetrachloride and the tetra- and tribromides. The tetrachloride was supplied by the Ames Laboratory, and the tetrabromide by the Radiation Laboratory at Berkeley. The tribromide was prepared in this laboratory (see "Observations on the Preparation of the Tribromide and Triiodide of Uranium" by E. D. Eastman, B. J. Fontana and R. A. Webster, Paper No. 2

in this volume).

Various halides of the alkali metals or alkaline earth metals were prepared in the anhydrous condition. Where necessary to prevent oxide formation, heating was carried out in a stream of hydrogen halide or in the presence of ammonium halides. Aside from possible loss of uranium by the formation of oxides, the attack on refractory materials by the fused salt baths was in general considerably less in oxide-free systems. All hygroscopic materials were handled in dry boxes.

With regard to refractories, pyrex glass was generally unsatisfactory, even aside from temperature limitations. Silica glass was fairly satisfactory; McDanel porcelain (mullite) was the best of the three materials. Attack of the mullite by a fused uranium tribromide - uranium metal mixture, the most corrosive material encountered, appeared to be limited to a relatively thin surface layer.

The type of electrolytic cell used and the behavior of the electrode materials are described below in the discussion of the individual experiments.

Electrolysis of Uranium Tetrachloride in Fused Salts

Unsuccessful attempts were made to determine the decomposition potential of uranium tetrachloride. A mixture of UCl_4 with 99% of the sodium chloride - potassium chloride eutectic was used at about $750^\circ C$. The electrolyte was contained in a silica glass tube, with a graphite anode inside a porous alumina thimble, and a sheet iron

cylinder cathode outside the thimble. No stable conditions were attained, even after prolonged electrolysis at low voltages. A modified set-up, in which the anode and cathode compartments were reversed (using an iron rod cathode), gave the same results. The salt in the anode compartment probably contained iron after the experiment; no indications of the presence of metallic sodium, potassium or uranium were found on the cathode. In the absence of uranium salt a reasonably sharp and reproducible "decomposition potential" was observed at 2.3 volts.

Electrolysis in the above set-up, or with the uranium salt in the thimble - cathode compartment only, at 6 - 7 volts and 0.8 - 1 ampere for 1/2 to 3/4 hour was attempted next. Metallic sodium or potassium formed at the cathode and burned at the surface of the melt. No metallic uranium was detected. Water-soluble material from both the anode and the cathode compartment was found to contain iron but no uranium. A dark residue, partially soluble in acid (without gas evolution) was recovered from the cathode compartment; it contained uranium and iron. No uranium whatsoever was detected in the anode compartment. Electrolysis at lower voltage (1 hour at 2.0 volts) gave similar results, except that no metallic sodium or potassium was formed.

A blank run was made in which the above conditions were duplicated but no current was passed. The dark, water-insoluble deposit containing mostly iron and some uranium again appeared, while water-soluble uranium and iron were found uniformly distributed throughout the cell..

A blank experiment, in which the uranium salt was omitted, left the iron cathode bright (instead of coated with a dark layer) and no insoluble deposits were formed. A blank experiment in which the uranium salt was present in the thimble, but with electrodes omitted, gave no dark deposits. The latter are formed therefore only in the presence of both metallic iron and uranium tetrachloride, with or without electrolysis.

Molybdenum, tungsten and tantalum were next tried as cathodes for 1 hour at 2.0 volts. In every case a dark material was produced, which dissolved partially with effervescence in warm dilute hydrochloric acid, leaving a black residue which was dissolved only slowly with aqua regia.

A series of runs with a tantalum cathode was made, holding the voltage constant at 0.2 volt intervals between 1.8 and 0.8 volts. The gas evolution observed on treating the cathode material with acid gradually decreased with decreasing voltage and was negligible in the 0.8 volt run. A black insoluble material was formed in every case. A blank run with the tantalum cathode but no current passed also produced a dark residue.

Using a barium bromide bath at about 90°C, electrolyses were run at 1.6, 1.8 and 2.0 volts with a tantalum cathode. Results were the same in each case. Neither the tantalum cathode, nor the material from the cathode compartment gave effervescence with hot water, but both evolved gas when treated with warm, dilute hydrochloric acid.

The acid soluble material was dark brown or black, and a dark and insoluble residue remained.

Electrolysis in Vacuum or Inert Atmosphere

It was felt that part of the changes observed in the above experiments, at least, were caused by the presence of atmospheric oxygen. To avoid them, subsequent experiments were performed either in vacuo or in an oxygen atmosphere. A long silica glass tube was used in the following experiments, with an arrangement which allowed the electrodes and the inner porous thistle to be raised from or lowered into the melt without exposure to the atmosphere. The uranium salt was introduced only into the thistle which served as the cathode compartment.

An electrolysis of uranium tetrabromide in the potassium chloride - sodium chloride eutectic mixture in vacuo was first attempted with a calcium metal anode and tantalum cathode. There was evidence of distillation of the uranium salt from the bath, dissolution of calcium metal in the anode compartment in addition to the anodic formation of calcium ions, and formation of alkali metal in the cathode compartment. After washing with water, the cathode gave a slight effervescence with acid, apparently due to uranium.

Electrolysis of a 5% uranium tetrachloride solution in a sodium chloride - potassium chloride - calcium chloride mixture in an argon atmosphere, using a molybdenum cathode, produced a rough, orange-brown coating on the cathode. It evolved only little gas in water, but

considerably more in dilute hydrochloric acid.

Numerous runs were made with both electrodes made of uranium (separated by a quartz plate instead of the porous thimble) using the sodium chloride - potassium chloride eutectic at 725°C and barium bromide at 900° to 1000°C , with or without added uranium tetrabromide. A coulometer was used in series with these cells, and the electrodes were weighed at the end of the experiments with view to determining changes in oxidation states. Both electrodes lost weight in most of the runs. The cathode weight loss was relatively small but definite. The anode weight changes corresponded to the oxidation states of uranium varying from 2.24 to 5.1. These extremely variable results would indicate, as does the cathode weight loss, that uranium is being oxidized both electrolytically and chemically. The weight lost by the cathode was always smaller in the absence of uranium salt.

At temperatures of about 1000°C , considerable uranium was found to dissolve in the tetrahalides even in the absence of any electrolytic current. The tetravalent state thus appears to be unstable in the presence of excess uranium. Obviously, in the electrolytic process, it is desirable to work with a halide which is stable with respect to the metal. Therefore, experiments with trihalides were attempted next.

Before passing on to these latter experiments it should be mentioned that loss in weight of tungsten, molybdenum and tantalum (increasing in this order) also was observed when these metals were heated

in vacuo in contact with 10% uranium tetrabromide dissolved in barium bromide. With uranium tribromide, none of these metals were attacked appreciably.

Electrolysis of Uranium Tribromide

The product of reaction of uranium tetrabromide with uranium metal at 900°C was used. The reacting proportions corresponded to a Br/U ratio of 1.6, but analysis of the product showed a ratio of 3. The electrolyte was barium bromide containing about 10% of the uranium bromide. The electrodes were both of uranium, separated by a silica plate in a silica glass cell. A current of 0.54 amperes was passed for 33 minutes at a temperature of 870° - 910°C in an argon atmosphere. A fibrous, bronze colored cathode deposit, resembling steel wool in texture, easily identified as metallic uranium was obtained. The deposit weighed only 42 mg, but in every previous electrolysis but one the uranium cathodes had lost weight. Some uranium also appeared loose in the salt. The ratio of faradays passed to gram-atoms of uranium lost at the anode was 1.78 in this experiment.

An electrolysis using 10% uranium tribromide in barium bromide with uranium anode and molybdenum cathode gave a small, spongy, non-adherent deposit of uranium on the cathode after 1 hour at 0.5 amperes and 900°C.

Uranium tribromide prepared from tetrabromide by reduction with hydrogen was electrolyzed in a 4% solution in barium bromide, using uranium electrodes at 900°C. A loose cathode deposit of metallic

uranium was obtained.

The electrolysis of pure, fused tribromide was then attempted, using a tungsten cathode and uranium anode in an argon atmosphere. The first run was made in a silica glass tube at 750°C . About 0.003 faraday was passed at 0.5 amp. per cm^2 , enough to produce nearly 0.5 gram of metal by direct reduction, but no metal was obtained. A second similar run at 850°C in a mullite boat again produced no metal. In a third run, also in a mullite boat, at 750°C , about 0.01 faraday was passed at 1.4 amps per cm^2 . A few small sprigs of metal were found at the cathode and a sandy deposit of metal grains was found extended along the floor of the boat after dissolving out the soluble salts with water.

Several electrolyses were made employing mixtures ranging from 10 to 20 mol % uranium tribromide in strontium bromide at 700°C , in an atmosphere of argon. In each case enough current was passed to reduce all of the tribromide to the divalent state, with sufficient excess to reduce a substantial quantity of the latter to metal. Metal was obtained in every case in the form of fibrous trees which rapidly bridged the electrodes even when the anode was vertically above the cathode. In one experiment, for example, with a mixture of 11.5 mole % uranium tribromide, 1.702 grams of metal was obtained in the form of a loose, fibrous deposit extending nearly the full 3-1/2 inches between the anode and cathode. The anode lost 1.781 grams, and the overall current efficiency in production of metal in this experiment was about 0.22 gram-atom per faraday.

Existence of Divalent Uranium at High Temperatures

The general behavior in electrolysis of systems containing uranium salts, as observed throughout the work reported above can perhaps best be explained on the assumption that a lower-than-trivalent oxidation state of uranium exists in melts in equilibrium with excess uranium metal. Considerable physico-chemical evidence indicating the existence of divalent uranium at high temperatures has been collected and is discussed elsewhere (cf. E. D. Eastman, C. D. Thurmond and R. A. Webster, paper \square in this volume). It should be pointed out, however, that all that has actually been established is an appreciable solubility of metallic uranium in melts containing trivalent uranium. Whether this solubility is due to the formation of divalent uranium, is, of course, open to question. Below, we shall describe experiments which supply additional evidence, electrochemical in nature, bearing on the phenomenon under consideration.

All of the electrolysis experiments to be described below were done in a cell divided into three compartments. The cell consisted of a millite boat in which two porous alundum plates were cemented into place by baking with alundum cement, thus forming three compartments - anode, middle and cathode - of equal size. The electrolyses were all done at about 850°C in an argon atmosphere.

Three experiments were run with all three compartments filled with pure uranium tribromide. In the first experiment, one faraday

per mole of tribromide contained in the cathode compartment (i.e., $1/3$ of total $U\text{Br}_3$ in the whole boat) was passed. No deposit was obtained at the cathode. The uranium anode was smoothly eaten away, and a considerable deposit of metal in the form of small, thin flakes or scales was found in the anode part of the salt. The latter form of metal is that always observed on cooling uranium salt melts in equilibrium with excess metal (cf. paper in this volume). In the second experiment, two faradays per mole of salt in the cathode compartment were passed. Again no deposit was found in the cathode compartment, but a thin deposit of granular metal along the bottom of the middle section was found, with much flaky metal in the salt in the anode compartment. The third run, passing three faradays per mole of salt in the cathode compartment, gave 22 mg of granular metal in the cathode compartment, 10 mg of the same type in the central section, and 800 mg of the metallic flakes in the salt in the anode compartment. The flakes of the anode section appear to be of different origin than the granular deposit found in the other two sections. The flakes are obtained, as previously mentioned, in the presence of excess metal whether current is passed or not.

The above observations are roughly in accord with the idea that all of the uranium in the cathode section must be reduced to the divalent state before any deposition of metal can occur. To make any accurate predictions it must be assumed first, that thorough mixing by convection occurs in the cathode section; and, secondly, that mass flow of liquid through the partitions is negligible. Further, the

amount of uranium passing the porous partition by electrical migration of ions must be known. If the transference number of uranium in the melt is assumed to be 0.5, it should require the passage of 1.2 faradays per mole of UBr_3 in the cathode compartment for the reduction of the uranium originally present, together with that migrating into the cathode compartment, to the divalent state. Under these conditions, then, only current in excess of this threshold should result in deposition of metal on the cathode. The experimental results observed above are in rough agreement with this picture. The total deposit obtained in the third run of three faradays corresponded to considerably less metal than should have been obtained assuming direct reduction to metal from the divalent state. Perhaps loss of metal occurs by dispersion into very fine particles; or, more probably, metal "bridging" partially short-circuits the cell. It should be noted that if a monovalent state had to be formed before the deposition of metal, the threshold value becomes three faradays per mole.

The electrolyses were made in which only the cathode compartment contained uranium tribromide, while the middle and anode sections contained pure strontium bromide. In the first run, 60% of the quantity of electricity required for reduction of all uranium tribromide to the dibromide was passed, and in the second run, 150% of this quantity. No metal could be detected in the cathode part in the first of these experiments. In the second, some fine metallic "wool" was obtained in the cathode section.



Two more electrolyses were made in which the cathode electrolyte was 32% by weight of uranium tribromide in strontium bromide, while the middle and anode sections again contained pure strontium bromide. The theoretical "threshold" in these experiments, as in the previous two is, of course, 1.0 faradays per mole. In the first run, 1.02 faradays per mole of uranium tribromide was passed and, in the second, 2.04. A small tree-like deposit was obtained on the cathode in the first run and a similar larger deposit extending to the dividing partition but not passing through it, was obtained in the second. The first deposit amounted to about 1.7×10^{-4} gram-atom, where 5.9×10^{-4} gram-atom should have been produced by direct reduction from U^{+3} to metal and 0.15×10^{-4} gram-atom of all U^{+3} were first reduced to U^{+2} , and the latter directly reduced to metal. In the second experiment, about 5.7×10^{-4} gram-atom of metal was obtained, where 19.1×10^{-4} should have been obtained by direct reduction, and 14.6×10^{-4} gram-atom by reduction through the divalent state. The somewhat "too large" recovery observed in the first experiment might have been caused by the equilibrium activity of U^{+2} (in the presence of U^{+3} and excess U^{+2}) being less than unity at the temperature of the experiment. The somewhat "too low" recovery in the second experiment would seem to indicate that some univalent strontium may be produced.

These experiments, though only roughly quantitative, indicate, if not in a perfectly straightforward way, the formation of uranium in oxidation states lower than $U(III)$ in electrolysis of fused salts at high temperatures.