# CCCXC.—*The Preparation and Some Properties of Amalgams of Titanium, Uranium, and Vanadium.*

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THE work on metals which are ordinarily very difficult to deposit electrolytically from aqueous solution, and hitherto reported for molybdenum by Merrill and Russell (J., 1929, 2389) and for tungsten by Jackson, Russell, and Merrill (*ibid.*, p. 2394), has now been extended to titanium, uranium, and vanadium. Conditions have been found for the deposition of these metals on a cathode of mercury by the electric current and, to a very small extent, indeed, on certain amalgams, by merely shaking the latter with acidified solutions of salts of such metals. The order has also been determined in which these metals are removed by oxidising solutions from their solution or suspension in mercury, relative to metals such as tin, bismuth, and copper, whose electrode potentials in mercury are accurately known. In no case are the positions those to be expected from a knowledge of the general chemical character of these three metals. In mercury, owing to compound formation, these metals behave less reactively than they do in the free state. The nature of these compounds is at present under investigation by us. The action of these amalgams in assisting the production of hydrogen at a zinc amalgam–dilute sulphuric acid interface has also been investigated.

## EXPERIMENTAL.

*Previous Work on Titanium, Uranium, and Vanadium.*—The only previous work on the electrolytic deposition of titanium is that of Becquerel (*Ann. Chim. Phys.*, 1831, [ii], **48**, 337), who claimed to have deposited the metal with iron on a platinum cathode from a solution of chlorides in hydrochloric acid. Except in presence of iron the deposition failed and this indicated to him that the deposit obtained was an alloy of the two metals. He did not work with a mercury cathode. The only previous work on the electrolytic deposition of uranium from aqueous solution is due to Férée (*Bull. Soc. chim.*, 1901, **25**, 622), who used a mercury cathode, an electrolyte of uranous chloride in hydrochloric acid, and small current densities for long periods. He protected the mercury against attack by chlorine. He found the amount obtained varied capriciously and did not give precise conditions for a positive yield. The only claim to have deposited vanadium from aqueous solution is that of Cowper-Coles (*Chem. News*, 1899, **79**, 147), who electrolysed a solution of sodium vanadate in hydrochloric acid with a platinum cathode. The work was repeated and not confirmed by Borchers (" Elektrometallurgie," Leipzig, 1902, 498) and by S. Fischer (*Trans. Amer. Electrochem. Soc.*, 1916, **30**, 175). Setterberg (*Öfvers. Finska Vet.-Soc.*, 1882, **39**, 10) failed to obtain a deposit of vanadium from aqueous solutions under a variety of conditions. Schicht (*Chem. News*, 1880, **41**, 280; **42**, 331), Gore (" Electrochemistry," London, 1906, 101), and Meyers (*J. Amer. Chem. Soc.*, 1904, **26**, 1124) could not reduce vanadium electrolytically below the bivalent state. The last was the only worker to use a mercury cathode; his electrolyte was sodium vanadate.

*Deposition of Titanium, Uranium, and Vanadium on a Mercury Cathode.*—The essentials for the successful deposition of each of these metals were found to be a high *C.D.* at the cathode, with adequate cooling of the apparatus, and separation of anode and cathode liquids. The cell used was a cylinder of glass 9 cm. long, and of 4 cm. internal diameter, drawn out to a diameter of 1·4 cm. at its base, where the cathode mercury was placed. Inserted in this to a depth of 5 cm. was a cylinder of unglazed porcelain, 9 cm. long and of 2 cm. internal diameter, shut at one end. Both glass and porcelain cylinders were supported vertically on a stand which could be gently rocked during an experiment. The anode was a rectangle of platinum foil, 0·5 cm.$^2$ in area, supported inside the porcelain cylinder 3 cm. above its base. The cathode was about 15 g. of mercury at the base of the glass cylinder. Owing to the heat generated, both glass cell and porcelain cylinder had to be kept cool. The former was cooled on its outside by a continuous stream of water emerging from a series of small holes in a rubber ring which encircled its top, the arrangement being such that every part of the surface was kept continuously wet. A spiral of thin glass through which water circulated, placed inside the porcelain cylinder, served to keep the anode liquid cool.

For titanium the most suitable cathode liquid was found to be a 7% solution of titanous chloride in $2N$-hydrochloric acid, and the best anode liquid $2N$-hydrochloric acid. The *C.D.* at the cathode was best kept at 5 amp./cm.$^2$. With this disposition, 0·2 g. of titanium was deposited in an hour. Variations in the concentration or nature of the acid appeared to be of minor importance, nor had the addition of ferric chloride any noticeable effect.

For uranium, the most suitable cathode solution was uranyl sulphate initially in $2N$-sulphuric acid; the anode liquid was the same acid. The *C.D.* at the cathode was best kept at 6 amp./cm.$^2$. Soon after the electrolysis had begun, the yellow colour of the electrolyte changed to the deep green of uranous sulphate. Later, a suspension, probably of hydrated $U_3O_8$, appeared and the current fell. This was counteracted by gradually increasing the acid strength by dropping concentrated sulphuric acid into the electrolyte. The deposition was slower than that of titanium, about 3 hours being required to obtain 0·5 g. of uranium. Under no condition of arrangement of cell, concentration, and *C.D.* could metal deposition from hydrochloric acid solution be detected, a result directly opposed to Férée's claim. For vanadium, sodium vanadate alone of many vanadium compounds tried was found suitable for the cathode liquid, a result at variance with that of Myers. It was found best to add this salt in fine suspension to $2N$-sulphuric acid to form the cathode liquid. The best anode liquid was found to be $4N$-sulphuric acid, and the best *C.D.* at the cathode from 4 to 5 amp./cm.$^2$. As with uranium, sufficient sulphuric acid was added from time to time to avoid fall of current or formation of a precipitate. The deposition was the slowest of the three, but 0·5 g. could be obtained in 4 hours without difficulty.

The amounts of titanium, uranium, and vanadium deposited were determined by analysis of the electrolyte before and after the experiment; also by dissolving the metals completely from the mercury by acidified permanganate, reducing them to the titanous, uranous, and (bivalent) vanadous states and at the same time removing dissolved mercury by shaking with zinc amalgam, and titrating with permanganate.

*Some Properties of the Amalgams.*—Each of the three metals was found to be 100% efficient as a reducing agent when shaken vigorously with acidified permanganate, dichromate, or ferric sulphate, *i.e.*, the weight of metal oxidised was exactly equivalent to the concentration of oxidant reduced. In such reductions the mercury was unchanged ultimately. (At first, mercury would be oxidised simultaneously with, say, titanium, but on further shaking the mercuric ions would be reduced to metal by the titanium.) Titanium in its amalgam was found to be oxidised to the titanic state by acidified permanganate, dichromate, quinquevalent vanadium, and ferric sulphate, but not beyond the titanous state by copper sulphate in sulphuric acid, the vanadium being then reduced to the quadrivalent state and the cupric ion to the metal. Uranium in its amalgam was less powerful. There was no appreciable oxidation of it by acidified copper sulphate. It was oxidised to the uranyl state by permanganate and by dichromate, but only slowly beyond the uranous state by quinquevalent vanadium, and not at all beyond uranous by ferric sulphate. Vanadium amalgam was very similar in its reducing action to that of titanium.

Each of the metals in its amalgam was found to be completely insoluble in mercury when the amalgam was passed more than once through a ground-glass filter of the Gooch type with pores just sufficiently large to allow mercury to pass freely when the arrangement was attached to an ordinary water-pump. In each case, the mercury which passed was found to be free from the other metal, as shown by attempts to detect them by any oxidation method or by the more sensitive catalytic test to be described.

The actions of titanium, uranium, and vanadium in assisting the production of hydrogen at a zinc amalgam–dilute sulphuric acid interface were investigated by the method of Russell and Rowell (J., 1926, 1885). The concentrations of sulphuric acid below which bubbles of hydrogen failed to appear within a minute when the acid was poured on to a 1% zinc amalgam containing titanium, uranium, or vanadium were found to be 0·0025, 0·01, and 0·025$N$ respectively. Titanium, thus, has an effect comparable with platinum, tungsten, and molybdenum, and vanadium is least catalytic. By diluting a known weight of titanium with mercury it was found that approx. $10^{-6}$ g. of titanium in 200 g. of mercury gave a detectable catalytic effect when a 1% zinc amalgam was covered with $2N$-sulphuric acid. The corresponding figure for both uranium and vanadium was found to be $10^{-5}$ g.

*Deposition of Metallic Titanium, Uranium, and Vanadium on Zinc and Other Amalgams by Displacement.*—The common metals of the B sub-group of the periodic classification may be divided sharply into two groups with regard to the behaviour of their ions in sulphuric acid solution towards zinc amalgam. The ions of tin and less reactive metals are quantitatively reduced to the metallic state by the amalgam; those of metals more reactive than tin are not reduced in detectable quantity. With titanium, uranium, and vanadium, however, as has been previously shown with tungsten and molybdenum (Russell and Rowell, *loc. cit.*), a very small concentration of the ions present was found to be reduced to the metallic state in certain circumstances and after very vigorous shaking. As with tungsten, the concentrations of uranium and vanadium so deposited were below those detectable by known chemical tests, but were easily detectable by the catalytic action of the metal described above. On the other hand, the small concentrations of titanium and of molybdenum similarly deposited were just detectable by sensitive chemical tests.

The procedure with zinc amalgam was as follows. Half of the amalgam was very vigorously shaken by hand for two minutes with a sulphuric acid solution of the ions of the metal under examination in a stoppered bottle. The other half was shaken equally vigorously for the same time with a solution of $2N$-sulphuric acid. The amalgams were then freed from their solutions by decantation, washed with distilled water, and covered with $2N$-sulphuric acid. The blank amalgam showed after a minute no bubbles of hydrogen, or perhaps a few bubbles only. The other, if traces of a metal which was catalytic had been deposited on it, showed a vigorous effervescence of hydrogen. Of the three metals, titanium, uranium, and vanadium, the second was most easily deposited by this shaking method, but, compared with tungsten and molybdenum, the amount deposited appeared to be very small. With titanium and vanadium, it was only after vigorous and prolonged shaking, that the deposition of these metals in this way was established. (Care had been taken to ensure that the solutions shaken with the zinc amalgam contained no traces of tungsten, molybdenum, or uranium, and that the amalgam itself was free from other catalytic metals.) Whenever the deposition had been established on zinc amalgam it was sought to establish it on amalgams of less reactive metals, such as tin and copper, and finally on mercury itself. In these attempts one-half of the amalgam or of the mercury was vigorously shaken with the solution to be tested, and the other similarly with dilute sulphuric acid. The amalgams or the mercury were then separated from the liquids with which they had been shaken, and well washed. Small quantities of zinc were added to all, and the amalgam was covered with $2N$-sulphuric acid. The presence of a uniform layer of bubbles, like pin-points, which formed within a minute on the surface of the amalgam that had been shaken with the ions of the solution to be tested, as contrasted with absence of bubbles on the blanks, was taken as evidence that traces of catalytic metal had been deposited on the amalgams or mercury. In this way, it was shown that titanium and uranium, but not vanadium, were deposited in traces on pure mercury and on copper and tin amalgams as well as on the more reactive zinc amalgam. Uranium was deposited most quickly and obviously of the three, and vanadium least, or not at all, on the amalgams tried. The concentrations of sulphuric acid below which bubbles failed to appear when zinc was added to an amalgam or to mercury shaken as described with solutions of titanium, uranium, and vanadium, were 0·0025, 0·01, and 0·025$N$ respectively. These values are identical with those obtained with the metals deposited electrolytically, and indicate that the catalytic effect produced is not due to the presence in the solutions of titanium, uranium, and vanadium of some common impurity which happens to be deposited on mercury and more reactive metals.

Whereas with tungsten and molybdenum, solutions of different salts so far tried appeared to give equally well a deposit of traces of the metal, there were marked differences with titanium. Mass for mass, the most active titanium solutions for this purpose were those of the sulphate in sulphuric acid which had been reduced by zinc and oxidised by permanganate more than once. When this solution was shaken vigorously with a pure zinc amalgam, sufficient titanium to give a marked evolution of hydrogen was deposited on the zinc. Often with more concentrated solutions, *e.g.*, with the 15% solutions of titanous sulphate and chloride supplied commercially, the catalytic effect produced was markedly less, although never zero. A precipitate of pure titanous hydroxide, freshly dissolved in hydrochloric or sulphuric acid, gave hardly more than a trace of catalytic effect. It was diluted and allowed to stand for some weeks, whereupon it hydrolysed, forming a deposit. This gave a vigorous catalytic effect when shaken with zinc amalgam. The cause of these variations is under investigation. Possibly a certain kind of ion capable of immediate reduction to the metallic state is formed in some solutions in greater concentration than in others. Similar variations were not observed with different uranium solutions; the deposition was obtained equally well from uranyl nitrate, chloride, and sulphate. With all vanadium solutions the catalytic effect was very hard to substantiate. Sodium vanadate in sulphuric acid seemed the least unsuitable solution for the purpose.

With tungsten and molybdenum, the deposition of traces of the metal on zinc amalgam began immediately the solution and the amalgam had been brought in contact; it is not an effect which occurs after the solutions have been reduced to the quadrivalent and tervalent states respectively, *i.e.*, the states of oxidation below which it has hitherto been thought that these solutions cannot be reduced by zinc or its amalgam. With titanium, uranium, and vanadium, the difficulty or slowness of deposition is so great that it cannot be said whether or not it occurs before the reduction to the tervalent, tervalent, and bivalent state of oxidation respectively.

It was expected that solutions of chromium and manganese salts when shaken with zinc amalgam would give sufficient deposition of the metal to be identified by catalytic action. These metals are similar in chemical character to vanadium, titanium, and molybdenum, and their deposition at a mercury cathode by the electric current is much more easily accomplished. An extended series of experiments with different chromium and manganese salts in solution failed to give the slightest trace of catalytic activity, however. The catalytic action of chromium deposited by electrolysis is doubtful, but manganese so deposited is a good catalyst (Russell and Rowell, *loc. cit.*). It would therefore appear that manganese is not deposited in traces by shaking, as are the other metals mentioned.

The ordinary chemical tests available for tungsten, uranium, and vanadium were insufficiently sensitive to identify the quantities of these metals deposited on zinc amalgam by shaking. This was possible, however, with molybdenum and titanium, and a rough estimate of the masses of these metals deposited on a 1% zinc amalgam by shaking it for 2 minutes with 100 c.c. of $N/10$-molybdenum or titanium ion in sulphuric acid was made. The amalgam on which the molybdenum had been deposited was shaken with excess of permanganate to oxidise the molybdenum completely in addition to the zinc. Molybdenum was determined in this solution colorimetrically by the addition of potassium cyanate and a fragment of zinc. The mean value obtained in a few experiments was approx. $10^{-5}$ g. Titanium was determined in a similar experiment by Das Gupta's method (*J. Indian Chem. Soc.*, 1929, **6**, 763). The mean value obtained in a few experiments was also approx. $10^{-5}$ g.

*Order of Removal of Titanium, Uranium, and Vanadium from Mercury by Oxidising Solutions.*—This work is a continuation of previous work summarised by Russell (J., 1929, 2398) and carried out by his methods. Titanium was oxidised after tin and lead and before bismuth and copper, uranium after iron and molybdenum and before cobalt and mercury, vanadium after titanium and before bismuth. The experiments to settle this order were easily carried out as soon as amalgams containing quantities of approx. 0·5 g. of titanium, uranium, or vanadium had been prepared. The behaviour of titanium amalgam towards oxidising agents described above suggested that titanium would probably be removed from mercury after tin and lead. An amalgam containing 0·5 g. of tin or lead and 0·5 g. of titanium was oxidised by acidified permanganate, dichromate, or ferric sulphate. The tin or the lead was found to be responsible for the whole of the reduction so long as a quantity in excess of a few mg. was present. When similar weights of bismuth or copper replaced the tin, the titanium did the whole of the reduction until its concentration had been reduced to a very small weight. As tin is known to precede lead, and bismuth copper, the order of removal becomes tin, lead, titanium, bismuth, copper. A similar series of experiments with an amalgam of uranium containing 0·5 g. of the metal in 200 g. of mercury mixed with similar quantities of iron, molybdenum, and cobalt, placed uranium after the first two and before the third. Analogous experiments with an amalgam of vanadium suggested that its position was very similar to that of titanium, and just inferior in the series. As with titanium, the positions assigned to uranium and vanadium are consistent with the behaviour of amalgams of these metals towards oxidising agents, a short account of which has been given above. The complete order of those metals investigated (omitting chromium, the redetermination of which is the subject of another investigation) is given in the summary.

### *Discussion of Results.*

The positions found for the three metals under investigation are not, of course, their positions in the free state because, if they were, ions of all three should be completely reduced to the metallic state by contact with zinc, just as are those of tin, bismuth, or copper. Uranium, for example, from its position appears hardly more reactive than mercury, yet uranyl ions are only reduced to the tervalent state by zinc after prolonged shaking, and are not reduced below the quadrivalent state by shaking with tin. The electrode potentials of titanium, uranium, and vanadium have not yet been accurately determined, but it is clear from observations on these metals in the literature that all are more reactive than tin, and this statement is consistent with the great difficulty experienced in reducing their ions by zinc below the tervalent, tervalent, and bivalent states, respectively, and possibly also with the difficulty in depositing them by the current. These metals, like other transition and pre-transition metals investigated (chromium, manganese, iron, nickel, cobalt, molybdenum, and tungsten), behave passively in mercury, effects most probably to be ascribed to compound formation. A preliminary account of some of these compounds has already been given by one of us (*Nature*, 1930, **125**, 89) and a full account will be published in due course.

The inversion of the ordinary phenomenon of displacement, *i.e.*, the deposition of traces of titanium and uranium on less reactive metals like copper and mercury by mere contact of one of the latter with solutions of salts of the former, is a rare occurrence. Von Hevesy (*Phil. Mag.*, 1912, **23**, 628) showed a similar effect by a radioactive method. He deposited radioactive isotopes of lead and bismuth, presumably as metal, on noble metals such as platinum, gold, mercury, and copper, in some cases quantitatively. He showed also that any radio-element, however reactive, could be deposited on a noble metal to a very small extent by mere contact of a solution of a salt of the former with the latter. These observations, as he showed, are consistent with Nernst's theory of electrode potentials. In the cases under investigation, the amounts of reactive metals deposited, *viz.*, $10^{-6}$ to $10^{-5}$ g., are greater than the mass of the surface layer permitted by Nernst's theory if the deposited metal forms no compound with the mercury, copper, or other metal. But there is no doubt that compound formation does occur with consequent removal of the surface layer of pure metal. It should thus be possible by sufficiently long and vigorous shaking to obtain masses of deposited metal identifiable by ordinary chemical tests.

If catalytic action is to occur, the deposited metal must form a separate phase in the mercury, and therefore must be deposited in excess of its solubility in mercury. Of the transition and pre-transition metals investigated, manganese alone has been found to possess a detectable solubility (approx. 0·001%) at ordinary temperature. It alone of the metals which are known to have a detectable catalytic action fails to show it when deposited by the shaking method. This is understandable because the amount of metal deposited by shaking as at present carried out is well below the limit of solubility of manganese. This argument cannot apply to chromium, the other metal which shows no catalytic action on shaking, but there the explanation is that the metal in no circumstances shows the usual catalytic action.

The present work is being extended by a study of compound formation of metals in mercury and of solubilities of transition and pre-transition metals therein.

## *Summary.*

1. Conditions for the electrolytic deposition of titanium, uranium, and vanadium from aqueous solutions on a mercury cathode have been investigated. High current densities at the cathode, separation of cathode and anode liquid, an efficient system of cooling, and proper choice of cathode electrolyte are essential. The most suitable of the last are titanous chloride in hydrochloric acid and uranyl sulphate or sodium vanadate in sulphuric acid.

2. The catalytic action of these three metals on the production of hydrogen at a zinc amalgam–dilute sulphuric acid interface has been investigated. Titanium is nearly as good a catalyst as platinum, tungsten, and molybdenum, and better than uranium, which, in turn, is better than vanadium.

3. Traces of metallic titanium, uranium, and vanadium have been deposited on zinc amalgam, and the first two, in addition, on tin and

copper amalgams and on mercury, by merely shaking solutions of salts of these metals with the amalgams or mercury. The quantity deposited is approx. $10^{-6}$ to $10^{-5}$ g., and its presence is demonstrated by catalytic action. Uranium is most easily deposited in this way, and vanadium with most difficulty. Titanium, alone of the three, has been identified also by chemical tests.

4. The order of removal of titanium, uranium, and vanadium from mercury by oxidising agents has been determined with respect to metals whose positions are known from earlier work. The order now is Zn, Cd, Mn, Tl, Sn, Pb, Ti, V, Bi, Cu, Fe, Mo, U, Co, Hg, Ni, W. Titanium and vanadium lie close together in this order and well above uranium.

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