

experiments designed to test the effect of carrier on the separation.

The data plotted in Fig. 8 are representative of the results of this series of experiments. As in the IR-1 experiments, the separation is decreased by the presence of carrier. However, the effect is much less pronounced in this case. It was the results of these experiments which led to the use of Dowex 50 for rare earth separation.<sup>4</sup> Not only is the degree of separation obtained by its use with trace quantities of rare earths many times greater than that obtained with IR-1, but also the effect of carrier is much less than the effect with IR-1, as may be seen by comparing the results of these two series of experiments. The column used in the Dowex 50 series was longer (although it had only a slightly larger volume) than that used with IR-1, so that quantitative comparison of the two series is not possible; however, the qualitative difference is obvious. The results of many subsequent experiments on gram quantities of rare earths have amply demonstrated the superiority of Dowex 50.

### Summary

The effects of several variables on the efficiency of an ion-exchange column for the applications of volume reduction and separation of several cationic fission products have been studied.

When the flow rate per unit area was held constant at 1.0 ml./sq. cm./min., the column area was

found to affect the width of the elution curve. The effect of column length on the width of the elution curve differed slightly from that predicted from theoretical considerations. Flow rate was an important factor in both volume reduction and separations column applications. The original form of the resin was found to be important. For obtaining the maximum volume reduction factor, it should be in the hydrogen form initially, and the elution of rare earths should be made with citrate at a pH of 3.3-3.5. These conditions are not optimum for separations. For this purpose it is preferable to elute the mixture of rare earths from a column of resin in the ammonium form using citrate at a lower pH. Addition of carrier had a deleterious effect on the separation of solutes. This was very pronounced when amberlite IR-1 was used, but was much less pronounced when Dowex 50 was employed.

The results of this investigation, together with data obtained previously, were used as a basis for the design of an ion-exchange column apparatus for separating and purifying fission products. The principles involved in this apparatus are applicable for the separation of other substances. The results of these experiments aid in the interpretation of the theory of ion-exchange column operation.

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## Chemistry of Aqueous Uranium(V) Solutions. I. Preparation and Properties. Analogy between Uranium(V), Neptunium(V) and Plutonium(V)<sup>1</sup>

BY KURT A. KRAUS, FREDERICK NELSON AND GORDON L. JOHNSON

### 1. Introduction

On the basis of rather detailed polarographic studies of uranium(VI) it has been concluded recently<sup>2,3,4</sup> that uranium(VI) can be reduced to uranium(V) at the dropping mercury electrode and that the electrode reaction for the first reduction wave (which occurs at about -0.180 v. vs. the S. C. E.) is



The formula  $\text{UO}_2^+$  for the uranium(V) ion in

(1) This document is based on work performed under Contract Number W-7405 eng 26 for the Atomic Energy Project at Oak Ridge National Laboratory. Part of this work has previously been published in the project reports Mon N-161 (August, 1946), Mon N-176 (September, 1946) and Mon N-194 (October, 1946). This paper was presented in part at the Meeting of the American Chemical Society, March 28, 1949.

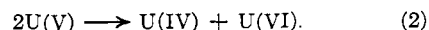
(2) W. E. Harris and I. M. Kolthoff, *THIS JOURNAL*, **67**, 1484 (1945).

(3) H. G. Heal, Report MC-95, October, 1944, *Nature*, **157**, 225 (1946).

(4) For summary of the polarographic work on uranium see references (1) and (2).

acid solutions was deduced from the acid independence of the U(V)/(VI) half-wave potential assuming  $\text{UO}_2^{++}$  as the formula of uranium(VI). Reaction (1) was shown to be reversible at the d. m. e. since  $\log i/(i_t - i)$  changes linearly with  $E$  (where  $i_t$  is the diffusion current and  $i$  the current at voltage  $E$ ) and since the line has a slope of close to the theoretical value 0.059 for an electrode reaction involving a one-electron change.

Harris and Kolthoff,<sup>2</sup> and Heal,<sup>3</sup> felt that  $\text{UO}_2^+$  exists only as a transient species which is too rapidly destroyed through the disproportionation reaction



to permit preparation of uranium(V) solutions of reasonable concentration.

Approximately simultaneously with this work on uranium(V) the +5 oxidation states of the elements neptunium and plutonium had been observed, and it had been concluded that these ions exist also as the species  $\text{XO}_2^+$  in acidic solu-

tions.<sup>5,6</sup> Similarly, it was found from potential measurements that the systems  $\text{XO}_2^+ - \text{XO}_2^{++}$  behave reversibly at a platinum electrode.

However,  $\text{NpO}_2^+$  is stable even in strongly acid solutions,<sup>7</sup> and  $\text{PuO}_2^+$ , although rapidly disproportionating at high acidities, can readily be prepared and kept for long periods of time at low acidities.<sup>8</sup>

In general the stability of these  $\text{XO}_2^+$  ions can be shown to increase with decreasing acidity and an optimum stability can be predicted for the  $\text{pH}$  range 2 to 4. Since in addition the rates of disproportionation were also expected to decrease with decreasing acidity the optimum conditions for the preparation of uranium(V) solutions appeared sufficiently well established to make a search promising.

**2. Analogy between Uranium, Neptunium and Plutonium. Optimum Stability Range of Uranium(V).**—It is now generally agreed that most elements in the last row of the periodic table form a rare earth type group of very similar properties, although there is some doubt as to the exact beginning of this series. The very great similarity between uranium and the trans-uranic elements leaves little doubt that surely these elements must be members of such a series.<sup>9</sup>

Uranium, neptunium and plutonium exist with oxidation numbers 3, 4, 5 and 6 in aqueous solutions. There is little doubt that the corresponding species<sup>10</sup> in acid solutions (*e. g.*, 1  $M$   $\text{HClO}_4$ ) are  $\text{X}^{+3}$ ,  $\text{X}^{+4}$ ,  $\text{XO}_2^+$  and  $\text{XO}_2^{++}$  whose properties for the various elements are very similar. The elements differ primarily in the values of the oxidation-reduction potentials of the various couples and consequently also in the relative stability of these ions with respect to disproportionation reactions.

The  $\text{X(V)}$  ions can be considered thermodynamically stable with respect to disproportionation if the difference in the half cell potentials  $\Delta E = E_{56} - E_{45}$  for the  $\text{X(V)}/(\text{VI})$  and  $\text{X(IV)}/(\text{V})$  couples is negative.

(5) T. J. LaChapelle, L. B. Magnusson, Report CN-3053, June, 1945.

(6) K. A. Kraus and G. E. Moore, Reports CL-P-395, March, 1945, Mon N-249, February, 1947.

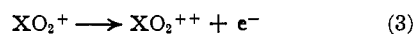
(7) L. B. Magnusson, J. C. Hindman and T. J. LaChapelle, Report ANL-WMM-115, December, 1946.

(8) L. H. Gevantman and K. A. Kraus, Report Mon N-80, May, 1946.

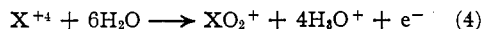
(9) The similarity in properties does not extend to Pa(V) whose properties appear to be much more similar to Ta(V) and Cb(V) than to U(V), Np(V) and Pu(V).

(10) These species are more properly represented as their aquo-complexes  $\text{X}(\text{H}_2\text{O})_i^{+3}$ ,  $\text{X}(\text{H}_2\text{O})_j^{+4}$ ,  $\text{XO}_2(\text{H}_2\text{O})_k^+$  and  $\text{XO}_2(\text{H}_2\text{O})_m^{++}$  where probably  $i = 8$ ,  $j = 8$ ,  $k = 6$ , and  $m = 6$ . However, in order not to encumber the equations unduly the simpler symbolism has been used in this paper. The tentative assumption,  $m = 6$ , rests primarily on the facts that uranyl ions tend to form hexahydrates, and that in certain U(VI) salts (uranates and  $\text{UO}_2$ ) the  $\text{UO}_2$  group is surrounded by six equidistant oxygens, as discussed in an earlier paper.<sup>17</sup> The assumption  $k = m$  is suggested from the reversibility of the  $\text{X(V)}/(\text{VI})$  potentials and from the fact that the differences in the hydrolytic properties of the  $\text{X(V)}$  and  $\text{X(VI)}$  ions are as expected from the differences in charge of the ions.<sup>11</sup>

In 1  $M$  acid, where the reactions



and



apply, only neptunium(V), of the elements under consideration, fulfills this condition ( $E_{56} = -1.135$  v.,  $E_{45} = -0.737$  v. in 1  $M$   $\text{HCl}$ .<sup>7,11</sup> For uranium  $E_{56} = -0.06$  v.<sup>2</sup> and  $E_{45}$  can be calculated using  $E_{56}$  and the potential  $E_{46}$  of the U(IV)/(VI) couple, whose value is quite uncertain under conditions where complexing is at a minimum. There are no values for 1  $M$  perchloric acid and values in 1  $M$   $\text{HCl}$  range from  $-0.59$  v.<sup>12</sup> to  $-0.33$  v.<sup>13</sup> Using the latter value  $E_{45} = -0.60$  v. and  $\Delta E = 0.54$  v. are found, indicating that uranium(V) is thermodynamically the least stable of these three elements in 1  $M$  acid, though only by 0.27 v. less stable than plutonium(V) ( $E_{56} = -0.93$  v.,<sup>6</sup>;  $E_{46} = -1.067$  v.,<sup>14</sup>  $E_{45} = -1.20$  v. for 1  $M$   $\text{HClO}_4$ ).

As indicated by equations (3) and (4),  $E_{56}$  is independent of acidity,  $E_{45}$  varies with the 4th power of the acidity (becoming more positive at the rate of  $4 \times 0.059$  v./ $\text{pH}$ ) and thus  $\Delta E$  becomes less positive with increasing  $\text{pH}$ , *i. e.*, the species  $\text{XO}_2^+$  more stable.

These acid-dependencies will pertain as long as equations (3) and (4) represent the half cell reactions. This in turn depends on the hydrolytic properties of the various oxidation states involved.

The +4 oxidation states of uranium and plutonium have been found to hydrolyze near  $\text{pH}$  1 according to the equation



the  $\text{pK}$  values for the reactions being 1.45 and 1.55 for uranium(IV) and plutonium(IV), respectively, at an ionic strength of 0.5 ( $\text{NaClO}_4$ ).<sup>15</sup> Near  $\text{pH}$  1.5, plutonium(IV) ( $2 \times 10^{-4}$   $M$ ) undergoes very rapid further hydrolysis to a polymer<sup>16</sup> whose approximate composition is  $\text{Pu}(\text{OH})_4$ , the rate of polymerization increasing with increasing concentration and  $\text{pH}$ . Precipitation of the hydroxide occurs at somewhat higher  $\text{pH}$ . Uranium(IV) behaves very similarly except that its rate of polymerization may not be very rapid even near  $\text{pH}$  2 for *ca.*  $10^{-3}$   $M$  solutions.<sup>15</sup> There is no evidence for a hydrolysis product intermediate between  $\text{XOH}^{+3}$  and the polymer nor is there evidence for amphoteric character of the hydroxides. There are no hydrolytic data on neptunium(IV), although its properties almost certainly are intermediate between uranium(IV) and plutonium(IV).

The ions  $\text{NpO}_2^+$  and  $\text{PuO}_2^+$  have been found<sup>17</sup>

(11) Since these elements form only weak chloride complexes the potentials in 1  $M$   $\text{HClO}_4$  and 1  $M$   $\text{HCl}$  are probably very similar.

(12) J. J. Howland, Report CN-2445, January, 1945.

(13) J. K. Taylor and E. R. Smith, Report A-1972, August, 1944.

(14) J. C. Hindman, Report CN-2289, November, 1944.

(15) K. A. Kraus and F. Nelson, Report ORNL-23, March, 1948.

(16) K. A. Kraus, Report CN-2289, November, 1944.

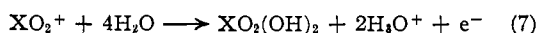
(17) K. A. Kraus and F. Nelson, Report CNL-19, February, 1948.

to hydrolyze according to the equation



with  $pK$  values *ca.* 8.9 and 9.7 for neptunium(V) and plutonium(V), respectively. Formation of negative species appears to occur between  $pH$  9 and 10. By analogy one would expect that the corresponding  $pK$  value for  $\text{UO}_2^+$  would be *ca.* 8 and that at  $pH$  somewhat above 8 negative species (*e. g.*,  $\text{UO}_2(\text{OH})_2^-$ ) would be formed.

The hydrolytic properties of the  $\text{XO}_2^{++}$  ions are not well understood. Their hydrolysis is concentration dependent and there is little doubt that polymerization reactions occur.<sup>16,18,19</sup> Without going into the mechanism of hydrolysis, one could summarize that for  $10^{-3} M$  solutions, the ions are 50% hydrolyzed (*i. e.*, have the average formula  $\text{XO}_2(\text{OH})_{0.5}^{1.5}$ ) near  $pH$  4, 4.7 and 5.4 for uranium(VI), neptunium(VI) and plutonium(VI), respectively.<sup>15</sup> At somewhat higher  $pH$  the average formula approaches  $\text{XO}_2(\text{OH})_2$  and the half-cell reaction can be approximated by the equation



Hydrolysis of the hydroxides to negatively charged species appears to occur between  $pH$  8 and 10.

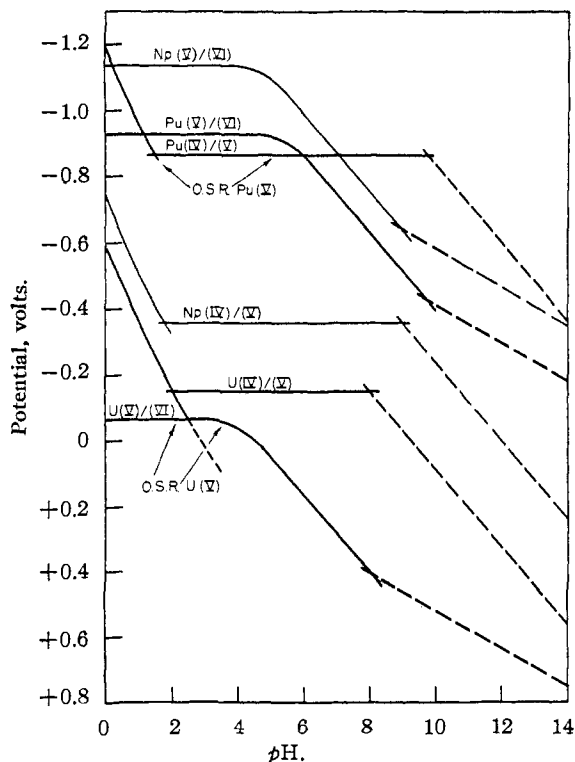


Fig. 1.—Potentials of X(IV)/(V) and X(V)/(VI) couples; optimum stability range of  $\text{XO}_2^+$ .

(18) D. A. MacInnes and L. G. Longworth, Report MDDC-911, November, 1942.

(19) J. Suttén, Report CRC-325, March, 1947.

On the basis of these hydrolytic and potential data the potential diagrams of Fig. 1 for the X(IV)/(V) and X(V)/(VI) couples were constructed. It can be seen that both potentials for the three elements are  $pH$  independent between  $pH$  2 and 4 (or 5) the half cell reactions being



and equation (3). In this region (the optimum stability range, O. S. R.)  $\Delta E$  is most negative and the thermodynamic stability of the ions  $\text{XO}_2^+$  at a maximum. It should be noticed that the O. S. R. of uranium(V) has been drawn to begin at a higher  $pH$  than that of plutonium(V) in view of the greater "reluctance" of uranium(IV) to form a polymer. As a result the greater instability of  $\text{UO}_2^+$  (compared with  $\text{PuO}_2^+$ ) in acid solutions becomes at least partially compensated. The strongly  $pH$  dependent U(IV)/(V) potential approaches the U(V)/(VI) potential over a longer  $pH$  range, thus considerably increasing the stability of  $\text{UO}_2^+$  over what would be expected if the hydrolysis of uranium(IV) were exactly like that of plutonium(IV) (for further discussion see also section 3.2). On the other hand, because of the differences in the hydrolysis of the X(IV) and X(VI) ions the O. S. R. of uranium(V) is considerably shorter than that of plutonium(V).

Consideration of the disproportionation rates also pointed to the possibility of finding a reasonably stable uranium(V). The rate of disproportionation of plutonium(V) was found<sup>8</sup> to decrease with decreasing acidity and the same was therefore expected for uranium(V). The observation of Koltzoff and Harris,<sup>20</sup> that at very high acidity the diffusion current of the U(V)/(VI) wave increases over its (constant) value at low acidities due to increasingly rapid disproportionation of uranium(V), to a certain extent substantiated the analogy. Heal<sup>3</sup> through study of the Becquerel effect came to the same conclusion and suggested that the rate of disproportionation of uranium(V) decreases approximately linearly with acidity.

### 3. Preparation and Properties of Solutions of $\text{UO}_2^+$

**3.1. Analytical Procedure, Equipment and Materials.**—The fact that the U(V)/(VI) couple behaves reversibly at the dropping mercury electrode<sup>2,3</sup> makes available a rather simple analytical procedure for  $\text{UO}_2^+$ .

The first wave in the polarogram of uranium(VI) results from the reduction of  $\text{UO}_2^{++}$  to  $\text{UO}_2^+$ . The mercury drop is thus the cathode and the cathodic diffusion current  $i_c$  (corrected for residual current) is proportional to the concentration of  $\text{UO}_2^{++}$ . Polarograms of  $\text{UO}_2^+$  solutions would show a very similar wave due to the oxidation of  $\text{UO}_2^+$  to  $\text{UO}_2^{++}$ . The direction of the current would

(20) I. M. Koltzoff and W. E. Harris, THIS JOURNAL, **68**, 1175 (1946).

be reversed, however, the mercury drop now being the anode. The (corrected) anodic diffusion current  $i_a$  would be proportional to the concentration of  $\text{UO}_2^+$ . In mixtures of  $\text{UO}_2^{++}$  and  $\text{UO}_2^+$  the wave would have both anodic ( $i_a$ ) and cathodic ( $i_c$ ) components, each in turn being proportional to the concentration of  $\text{UO}_2^+$  and  $\text{UO}_2^{++}$  (see also Fig. 3). The three types of waves (anodic, cathodic and mixed) would thus all be similar, would have the same shape and half-wave potential and would differ primarily in their displacement from the zero-current line.

One would also expect, in general, a difference in height of the anodic and cathodic waves at constant uranium concentration because of differences in the diffusion current constants  $K_5$  and  $K_6$  of uranium(V) and uranium(VI). Actually, as will be discussed below, no significant difference was found and for all calculations  $K_5 = K_6$  was assumed.

For the early polarographic work a Heyrovsky, Model XII, polarograph was used, and for the later work a Sargent, Model XX1, recording polarograph. All work was carried out in a constant temperature room at  $25 \pm 0.5^\circ$ , the temperature of the solutions measured, and the diffusion currents "normalized" to  $25.0^\circ$ , assuming a temperature coefficient of 0.015 per  $^\circ$ . Practically all work was carried out at a dilution where no maxima occurred in the polarograms and therefore no maximum suppressor was used.

The reference (non-polarizable) electrode was a silver strip on which silver chloride had been deposited electrolytically. This reference electrode was very satisfactory and kept a constant reference potential for a period of months.

To keep mixing of the solutions at a minimum the reference electrode was separated from the electrolysis compartment by a partially greased closed stopcock.

This arrangement is illustrated in Fig. 2 which shows a diagram of a combined polarograph and electrolysis cell. A mercury pool with large surface was used as anode which yielded insoluble mercurous chloride on oxidation. The anode compartment was filled with the same "supporting" electrolyte as the cathode compartment (e. g., 0.1  $M$  KCl) and the two compartments were separated by a sintered glass disk. A large sheet of platinum served as cathode. Using this arrangement, 0.1  $M$  KCl as electrolyte, and a cathode compartment of 7.5 sq. cm. cross-section, electrolyses were carried out at *ca.* 5 mamp. with an applied potential of *ca.* 0.6 v. For some work the polarograph cell was similarly constructed, but without an electrolysis compartment in order to prevent slow changes in uranium concentration through diffusion across the sintered glass disk. The uranium(V) solutions were then prepared in a separate electrolysis cell and jetted with nitrogen into the polarograph cell.

All equipment and solutions were carefully

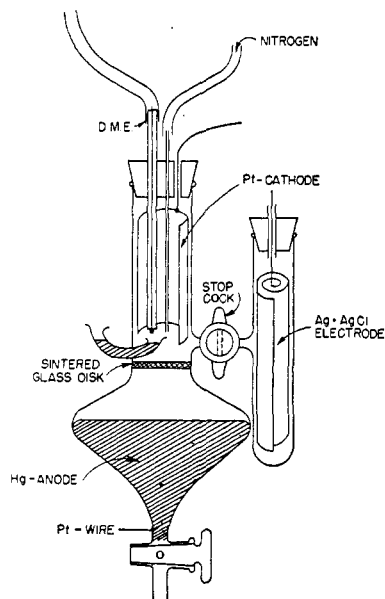


Fig. 2.—Apparatus for electrolysis and polarography.

freed of oxygen by a stream of nitrogen which was purified by passing it over copper turnings at *ca.*  $500^\circ$ .

Most experiments were carried out with uranium(VI) chloride solutions using 0.1  $M$  KCl as supporting electrolyte. Solutions of higher chloride concentration as well as perchlorate solutions were also investigated. The solutions were prepared from reagent grade uranyl chloride and purified through ammonia precipitations, washing and dissolution in the appropriate acid. The solutions were analyzed by oxidimetry<sup>21</sup> (reduction in a Jones reductor followed by ceric sulfate oxidation), "diuranate" precipitation with carbonate-free ammonia and ignition to  $\text{U}_3\text{O}_8$  of a spectrographically pure salt-free stock solution.

**3.2. Preparation of Solutions of  $\text{UO}_2^+$ .**—Most of the  $\text{UO}_2^+$  solutions were prepared by electrolytic reduction of  $\text{UO}_2^{++}$  solutions. The pH was in the O. S. R. described in section 2 and most preparations were carried out between pH 2.5 and 3.

It appeared desirable to prepare the uranium(V) solutions without producing at the same time considerable amounts of uranium(IV). Selective reduction of uranium(V) can be achieved taking advantage of the irreversibility of the uranium(IV)/(V) couple and the resulting slow rate of reduction of uranium(V). Thermodynamically, of course, a potential sufficiently negative to reduce uranium(VI) to uranium(V) should also be able to reduce uranium(V) to uranium(IV). In practice, however, considerable overvoltage is required as shown by the large difference (*ca.* 0.7 v. near pH 2.7) between the half-wave potentials of the U(VI)–U(V) and the U(V)–U(IV)–U(III)

(21) We are indebted to the Analytical Section for most of the analyses.

waves. Taking advantage of this overvoltage the reductions were carried out at a potential located approximately half way between these two half-wave potentials (*ca.* 0.6 v. vs. 0.1 M KCl-calomel electrode).

The polarogram of an electrolytically reduced solution is shown in Fig. 3 together with the polarogram of the original uranium(VI) solution. As shown by the relative magnitudes of the anodic ( $i_a$ ) and cathodic ( $i_c$ ) currents, the reduction in this particular sample was approximately 85% complete.

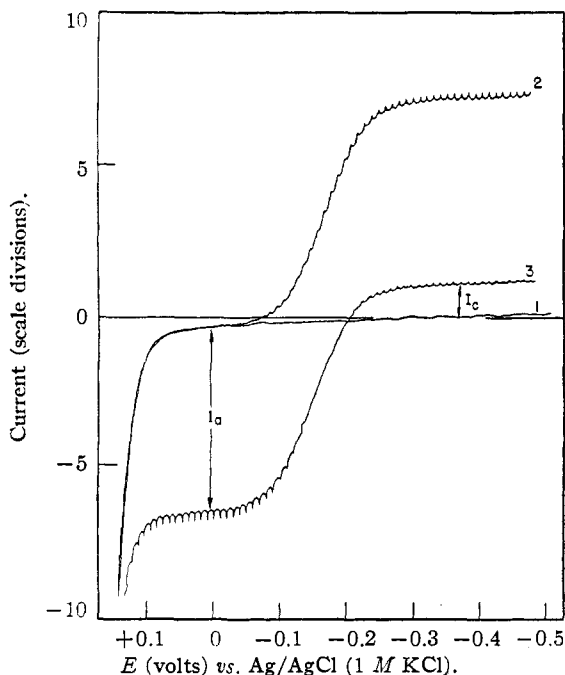


Fig. 3.—Polarogram of  $\text{UO}_2^{+}$ - $\text{UO}_2^{++}$  mixture: 1, residual current; 2,  $\text{UO}_2\text{Cl}_2$  solution (0.1 M KCl); 3, electrolytically reduced solution (*ca.* 85%  $\text{UO}_2^{+}$ );  $I_c$ , cathodic diffusion current;  $I_a$ , anodic diffusion current.

The anodic and cathodic parts of such mixed U(V)-U(VI) waves merge smoothly, without discontinuity. Irrespective of the ratio of the concentrations of uranium(V) and uranium(VI), plots of  $\log i/(i_t - i)$  vs.  $E$  ( $i_t = i_a + i_c$ ) yield, straight lines with slopes  $0.060 \approx 0.002$  for *ca.*  $-1.3 \leq \log i/(i_t - i) \leq ca. +1.3$ , confirming that the reaction is reversible and involves a one-electron change, as previously suggested from polarograms of uranium(VI) solutions.

Aside from controlled electrolytic reduction a number of other methods have been investigated for the preparation of uranium(V) solutions.

Of these attempts, the following may be mentioned: (a) reduction of uranium(VI) solutions with hydrogen using a strip of platinized platinum as a catalyst, (b) reduction of uranium(VI) solutions with zinc amalgam, (c) dissolution of solid uranium pentachloride, and (d) reduction of uranium(VI) solutions with uranium(IV).

The results of the dissolution experiments of uranium pentachloride and of the reduction of uranium(VI) by uranium(IV) will be described in a subsequent paper.<sup>22</sup> Suffice it here to say that by these methods solutions of  $\text{UO}_2^{+}$  containing also uranium(IV) and uranium(VI) can be prepared.

Near pH 2.5 reduction of  $\text{UO}_2^{++}$  to  $\text{UO}_2^{+}$  occurs rapidly with hydrogen. However, since the amount of hydrogen introduced was not controlled, further reduction to uranium(IV) occurred. It appeared difficult to control the experiments so that they would yield only uranium(V).

Reduction of uranyl chloride solutions (*ca.*  $1.5 \times 10^{-3}$  M U, *ca.* 0.1 M KCl, pH *ca.* 2.5) with zinc amalgam (20% Zn by weight) in less than two minutes yielded uranium(V) with considerably better than 50% yield and little reduction to uranium(IV). On longer shaking with zinc amalgam, however, rapid disproportionation of uranium(V) occurred.

With all methods of preparation, solutions of uranium(V) were often prepared which were very stable toward disproportionation for a long time and suddenly began to disproportionate rapidly. It is believed that these autocatalytic effects result from polymerization of uranium(IV) which is formed during the reductions or disproportionations. Apparently at high dilution the monomeric hydrolysis products of uranium(IV) (probably  $\text{UOH}^{+3}$ ) are metastable with respect to polymerization. Hence the whole system is in a metastable state. Once polymer forms, whose rate of formation must be highly concentration dependent, the whole system will seek its true equilibrium position, accelerated by the appearance of a new mechanism for disproportionation such as disproportionation on the surface of the polymer.

Thus, while uranium(V) solutions can be prepared readily by reduction of uranium(VI) solutions, one cannot, in general, expect to prepare them through oxidation of uranium(IV) solutions for the following reasons: (a) Except perhaps at very low acidities<sup>22</sup> any oxidizing agent sufficiently strong to effect oxidation of uranium(IV) to uranium(V) will also be strong enough to cause oxidation of uranium(V) to uranium(VI). (b) Since the uranium(IV)/(V) couple apparently is the irreversible step in the U(IV)/(VI) system and the U(V)/(VI) couple the reversible one, it is to be expected that uranium(V) would be oxidized as rapidly as it is formed. (c) Using uranium(IV) at any reasonable concentration as starting material will seriously restrict the useful pH range since at low acidities it could change into the polymer and thus disturb the metastable equilibrium, which appears so important for the success of preparations of uranium(V) solutions.

**3.3. Disproportionation of  $\text{UO}_2^{+}$ .**—The rate of disproportionation, which is very slow<sup>23</sup> in the

(22) K. A. Kraus and F. Nelson, *THIS JOURNAL*, **71**, 2517 (1949).

(23) As shown in a subsequent paper,<sup>22</sup> in this pH range equilibrium mixtures of U(IV), U(V) and U(VI) containing large amounts of U(V) can also be prepared.

O.S.R. (except for occasional catalysis by uranium(IV) polymer), increases rapidly with increasing acidity and the rate constant at any acidity divided by the acidity is approximately constant.

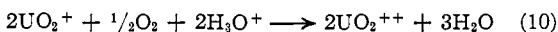
The disproportionation of uranium(V) follows a second order law, *i. e.*, it can be described by the equation

$$d[U(V)]/dt = -k[U(V)]^2 \quad (9)$$

where brackets indicate concentrations in moles/liter. As predicted from equation (9) a plot of  $1/[U(V)]$  vs. time was found to be a strictly linear function within experimental error under conditions where the uranium(V) concentration is considerably larger than its equilibrium concentration in the U(IV)-U(V)-U(VI) system.<sup>22</sup> For these studies the solutions were prepared by electrolytic reduction near pH 2.5 and then acidified. Using the Sargent polarograph, a continuous record of the anodic diffusion current was obtained and from it the uranium(V) concentrations calculated (assuming  $K_5 = K_6$ ). As an example, a second order rate constant of  $3.96$  (moles/liter)<sup>-1</sup> sec.<sup>-1</sup> was found for a  $1.983 \times 10^{-3}$  M uranium solution ( $0.14$  M Cl<sup>-</sup>,  $0.04087$  M H<sub>3</sub>O<sup>+</sup>). In general the rate constants found for chloride solutions were in fair agreement with those obtained by Kern and Orlemann<sup>24</sup> for perchlorate solutions. Further details on the kinetics of these systems will be given in subsequent papers.

**3.4. Oxidation of Uranium(V).**—It was found that uranium(V) is readily oxidized by a number of oxidizing agents including atmospheric oxygen. Although no systematic investigation was carried out, the rate of oxidation by oxygen appeared to increase with increasing acidity. Up to pH 3, however, the rate of oxidation by oxygen is sufficiently fast to make it impossible to prepare uranium(V) solutions successfully if the solutions are not carefully deoxygenated.

A number of attempts were made to verify the assignment of the formula UO<sub>2</sub><sup>+</sup> for uranium(V) by measuring the change in acidity of the solutions on oxidation by oxygen with a glass electrode assembly. If the oxidation follows the equation



1 mole of oxonium ions should be used up per mole UO<sub>2</sub><sup>+</sup> oxidized. The results in general confirmed the validity of equation (10). However, the precision of the experiments was not sufficiently high to permit a conclusive answer by the use of this method, the deviations from the theoretical value being *ca.* 10%.

Other reagents used for the oxidation of uranium(V) were iron(III) and cerium(IV). With either reagent rapid oxidations were obtained near pH 2.

**3.5. The Diffusion Coefficient of UO<sub>2</sub><sup>+</sup>.**—The precision of the analytical (polarographic) procedure is directly related to the estimation of the

diffusion current constant  $K$  in the Ilkovic equation

$$i_d = K C m^{2/3} t^{1/6} \quad (11)$$

where  $i_d$  is the diffusion current (*i. e.*,  $i_a$  for UO<sub>2</sub><sup>+</sup> and  $i_c$  for UO<sub>2</sub><sup>++</sup>),  $C$  the concentration of the ions in millimoles/liter ( $C_5$  for UO<sub>2</sub><sup>+</sup>,  $C_6$  for UO<sub>2</sub><sup>++</sup>), where  $K = 605 n D^{1/2}$  and where  $n$ ,  $D$ ,  $m$  and  $t$  have their usual definitions.<sup>25</sup> Using uranyl ions for standardization, and assuming that  $m^{2/3}$  does not change with applied potential, the concentration  $C_5$  can be obtained directly from the relationship

$$\frac{i_a}{i_c} = \frac{K_5 C_5 t_5^{1/6}}{K_6 C_6 t_6^{1/6}} = R \frac{C_5}{C_6} \left(\frac{t_5}{t_6}\right)^{1/6} \quad (12)$$

provided  $R$ , the ratio of the diffusion current constants, and the ratio of the drop times  $t_5$  and  $t_6$  (obtained at the potentials where  $i_a$  and  $i_c$  are measured) are known.

To determine  $R$ ,  $C_5$  was estimated by the following methods: (a) From the decrease in  $i_c$  on reduction ( $C_4 + C_5$ ) can be obtained, where  $C_4$  is the concentration of uranium(IV). Using ceric sulfate oxidation after complete disproportionation in oxygen-free acid (HCl or H<sub>2</sub>SO<sub>4</sub>) ( $2C_4 + C_5$ ) was obtained. Using  $t_5 = 2.97$  sec. and  $t_6 = 3.27$  sec.  $R$  was found to be 1.01, 1.02 and 1.03 for three  $1.983 \times 10^{-3}$  M uranium solutions which were prepared near pH 3 in 0.1 M KCl, and which contained 70–80% uranium(V) and less than 2% uranium (IV). (b) From the increase of  $i_c$  on oxidation of a U(IV)-(V)-(VI) mixture, prepared by dissolution of uranium pentachloride, a ratio  $i_a/i_c = 1.00$  was found,<sup>22</sup> and thus  $R = 1.02$ . (c) From the change in  $i_a$  and  $i_c$  on disproportionation of uranium(V), where it can be assumed that the increase in concentration of UO<sub>2</sub><sup>++</sup> is one-half the decrease in the concentration of UO<sub>2</sub><sup>+</sup>,  $R = 1.02 \pm 0.02$  was found.

Thus  $R$  appears to be sufficiently close to unity, to permit the simplification  $K_5 = K_6$  for most calculations.

Using  $R = ca. 1.02$ , the ratio of the diffusion coefficients  $D_5/D_6$  of UO<sub>2</sub><sup>+</sup> and UO<sub>2</sub><sup>++</sup> is found to be *ca.* 1.04. This practical identity of the two diffusion coefficients appears at first surprising since one would expect that the difference in charge between these two ions would be reflected in a corresponding difference in the diffusion coefficients. Conversely, however, this close agreement of the diffusion coefficients of these two ions appears to be supporting evidence that the essential structure of these two ions is the same at least in the first coordination sphere as would be indicated by the formulas UO<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub><sup>+</sup> and UO<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub><sup>++</sup>.<sup>10</sup>

Using equation (11)  $D_6$  was determined for 1.666 and  $1.983 \times 10^{-3}$  M uranium(VI) solutions in 0.1 M Cl<sup>-</sup> at an applied potential of  $-0.5$  v. vs. Ag/AgCl in 0.1 M KCl. It was found that  $D_6 =$

(24) D. M. H. Kern and E. F. Orlemann, MDDC-1703, December, 1497.

(25) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., revised reprint, 1946.

$0.67 \pm 0.01 \times 10^{-5}$  ( $pH$  1 to 3) and  $0.63 \times 10^{-5}$   $cm.^2$   $sec.^{-1}$  ( $pH$  2 to 3) for capillaries with  $m^{2/3}t^{1/3} = 1.735$  and  $2.468$   $mg.^{2/3}sec.^{-1/3}$ , respectively. Harris and Kolthoff<sup>2</sup> using a capillary with  $m^{2/3}t^{1/3} = 2.70$   $mg.^{2/3}sec.^{-1/3}$  and working in  $0.1$   $M$   $KCl$ - $0.01$   $M$   $HCl$  solutions found  $D_6 = 0.62 \times 10^{-5}$   $cm.^2$   $sec.^{-1}$  for uranyl solutions of approximately the same concentration which also contained  $2 \times 10^{-4}$  % thymol as maximum suppressor. These differences in the values of  $D_6$  appear to be outside of the experimental error, and are probably due to the fact that the Ilkovic equation is not strictly applicable as was shown by Lingane and Loveridge for lead solutions<sup>26</sup> where the diffusion current constants showed a similar change with  $m^{2/3}t^{1/3}$ . The value  $D_6 = 0.68 \times 10^{-5}$   $cm.^2$   $sec.^{-1}$  for  $0.1$   $M$   $ClO_4^-$  solutions (reported by Kern and Orlemann) for a capillary with  $m^{2/3}t^{1/3} = ca. 2.13$   $mg.^{2/3}sec.^{-1/3}$  is considerably higher than that expected for chloride solutions for the same capillary characteristics. This difference in the diffusion coefficients of  $UO_2^{++}$  in chloride and perchlorate solutions may be due to the differences in the media. The conclusion of Kern and Orlemann, that this difference is due to complexing of  $UO_2^{++}$  by chloride ions, does not appear to be substantiated by the potential data, as is discussed below.

**3.6. The Formal Potential of the U(V)/(VI) Couple.**—Using the polarograms of a number of electrolytically prepared U(V)-U(VI) mixtures in  $0.1$   $M$   $Cl^-$  near  $pH$  3 the formal oxidation-reduction potential  $E_{56}$  of the U(V)/(VI) couple was found to be  $-0.062 \pm 0.002$  v. vs. the standard hydrogen electrode. For the calculations the standard potential of the Ag/AgCl electrode was assumed to be  $-0.2222$  v.<sup>22,27</sup> and the mean activity coefficient of potassium chloride<sup>27</sup> was used as the activity coefficient of  $Cl^-$ . Liquid junction errors should be negligible since the solutions in either half-cell had the same potassium chloride and total uranium concentrations.

The value of  $E_{56}$  found here agrees with that found by Harris and Kolthoff<sup>2</sup> for chloride solutions and by Kern and Orlemann<sup>24</sup> for perchlorate solutions of ionic strength  $\mu = 0.5$  ( $E_{56} = -0.062$  v., before correction for differences in the diffusion coefficients of  $UO_2^+$  and  $UO_2^{++}$ ).<sup>28</sup> Actually, the agreement is so close as to preclude the possibility of appreciable complexing of  $UO_2^{++}$  by chloride ions in  $0.1$   $M$   $KCl$  if the assumptions are made that there is a considerable difference in the stabil-

ity constants of the chloride complexes of  $UO_2^+$  and  $UO_2^{++}$ , and that the ratios of the activity coefficients of  $UO_2^+$  and  $UO_2^{++}$  are approximately the same at  $\mu = 0.1$  and  $\mu = 0.5$ . Further observations on the potentiometry of the system will be given in a subsequent paper.<sup>22</sup>

**3.7. The Absorption Spectrum of  $UO_2^+$ .**—The absorption spectra of electrolytically reduced  $UO_2^{++}$  solutions containing *ca.* 70%  $UO_2^+$  and at most a few per cent. of uranium(IV) have been determined with a Beckman Quartz Spectrophotometer, Model DU. After correcting the absorption curves for absorption due to  $UO_2^{++}$  it was found that  $UO_2^+$  has no strong absorption bands between *ca.* 360 and 1000 millimicrons ( $m\mu$ ), the corrected extinction coefficients ( $\epsilon$ ) being less than 1.5. It is possible that a considerable fraction of the absorption found is due to a small amount of uranium(IV) in the solutions. A corresponding correction, however, could not be made at this time since the absorption characteristics of uranium(IV) near  $pH$  2.5 have not been determined.

Below 350  $m\mu$  absorption due to  $UO_2^+$  increases rapidly and extinction coefficients of the order of 100 are reached near 280  $m\mu$ . This rapidly increasing absorption in the ultraviolet is similar to that observed with  $UO_2^{++}$  for which a similar absorption edge lies at slightly longer wave lengths.

The absorption spectrum of  $UO_2^+$  has some similarity to that of  $NpO_2^{++}$  with which it is isoelectronic. The latter also does not show intense and sharp absorption bands, which are so typical for most of the oxidation states in this group of elements. Furthermore,  $NpO_2^{++}$  also shows a strong absorption edge at short wave lengths. The main differences between the absorption spectra of  $UO_2^+$  and  $NpO_2^{++}$  are some subsidiary broad absorption bands of low intensity, and location of the steep absorption edge at considerably longer wave lengths in the case of  $NpO_2^{++}$  ( $\epsilon = ca. 100$  at 350  $m\mu$ ).

#### 4. Summary

1. Comparing the chemistry of uranium, neptunium and plutonium and utilizing the available data on the hydrolytic properties of these elements, it is shown that uranium(V) should have an optimum stability range between *ca.*  $pH$  2 and 4.

2. Uranium(V) solutions have been prepared by reduction of uranium(VI) solutions. In the optimum stability range uranium(V) solutions can be preserved without appreciable disproportionation for considerable periods of time.

3. Using uranium(V)-uranium(VI) mixtures and a polarographic method of analysis verification of the formula  $UO_2(H_2O)_n^+$  for uranium(V) was obtained. Furthermore, the potential of the U(V)/(VI) couple in  $0.1$   $M$  potassium chloride was determined as well as the diffusion coefficient

(26) J. J. Lingane and B. A. Loveridge, *THIS JOURNAL*, **66**, 1425 (1944).

(27) W. M. Latimer, "Oxidation Potentials," Prentice-Hall Inc., New York, N. Y., 1938.

(28) NOTE ADDED IN PROOF: Since this paper was written, Kern and Orlemann (*THIS JOURNAL*, **71**, 2103 (1949)) revised their value for the diffusion coefficient of  $UO_2^+$ . While their earlier value<sup>24</sup> gave  $D_5/D_6 = 1.26$ , the newer value gives  $D_5/D_6 = 1.03$  for perchlorate solutions in good agreement with the ratio obtained here for  $0.1$   $M$   $Cl^-$  solutions. Their potential data for perchlorate solutions thus agree now very well with those obtained here for chloride solutions.

of uranium(V), and its absorption spectrum. Some observations on the oxidation of uranium(V) by oxygen and other oxidizing agents and on its

disproportionation into uranium(IV) and uranium(VI) have been included.

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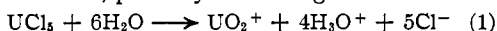
[CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY]

## Chemistry of Aqueous Uranium(V) Solutions. II. Reaction of Uranium Pentachloride with Water. Thermodynamic Stability of $\text{UO}_2^+$ . Potential of U(IV)/(V), U(IV)/(VI) and U(V)/(VI) Couples<sup>1</sup>

BY KURT A. KRAUS AND FREDERICK NELSON

### I. Introduction

In the previous paper<sup>2</sup> it was shown that aqueous uranium(V) solutions of considerable stability could be prepared by controlled reduction of uranium(VI) solutions in the absence of oxygen in (or near) the  $p\text{H}$  range where maximum stability of  $\text{UO}_2^+$  could be predicted. If similarly stable solutions of  $\text{UO}_2^+$  could be prepared by dissolution of solid anhydrous uranium pentachloride in water in this expected maximum stability range, information regarding the formation of the oxygenated ion  $\text{UO}_2^+$  from uranium pentachloride, possibly according to the reaction



could be obtained. It was planned to follow the rate of formation of  $\text{UO}_2^+$  from uranium pentachloride polarographically and through simultaneous  $p\text{H}$  measurements to provide an independent check on the formula  $\text{UO}_2^+$  for uranium(V) in aqueous solutions.

It was found that the initial reaction products of uranium pentachloride and water are uranium(IV) ( $\text{UOH}^{+3}$ ) and uranium(VI) ( $\text{UO}_2^{++}$ ) near  $p\text{H}$  2 and that these initial products react with each other to yield uranium(V) ( $\text{UO}_2^+$ ) as will be discussed in section 3.1.

The reaction of  $\text{UOH}^{+3}$  with  $\text{UO}_2^{++}$  was found to come rapidly to equilibrium near  $p\text{H}$  2 and from the oxidation-reduction potential of the mixture the (formal) potentials of the uranium(IV)/(V), uranium(V)/(VI) and uranium(IV)/(VI) couples near  $p\text{H}$  2 were obtained as will be discussed in section 3.2.

Using the hydrolytic data available for the various species the potentials of the uranium couples in 1  $M$  perchloric acid were estimated as shown in section 3.4.

The  $p\text{H}$  measurements which were carried out afford a check on the assignment of ionic species made for the various oxidation states of uranium in the solutions as shown in section 3.3.

### (2) Experimental

Two batches of uranium pentachloride were used in the experiments both having been prepared by the chemistry

(1) This document is based on work performed under Contract Number W-7405 eng-26 for the Atomic Energy Project at the Oak Ridge National Laboratory.

(2) K. A. Kraus, F. Nelson and G. L. Johnson, *THIS JOURNAL*, **71**, 2510 (1949).

group of the Electromagnetic Plant (Y-12) at Oak Ridge. The first batch, of unknown purity, was used in the preliminary experiments. The second batch, freshly prepared and carefully handled in dry-boxes throughout was analyzed by the Y-12 group and the analytical section of our laboratory and found to have a uranium chloride ratio of 4.95-0.05. This value appeared sufficiently close to 5.00 to permit assumption of the composition of uranium pentachloride for all calculations.

Thin-walled glass bulbs were filled with weighed samples of uranium pentachloride in a dry, oxygen-free, nitrogen atmosphere. At the appropriate time, the uranium pentachloride was dissolved in potassium chloride solutions of low acidity and ionic strength  $\mu = 0.1$  by breaking the bulb in the deaerated solutions.

From the instant of dissolution, polarographic analysis with a Sargent Model 21 recording polarograph was carried out in the cell previously described.<sup>2</sup> A silver strip, coated with silver chloride, immersed in 0.1  $M$  potassium chloride was used as the non-polarizable (reference) electrode. The cell was fitted with a glass-saturated potassium chloride-calomel electrode assembly to permit simultaneous  $p\text{H}$  measurements. For the potentiometric measurements a recording instrument consisting of a vibrating reed electrometer, Rubicon Precision Potentiometer and Brown Electronik strip chart recorder was used, a description of which will be given elsewhere.

All experiments were carried out in a thermostated room at  $25 \pm 0.5^\circ$ .

### (3) Results

**3.1 Formation of  $\text{UO}_2^+$  from Uranium Pentachloride. Reaction of Uranium(IV) with Uranium(VI) to form Uranium(V).**—The polarographic curves which are obtained after dissolution of uranium pentachloride are very similar to those which one obtains from  $\text{UO}_2^+ - \text{UO}_2^{++}$  mixtures prepared by controlled reduction.<sup>2,3</sup> From the similarity between these curves it can be concluded that  $\text{UO}_2^+$  and  $\text{UO}_2^{++}$  are products of the reaction of uranium pentachloride with water.

The polarograms can be subdivided into three sections as indicated in Fig. 1, which represents a polarogram of a uranium pentachloride solution about one-half hour after dissolution. Section A of the curve represents the cathodic part of the wave due to reduction of  $\text{UO}_2^{++}$  to  $\text{UO}_2^+$ . The cathodic diffusion current  $i_c$  (after correction for residual current) can be assumed to be proportional to the concentration of  $\text{UO}_2^{++}$ . Section B of the curve represents the anodic current due to oxidation of  $\text{UO}_2^+$  to  $\text{UO}_2^{++}$ . The anodic

(3) D. M. H. Kern and E. F. Orlemann, *MDDC-1703*, December, 1947.