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.

OAK RIDGE, TENN. RECEIVED JANUARY 31, 1949

[CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY]

Chemistry of Aqueous Uranium(V) Solutions. II. Reaction of Uranium Pentachloride with Water. Thermodynamic Stability of UO_2^+. Potential of U(IV)/(V), U(IV)/(VI) and U(V)/(VI) Couples[1]

BY KURT A. KRAUS AND FREDERICK NELSON

I. Introduction

In the previous paper[2] 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*H range where maximum stability of UO_2^+ could be predicted. If similarly stable solutions of 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 UO_2^+ from uranium pentachloride, possibly according to the reaction

$$UCl_5 + 6H_2O \longrightarrow UO_2^+ + 4H_3O^+ + 5Cl^- \quad (1)$$

could be obtained. It was planned to follow the rate of formation of UO_2^+ from uranium pentachloride polarographically and through simultaneous *p*H measurements to provide an independent check on the formula UO_2^+ for uranium(V) in aqueous solutions.

It was found that the initial reaction products of uranium pentachloride and water are uranium (IV) (UOH^{+3}) and uranium(VI) (UO_2^{++}) near *p*H 2 and that these initial products react with each other to yield uranium(V) (UO_2^+) as will be discussed in section 3.1.

The reaction of UOH^{+3} with UO_2^{++} was found to come rapidly to equilibrium near *p*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*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*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 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.[2] 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*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 ± 0.5°.

(3) Results

3.1 Formation of 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 UO_2^+–UO_2^{++} mixtures prepared by controlled reduction.[2,3] From the similarity between these curves it can be concluded that UO_2^+ and 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 UO_2^{++} to UO_2^+. The cathodic diffusion current i_c (after correction for residual current) can be assumed to be proportional to the concentration of UO_2^{++}. Section B of the curve represents the anodic current due to oxidation of UO_2^+ to UO_2^{++}. The anodic

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(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).

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

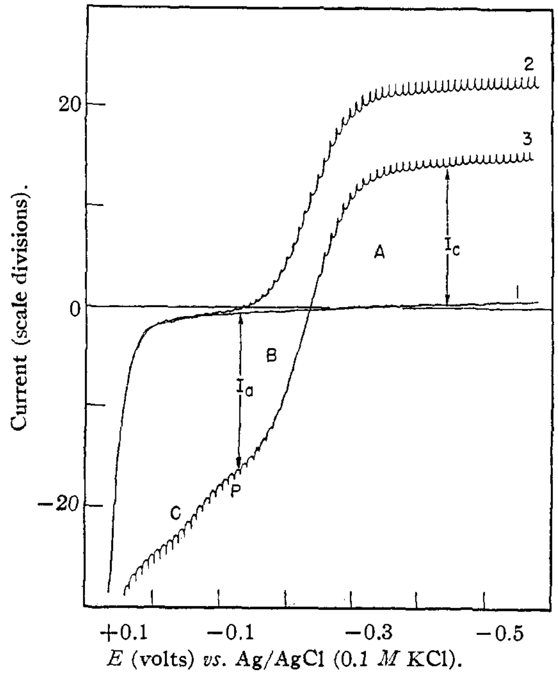

Fig. 1.—Polarogram of UCl_5 solution: 1, residual current; 2, UO_2Cl_2 solution (0.1 *M* KCl); 3, UCl_5 solution (*ca.* 5×10^{-3} *M* H_3O^+); A, cathodic (UO_2^{++}) section; I_c = cathodic diffusion current; B, anodic (UO_2^+) section; I_a = anodic diffusion current; C, anodic (U(IV), Hg) section.

diffusion current i_a (corrected for residual current) measured from the inflection point "P" can be assumed to be proportional to the concentration of UO_2^+. Using uranium(IV) solutions of similar *p*H it could be shown that section C of the curve is a superposition of the anodic currents resulting from oxidation of mercury and oxidation of uranium(IV) whose concentration in the uranium pentachloride solutions is approximately equal to that of uranium(VI). It is apparent that the half-wave potential of the anodic uranium(IV)/(V) wave in these solutions is only little more positive than the half-wave potential of the uranium(V)/(VI) wave, while it is considerably more positive at higher acidities.[4]

There is no doubt that the cathodic and anodic sections A and B are due to UO_2^{++} and UO_2^+ since the wave has the proper half-wave potential (*ca.* 0.06 v. *vs.* the standard hydrogen electrode—S. H. E.—see section 3.2) as well as the proper shape for such a mixture. The usual plots of log $i/(i_t - i)$ *vs.* E, where $i_t = i_a + i_c$ and i the observed current at voltage E, are a strictly linear function with slope 0.060 ± 0.02 close to the theo retical value of 0.059. Actually these plots are indistinguishable from those obtained from polarograms of uranium(VI) solutions or U(V)–U(VI) mixtures, prepared by controlled reduction of uranium(VI).[2]

After dissolution of uranium pentachloride polarographic analysis was started as soon as possible and continued for several hours. It was found that the anodic current i_a increases rapidly at first, continues to increase for about one-half hour and after this time levels off to a constant value. Simultaneously with the increase in i_a there is a decrease in the cathodic current i_c. The latter also approaches a constant value after approximately one-half hour. A plot of i_a and i_c as a function of time (t) is shown in Fig. 2. In constructing the graphs it was assumed that at $t = 0$, $i_a = 0$ and $i_c = {}^1/_2 i_{ox}$, where i_{ox} is the diffusion current after complete oxidation of the solutions.

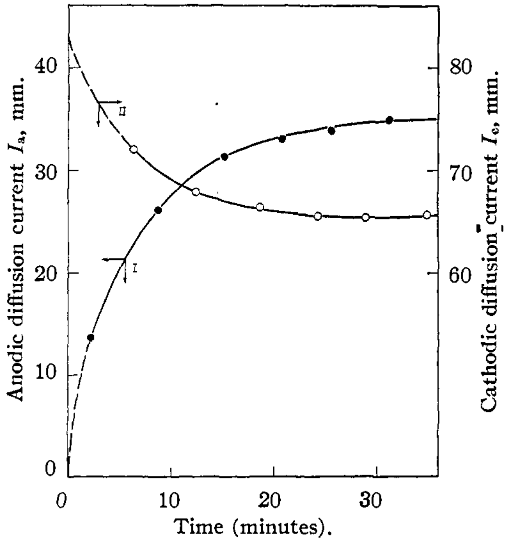

Fig. 2.—Change of anodic and cathodic current with time: I, anodic current (formation of UO_2^+); II, cathodic current (reduction of UO_2^{++}).

This "slow" formation of UO_2^+ from uranium pentachloride cannot be due to the change of a metastable uranium(V) species to UO_2^+. Rather it must be due to the comparatively slow reaction

$$\text{U(IV)} + \text{U(VI)} \longrightarrow 2\text{U(V)} \qquad (2)$$

since the half-wave potential does not change during the reaction and since the increase in UO_2^+ concentration occurs simultaneously with a decrease in the UO_2^{++} concentration. Since furthermore after about one-half hour the concentrations of UO_2^+ and UO_2^{++} remain constant (near *p*H 2) for at least several hours, it appears evident that in these solutions an equilibrium (or steady state) between uranium(IV), uranium (V) and uranium(VI) exists. This interpretation was verified by showing (polarographically) that uranium(V) is formed at the expected rate on addition of a uranium(IV) chloride solution to a solution of uranyl chloride near *p*H 2.2.

A further check of equation (2) can be obtained

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[4] This shift of the anodic U(IV)/(V) half-wave potential toward more negative values with increasing *p*H is paralleled by a similar shift of the oxidation–reduction potential of the couple and by an increased rate of reaction of U(IV) with U(VI) to yield U(V).

by measuring the relative magnitudes of i_a and i_c as a function of time. Assuming that the diffusion coefficients of UO_2^+ and UO_2^{++} are the same, as was suggested previously,[2] and that by stoichiometry the concentration of uranium(IV) should equal that of uranium(VI), the sum ($i_a + 2i_c$) should remain constant and equal to the total diffusion current i_{ox} after complete oxidation. Such oxidation was carried out through careful addition of a solution of ammonium hexanitrato cerate; a diffusion current $i_{ox} = 166.1$ mm. was found after correcting the data for the dilution occurring on addition of the reagent. The calculated sum of the currents ($i_a + 2i_c$) is given in Table I. It can be seen that this sum is constant and averages 165.9 mm., in close agreement with the diffusion current for the oxidized solution which was determined at the same sensitivity of the instrument. This close agreement appears to be further proof that the diffusion coefficients of UO_2^+ and UO_2^{++} are practically the same.[2]

Since at the *p*H in question U(VI) is primarily UO_2^{++}, U(V) primarily UO_2^+, and U(IV) probably primarily UOH^{+3} (see also section 4), the initial (practically) instantaneous reaction of uranium pentachloride can be approximated by the equation

$$2UCl_5 + 8H_2O \longrightarrow UOH^{+3} + UO_2^{++} + 10Cl^- + 5H_3O^+ \quad (3)$$

TABLE I

REACTION OF URANIUM PENTACHLORIDE WITH WATER, 3.57×10^{-3} UCl_5

Final acidity 9.56×10^{-3} *M*; $\mu = 0.1$ (potassium chloride); sensitivity, 0.06 μ amp./mm.

Time, minutes	i_a (mm.) (U(V))	i_c (mm.) (U(VI))	i_{total}[a] (mm.) (calcd.)
2.2	13.8	(77.6)[b]	168.8
6.5	(22.6)	72.0	166.6
8.8	26.1	(70.0)	166.1
12.6	(29.6)	67.9	165.4
15.3	31.3	(67.0)	165.3
18.8	(32.6)	66.4	165.6
20.9	33.0	(66.0)	165.0
24.4	(33.7)	65.5	164.6
25.7	33.9	(65.5)	164.9
29.0	(34.5)	65.3	165.1
ca. 33	34.9	65.6	166.1
ca. 42	34.7	65.7	166.1
ca. 57	35.0	65.3	165.5
ca. 105	35.1	65.7	166.5
ca. 145	35.2	65.7	166.6

[a] Calculated as $i_{total} = i_a + 2i_c$. [b] Values in parentheses are extrapolated.

The slow reaction which follows is then primarily

$$UO_2^{++} + UOH^{+3} + 4H_2O \longrightarrow 2UO_2^+ + 3H_3O^+ \quad (4)$$

In equations (3) and (4) the small concentration of U^{+4} present in these solutions was neglected.[5]

The initial formation of uranium(IV) and uranium(VI) from a uranium(V) compound, under conditions where considerable concentrations of U(V) (UO_2^+) are stable is surprising. One might explain this by either assuming that uranium pentachloride is a compound containing uranium(IV) and uranium(VI) ions as distinct entities in the solid state, or that the uranium(IV) and uranium(VI) ions are formed in the dissolution process.

The former hypothesis, namely, that solid uranium pentachloride contains uranium(IV) and uranium(VI) as distinct entities appears unlikely. The formula $UCl_4 \cdot UCl_6$ for UCl_5 was suggested by Sterrett and Calkins[6] on the basis of spectrophotometric studies of solutions of uranium tetrachloride, uranium pentachloride, and uranium hexachloride in carbon tetrachloride and thionyl chloride as well as on the basis of some incidental considerations. They found typical uranium hexachloride absorption bands in solutions of uranium pentachloride and ruled out the possibility of disproportionation on the basis of solubility considerations. However, their evidence is not convincing since their data apply only to solutions of uranium pentachloride rather than the solid.

Zachariasen has shown[7] through X-ray diffraction studies that all uranium atoms in uranium pentachloride are equivalent and that the compound cannot be considered a solid solution of uranium tetrachloride in uranium hexachloride (or *vice versa*) in agreement with the usual assumptions regarding the composition of this compound.[8] The geometrical equivalence of the uranium atoms in the solid indicates that they are all of the same oxidation state and that uranium pentachloride is a compound of uranium (V) rather than of uranium(IV) and uranium(VI).

Since uranium(IV) and uranium(VI) are the initial solution products of this uranium(V) compound they must be formed during the dissolution process either directly or through a metastable species of uranium(V), different from $UO_2(H_2O)_n^+$ (*e. g.*, $U(H_2O)_x^{+5}$), which very rapidly disproportionates into uranium(IV) and uranium(VI). The more stable uranium(V) species, $UO_2(H_2O)_n^+$, would then be formed in the secondary process.[9] The experiments at hand do not appear to permit a decision regarding these mechanisms.

3.2 Formal Potentials of the U(IV)/(V), U(IV)/(VI) and U(V)/(VI) Couples in Chloride Solutions near *p*H 2.—It was shown in section 3.1 that approximately one-half hour after dissolution of uranium pentachloride uranium(IV),

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[5] For the sake of simplicity the water molecules of hydration have been omitted in describing the various species. A more correct and elaborate symbolism would be $UO_2(H_2O)_n^{++}$, $UO_2(H_2O)_m^+$, $U(H_2O)_k^{+4}$ and $U(H_2O)_{k-1}(OH)^{+3}$ where probably $n = 6$, $m = 6$, and $k = 8$.

[6] C. C. Sterrett and V. P. Calkins, Report H-8.385.11, December, 1946.

[7] W. H. Zachariasen, Report ANL-4012, July, 1947.

[8] E. I. Rabinowitch, J. J. Katz, The Chemistry of Uranium, Chapter 14 (Report ANL-JJK-24. May, 1947).

[9] It is not possible that initially metastable species of uranium (IV) and uranium(VI) are formed without also assuming a metastable species of uranium(V) since in that case the metastable equilibrium would be shifted more in favor of uranium(V).

uranium(V) and uranium (VI) are in equilibrium with each other. Thus, a single determination of the oxidation-reduction potential of the system, together with an estimation of the concentration of each species, should permit evaluation of the formal potentials E' of the various uranium couples.[10]

The potential of the system was determined using the polarograph as a null detector by adjusting the input voltage to a point where the polarographic current was zero and then measuring this input potential with a potentiometer. Using the polarograph in this way, errors due to poor estimation of the iR drop can be avoided. The potential thus measured should, in a reversible system or in a system in equilibrium with a reversible system, be the thermodynamic potential at the given concentration of the species. If the system behaves "properly," the potential found in this way should be the same as that observed on a noble metal electrode.[11] The formal potentials E' of the various couples can then be evaluated by use of the Nernst equation

$$E_{\text{obs.}} = E' - \frac{0.0591}{n} \log \frac{C_{\text{ox}}}{C_{\text{red}}} \tag{5}$$

The concentration of the various oxidation states was estimated as described in section 3.1, *i. e.*, the concentrations of uranium(V) and uranium(VI) were determined from the U(V)/(VI) wave of the mixture and the uranium(IV) concentration was taken as the difference in height of the uranium(VI) wave after complete oxidation and the uranium(V)/(VI) wave of the mixture. The concentrations of uranium(IV) and uranium(VI) were found to be practically the same.

The reference electrode in the potential measurements was the silver/silver chloride electrode (in 0.100 M potassium chloride) which was also used as the non-polarizable electrode in the polarographic analyses as mentioned earlier. The potential of this electrode *vs.* a saturated potassium chloride-calomel electrode was taken several times after the calomel electrode had been standardized against a hydrogen electrode in 0.100 M hydrochloric acid. Assuming the activity coefficients $\gamma_{\pm\text{KCl}} = \gamma_{\text{Cl}^-} = 0.769$ for 0.100 M potassium chloride[12] and $\gamma_{\text{H}_3\text{O}^+} = 0.841$ for 0.100 M hydrochloric acid[13] the potential of the standard silver/silver chloride electrode was calculated and was found to agree within a millivolt with the value -0.2222 v. given in the literature.[12] This value was therefore assumed for the calculations. The results of the experiments are shown in Table II for two solutions of acidity 7.29 and 9.56 $\times$ 10^{-3} M. The acidities were measured simultaneously with the potential measurements as described in the next section.

The formal potential $E'_{5/6}$ of the uranium(V)/(VI) couple was found to be -0.060 and -0.062 v. in good agreement with the potentials found by Kern and Orlemann[3] (-0.062 v. *vs.* S.H.E. not corrected for differences in the diffusion coefficients of uranium(V) and uranium(VI))[13a] for electrolytically reduced perchlorate solutions of ionic strength $\mu = 0.5$, by Kraus, Nelson and Johnson[2] (-0.062 v. *vs.* S. H. E.) for electrolytically reduced chloride solutions of ionic strength $\mu = 0.1$ and by Harris and Kolthoff[14] (0.180 v. *vs.* S. C. E.) from polarograms of uranium(VI) solutions in 0.1 M Cl^-. The close agreement of the various potential data leaves no doubt that in these uranium pentachloride solutions the same electrode reaction

TABLE II

POTENTIALS OF THE U(IV)/(V), U(V)/(VI) AND U(IV)/(VI) COUPLES IN 0.1 M HCl

	Solution 1	Solution 2
M U $\times$ 10^3	3.57	2.48
M H_3O^+ $\times$ 10^3	9.56	7.29
[U(VI)]/[U(V)]	1.87	1.21
[U(IV)]/[U(V)]	1.86	1.21
E observed (volts)	0.2119	0.2210
$E'_{4/5}$ (volts)	− .092	− .072
$E'_{5/6}$ (volts)	− .060	− .062
$E'_{4/6}$ (volts)	− .076	− .067

$$\text{UO}_2^+ \longrightarrow \text{UO}_2^{++} + \text{e}^- \tag{6}$$

holds for the uranium(V) solutions prepared by other means.

The formal potentials $E'_{4/5}$ for the uranium(IV)/(V) couple were found to be -0.072 and -0.092 v. (*vs.* S. H. E.) in 7.29 and 9.56 $\times$ 10^{-3} M acid ($\mu = 0.1$), respectively. This difference of 20 mv. in the potentials is close to that expected if the electrode reaction is principally

$$\text{U(OH)}^{+3} + 4\text{H}_2\text{O} \longrightarrow \text{UO}_2^+ + 3\text{H}_3\text{O}^+ + \text{E}^- \tag{7}$$

for which a difference of 20.9 mv. can be calculated.[15] The corresponding formal potentials $E'_{4/6}$ for the uranium(IV)/(VI) couples are -0.067 and -0.076 v.

3.3 *p*H Measurements. Verification of the Formula UO_2^+.—The acidity of the solutions was measured with a glass electrode assembly with the object of measuring the amount of acid liberated on dissolution of uranium pentachloride.

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(10) The term "formal potential" denotes the potential of a couple at unit ratio of oxidized to reduced form under the conditions of the experiments and thus differs materially from the standard potentials of a couple where all species occurring in the electrode reaction are at unit activity.

(11) Attempts to measure the potential of the system with a platinum electrode were not successful since the observed potentials drifted rather severely except when the solutions were thoroughly stirred. In this case, the readings with the platinum electrode were in fair agreement with those determined by the polarograph null-point method.

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

(13) G. Scatchard, THIS JOURNAL, **47**, 696 (1925).

(13a) See also ref. 2, footnote 28.

(14) W. E. Harris and I. M. Kolthoff, *ibid.*, **67**, 1484 (1945).

(15) If the small amount of U^{+4} in equilibrium with UOH^{+3} is also taken into consideration the calculated difference in potential is 21.5 mv.

Combination of this information with the analytical data regarding the concentrations of the various oxidation states appeared to provide a check on the assignment of the formulas for the various species.

As soon as the bulb containing uranium pentachloride is broken, there is a very rapid initial increase in acidity. A further, though smaller, increase in acidity occurs as reaction (4) proceeds. The acidity approaches a constant value as the polarographic data become constant. The initial change in acidity was in reasonable agreement with that calculated, assuming that equation (3) represents the initial dissolution reaction, although the initial changes in acidity are too rapid to permit a careful evaluation.

The glass electrode assembly was calibrated with standard hydrochloric acid solutions of ionic strength $\mu = 0.1$ potassium chloride. It was found that in the acid range in question the potential of the cell changed 0.0591 v. for a tenfold change in acidity indicating that the activity of the oxonium ions does not change materially with acidity in the range studied. The potentials developed by the glass electrode assembly in the uranium solutions were compared with that of a 2.5×10^{-3} *M* hydrochloric acid solution. Assuming that the activity coefficients of the oxonium ions and the liquid junction potentials are the same for the uranium and hydrochloric acid solutions since their ionic strength was the same, the ratio of acidities and hence also their concentrations can be calculated from the potential differences. The results of the experiments are given in Table III, where the observed concentrations of acid are compared with those calculated assuming the formulas UO_2^{++}, UO_2^+, UOH^{+3} and U^{+4} for the various oxidation states.[16] The ratio of the concentrations of UOH^{+3} and U^{+4} was calculated using $pK = 1.15$ for the reaction

$$U^{+4} + 2H_2O \longrightarrow UOH^{+3} + H_3O^+ \qquad (8)$$

which was found[17] for chloride and perchlorate solutions of ionic strength $\mu = 0.1$. The agreement between observed and calculated acidities is considered to be within experimental error and thus substantiates the formulas assumed for the various species.

TABLE III

ESTIMATION OF THE AMOUNT OF ACID LIBERATED ON DISSOLUTION OF URANIUM PENTACHLORIDE

	Solution 1	Solution 2
M U $\times 10^3$	3.57	2.48
% UO_2^{++}	39.5	35.5
% UO_2^+	21.2	29.2
% U(IV)	39.3	35.4
% $U(OH)^{+3}$	34.6	31.9
% U^{+4}	4.7	3.5
M $H_3O^+ \times 10^3$ (calculated)	9.9	7.2
M $H_3O^+ \times 10^3$ (observed)	9.56	7.23

3.4 Potentials of the Uranium Couples as a Function of Acidity.—In Fig. 3 a diagram is given of the approximate formal potentials E' as a function of the oxonium ion activity (a_h). The possible metastability of the systems[2] at low acidity due to metastability of UOH^{+3} with respect to polymeric uranium(IV) was neglected. The diagram was constructed on the basis of the general considerations previously described[2] using the formal potentials near *p*H 2 given in section 3.2. Since these potentials were obtained under conditions where complexing of the various uranium ions is negligible the diagrams apply only to such solutions.

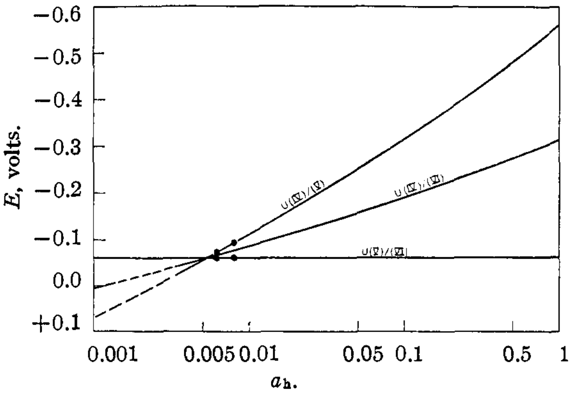

Fig. 3.—Potential of U(IV)/(V), U(V)/(VI) and U(IV)/(VI) couples as function of a_h.

At high acidity the diagrams are only very approximate, since for such solutions the ionic strength would by necessity be larger than 0.1, the value at which the experiments were carried out. Due to lack of suitable data, however, the corresponding changes in the ratios of the activity coefficients of the various uranium ions had to be neglected. There is a similar uncertainty in the value of the acid constant of uranium(IV) (equation 8), which is to be selected. For Fig. 3 the acid constant $K = 3.5 \times 10^{-2}$ was chosen, although it applies to an ionic strength $\mu = 0.5$.[17]

From the diagrams the formal potentials (*vs.* S. H. E.) of the uranium(IV)/(V) and uranium(IV)/(VI) couples at unit oxonium ion activity can be estimated to be *ca.* −0.55 and −0.31 v., respectively. They are believed to be within 20 to 30 mv. of the true potential. These potentials are in good agreement with the value $E = -0.334$ for the reaction

$$U^{+4} + 4H_2O \longrightarrow UO_2^{++} + 2H_3O^+ + H_2 \qquad (9)$$

found by Taylor and Smith[18] for molal hydro-

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(16) As mentioned in a previous paper[2] the only other hydrolysis product of uranium(IV) requiring consideration is the polymer of approximate formula $U(OH)_4$. The solutions, however, almost certainly did not contain appreciable amounts of this polymer, since its characteristic color could not be detected visually, and no catalytic acceleration of the disproportionation reaction occurred.

(17) K. A. Kraus and F. Nelson, Report ORNL-23, March, 1948. The given *pK* value applies if the molarities, rather than the activities, of all species are used.

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

chloric acid solutions under the assumption that $\gamma_{UO_2^{++}}/\gamma_{U^{+4}} = 1$ and $\gamma_{H^+} = \gamma_{\pm HCl} = 0.809$.

(4) Summary

Polarographic, *p*H and potential measurements on solutions of uranium pentachloride in water have been carried out.

It was found that uranium pentachloride reacts with water to yield initially uranium(IV) and uranium(VI) and that near *p*H 2 uranium(IV) and uranium(VI) react rapidly to yield appreciable concentrations of uranium(V).

Near *p*H 2 the species U^{+4}, UOH^{+3}, UO_2^+ and UO_2^{++} can exist in equilibrium with each other. Verification of the assignment of the species was obtained through *p*H measurements.

The potentials of the uranium(IV)/(V), uranium(IV)/(VI) and uranium(V)/(VI) couples have been determined near *p*H 2. Utilizing the available knowledge of the hydrolytic behavior of the species involved, the potentials of these couples were estimated for unit activities of oxonium ions. The values for the potentials of the uranium(IV)/(V) and uranium(IV)/(VI) couples at this acidity were found to be approximately −0.55 and −0.31 v., respectively.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Structure and Activity of Supported Nickel Catalysts

BY FRED N. HILL[1] AND P. W. SELWOOD

The purpose of this work was to use magnetic, and other, methods to study the structure of supported nickel; and to relate the structural information, so far as possible, to actual catalytic activity.[2] This work was carried on simultaneously with related studies on supported manganese and iron. During the course of all the work there emerged the principle of valence inductivity.[3] Applications of the principle to supported nickel are included in the present paper.

Preparation of Materials

Magnesia.—This material was prepared as follows: 290 g. of magnesium chloride hydrate was dissolved in 15 liters of distilled water. To this there was added a solution of 160 g. of potassium hydroxide in 3 liters of distilled water. The finely divided precipitate was allowed to settle for twelve hours. The supernatant liquid was removed, and a cycle of washings by decantation was begun. After three washings, the mixture was heated to 70° for ten minutes, and then allowed to cool. This procedure allowed a partial agglomeration of the finer particles, and decreased the difficulty of filtration. The mixture was filtered, the precipitate again washed by decantation, and once more filtered. No chloride ion could be detected in the final wash water. The precipitate was dried at 110° for two days, ground in an agate mortar, then finally ignited at 360° for fourteen hours.

The final product showed no X-rays lines except those due to magnesium oxide. The magnetic susceptibility of this material was approximately -0.3×10^{-6}, and independent of temperature. The surface area of the magnesia was 138 ± 2 sq. m. per g. as determined by low temperature nitrogen adsorption.

γ-Alumina.—This support was prepared by a standard procedure. Aluminum metal shot was dissolved in potassium hydroxide solution. The resulting solution was filtered, partially neutralized with nitric acid, then treated with carbon dioxide until precipitation was complete. The precipitate was decanted, washed until the wash water was neutral, then filtered, dried at 110°, ground, and finally ignited at 450° for sixteen hours.

The X-ray diffraction pattern of this material gave no lines other than those of γ-alumina, although traces of *boehmite* may have been present. The X-ray pattern was somewhat diffuse. The magnetic susceptibility of the alumina was approximately -0.3×10^{-6}, substantially independent of temperature down to −190°. The surface area of the alumina was 230 ± 5 sq. m. per g.

Rutile.—This material was obtained from the National Lead Company, Titanium Division. The X-ray pattern showed no lines other than those due to *rutile*. The magnetic susceptibility was approximately -0.3×10^{-6}, and was independent of temperature. The surface area was 126 ± 5 sq. m. per g. Neither the surface area nor the magnetic susceptibility of the *rutile* were appreciably altered by a twelve hour ignition at 450°.

Nickel Oxide on Magnesia.—This system was prepared by impregnation of the high-area magnesia with nickel nitrate solution. The mixture was then dried and ignited. Details of preparation were similar to those described more fully below for the nickel-alumina system. It was noted that quite dilute nickel nitrate solution sufficed for appreciable nickel concentrations in the finished catalyst. The supported oxide ranged in color from gray to black.

Nickel Oxide on Alumina.—Between 5 and 10 g. of *gamma*-alumina was stirred with nickel nitrate solution for five minutes. The volume of solution was usually 10 cc. per gram of support. This is much in excess of the amount of solution necessary to saturate the alumina. The slurry was filtered with suction, then dried at 110° and ignited for twelve hours at 450°. Samples were prepared in this way ranging from 2 to 24 weight per cent. of nickel. The nickel content was, of course, related to the nickel concentration in the solutions used for impregnation. For instance 5 g. of alumina impregnated with 50 cc. of 3.28 *M* nickel nitrate solution yielded an ignited sample containing 22.9% nickel.

The above procedure is believed to yield a more homogeneous product than the commonly used method of adjusting the volume of impregnation solution to that just necessary to saturate the support. Nevertheless, it is difficult to obtain microscopic homogeneity. There are always formed small clumps of massive nickel oxide, through drying and ignition of occluded solution. The magnetic data thus all tend to be low because dispersed nickel oxide has a much higher magnetic susceptibility than has the massive oxide.[4]

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[2] This is the seventh paper on the susceptibility isotherm from this Laboratory. The sixth appeared in THIS JOURNAL, **71**, 2181 (1949).

[3] Selwood, THIS JOURNAL, **70**, 883 (1948).

[4] The term "massive" oxide is here used to mean a well-crystallized, pure compound, in contrast to a dispersed or attenuated oxide such as a supported compound or a gel-like substance.