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Studies on Metal Carbonate Equilibria. 7. Reduction of the Tris(carbonato)dioxouranate(VI) Ion, $UO_2(CO_3)_3^{4-}$, in Carbonate Solutions

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The redox equilibria between U(VI) and U(V) have been studied at 25 °C in an aqueous carbonate–perchlorate medium with a constant perchlorate concentration of 3 M, by measuring the potential of inert mercury and platinum electrodes against a hydrogen half-cell. From these measurements we established that the limiting uranium(V) carbonate complex had the composition $UO_2(CO_3)_3^{5-}$. The experimental data at acidities between 10^{-12} and 10^{-11} M could be explained by the equilibrium $UO_2(CO_3)_3^{4-} + e^- \rightleftarrows UO_2(CO_3)_3^{5-}$ ($E° = -0.5236 \pm 0.0003$ V). By combining these data with the results of a previous work, we obtain the formation constant for the reaction $UO_2^+ + 3CO_3^{2-} \rightleftarrows UO_2(CO_3)_3^{5-}$ ($\log \beta_3 = 13.3 \pm 0.4$). Additional measurements in the acidity range between 10^{-11} and 10^{-9} M, combined with the results of a previous work,[1] have shown that uranium species in the oxidation states +6, +5, and +4 are formed according to the equilibrium $2UO_2(CO_3)_3^{5-} + 4HCO_3^- \rightleftarrows UO_2(CO_3)_3^{4-} + U(CO_3)_5^{6-} + 2CO_3^{2-}$ ($\log K = 4.98 \pm 0.07$). A recalculation of previous redox data[13] of the Am(VI)/Am(V) couple in carbonate media indicates that Am(V) forms a limiting carbonate complex $AmO_2(CO_3)_3^{5-}$ with approximately the same stability constant as found for U(V).

In three previous publications, we have reported equilibrium studies in the U(IV)[1]– and U(VI)[2,3]–carbonate systems.

Substantial qualitative evidence exists for the formation of carbonate species of U(V). Electrochemical and spectroscopic methods have been used by several authors to demonstrate the presence of uranium in this oxidation state in carbonate solutions. A brief review has been given by Wester and Sullivan,[4] which indicates that no quantitative equilibrium data are available on the U(V)–carbonate system. McClaine et al.[5] observed that potential measurements, with inert electrodes (Hg, Pt, Cu), in carbonate–bicarbonate solutions containing uranium(VI) and -(IV) appeared to be reversible. This was unexpected, due to the large structural changes introduced by the loss of the two axial oxygens following the reduction of U(VI) to U(IV).

They assumed this observation to indicate that the actual electrode reaction is a one-electron exchange involving uranium(VI) and -(V) carbonato complexes. By analogy with the U(VI) they suggested for the U(V) complex the probable composition $UO_2(CO_3)_3^{5-}$. This assumption is given additional support from the observation[6] that solids of the composition $K_5[MO_2(CO_3)_3]$, M = Np and Am, are formed at high carbonate concentrations.

In this paper, we describe the conditions under which U(V) may be stablized in carbonate media and the composition and the equilibrium constants of the species formed.

Notations

B = total concentration of uranium

c = concentration of CO_3^{2-}

c_0 = concentration of CO_3^{2-} in the initial test solution where $B = [UO_2(CO_3)_3^{4-}]$

d = concentration of HCO_3^-

d_0 = concentration of HCO_3^- in the initial test solution where $B = [UO_2(CO_3)_3^{4-}]$

$R = d^4c^{-2}$

h = concentration of H^+

$H = [ClO_4^-] - [Na^+] - 2B$ = analytical concentration excess of H^+ in the initial test solution.

w = moles of electrons introduced by cathodic reduction

$\theta = w/V$ = analytical concentration excess of electrons, referred to U(VI) as the zero level

$Z = \theta/B$ = average number of electrons per uranium atom

$K_{6,i}$ = conditional equilibrium constant for $p\mathrm{U(VI)} + (6p - i)e^- \rightleftarrows \mathrm{U}_p(i)$

$\beta_{1,r,q}$ = equilibrium constant for $UO_2(CO_3)_3^{4-} + e^- + (r-3)CO_3^{2-} + qH_2O \rightleftarrows UO_2(CO_3)_r(OH)_q^{1-2r-q} + qH^+$

Method

The redox equilibria at $h < 10^{-11}$ M were studied in carbonate solutions containing U(VI) and varying amounts of uranium in lower oxidation states, produced coulometrically. The redox potential was measured at 25 °c in 3 M (Na)ClO$_4$ by using mercury and platinum as inert electrodes. The experiments were performed as titrations. In each series, the total uranium concentration, B, and the proton concentration, h, were kept constant, whereas the analytical excess of electrons, θ, was varied by constant-current coulometry.

The values of B, h, H, and H/B were varied in the ranges $1 \times 10^{-3} < B < 1 \times 10^{-2}$ M, $1.4 \times 10^{-12} < h < 6 \times 10^{-12}$ M, $0.2 < -H < 0.7$ M, and $23 < -H/B < 210$. These limits were imposed for the following reasons: (1) A black precipitate (possibly UO_2) forms at low values of h. (2) Yellow precipitates (possibly both $Na_4UO_2(CO_3)_3$ and UO_3) form at high values of B and h. (3) At low values of B, the low redox-buffer capacity of the solutions makes the potential less reliable and errors due to oxidizing impurities are not negligible. (4) The solubility of Na_2CO_3 in 3 M $NaClO_4$ limits the h range that can be studied.

A known volume, V, of a test solution of initial composition

$$S_0\text{: } B\ \mathrm{M\ U(VI)},\ H\ \mathrm{M\ H^+},\ (3 - H - 2B)\ \mathrm{M\ Na^+},\ 3\ \mathrm{M\ ClO_4^-}$$

was introduced in the titration vessel. A low stream of 99.99% pure N_2 was first passed through two washing bottles containing 0.1 M Cr(II) on Zn(Hg) and 3 M $NaClO_4$, respectively. The gas was then bubbled through the solution for at least 5 h to displace O_2 prior to

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(1) L. Ciavatta, D. Ferri, I. Grenthe, F. Salvatore, and K. Spahiu, *Inorg. Chem.*, **22**, 2088 (1983).

(2) L. Ciavatta, D. Ferri, I. Grenthe, and F. Salvatore, *Inorg. Chem.*, **20**, 463 (1981).

(3) D. Ferri, I. Grenthe, and F. Salvatore, *Acta Chem. Scand., Ser. A*, **A35**, 165 (1981).

(4) D. W. Wester and J. C. Sullivan, *Inorg. Chem.*, **19**, 2838 (1980).

(5) L. A. McClaine, E. P. Bullwinkel, and J. C. Huggins, *Proc. Int. Conf. Peaceful Uses At. Energy, 3rd*, **8**, 26 (1955).

(6) D. S. Gorbenka-Germanov and R. A. Zenkova, *Russ. J. Inorg. Chem. (Engl. Transl.)*, **11**, 282 (1966).

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the generation of uranium at lower oxidation states. The composition of S_0 was varied by increasing stepwise the analytical concentration of electrons θ by coulometric reduction with the circuit

$$- \mathrm{Hg}|\mathrm{TS}|3\ \mathrm{M\ NaClO_4}|3\ \mathrm{M\ ClO_4^-},\ 2.9\ \mathrm{M\ Na^+},\ 0.05\ \mathrm{M\ Hg_2^{2+}}|\mathrm{Hg}\ + \qquad \text{(A)}$$

The test solution had the general composition

$$\mathrm{TS:}\ B\ \mathrm{M\ U},\ \theta\ \mathrm{M\ e^-},\ (H+\theta)\ \mathrm{M\ H^+},\ (3-H-2B)\ \mathrm{M\ Na^+},\ 3\ \mathrm{M\ ClO_4^-}$$

The electrolysis was carried out at lower densities than 1×10^{-3} A/cm^2 in order to ensure 100% current efficiency. This was checked as described previously.[1]

Equilibrium was reached very rapidly as shown by the stable potential of the redox electrodes that was attained 5–10 min after each step of electrolysis and remained constant for several hours within 0.02 mV. The potential of two mercury and two platinum electrodes always agreed within 0.05 mV.

The redox potential was measured with the cells

$$- \mathrm{Hg,\ Pt}|\mathrm{TS}|\mathrm{RE}\ + \qquad \text{(B)}$$

where RE denotes the half-cell

$$3\ \mathrm{M\ NaClO_4}|0.0185\ \mathrm{M\ AgClO_4},\ 2.982\ \mathrm{M\ NaClO_4}|\mathrm{AgCl(s),\ Ag}$$

From E_B, the emf of cells B, the potential E referred to the normal hydrogen electrode was calculated as shown in part 4[1] of this series.

h was measured by means of the cell

$$- \text{glass electrode}|\mathrm{TS}|\mathrm{RE}\ + \qquad \text{(C)}$$

The emf of cell C is equal to

$$E_C = E_C^\circ - 0.05916 \log h + E_j$$

where E_C° is a constant and E_j the liquid-junction potential arising between TS and 3 M $NaClO_4$. In a previous study,[2] we found $E_j = 7.2 \times 10^{-3}(H + 2B)$ V.

The value of E_C is constant within a few tenths of 1 mV; thus, h does not vary appreciably in the course of a titration. This simplifies the treatment of the data. The experimental data $(E,\theta)_B$ were recalculated in the form of $Z = \theta/B$ as a function of $\log x = -E/0.05916$. The sets of $Z(\log x)$ data reported in Table I (supplementary material) form the basis of the following mathematical treatment.

The measurements at $h \simeq 10^{-10}$ M were carried out with a slightly modified procedure. The N_2 stream was adjusted to the proper partial pressure of CO_2 by passing it through a series of washing bottles containing $NaHCO_3$ and Na_2CO_3 at the same ratio as in the test solution.

Test solutions with a high $-H/B$ ratio ($\sim$100) were studied in order to minimize the variation of c and d as compared to the initial concentrations c_0 and d_0. Thus, approximate values of $R = d^4c^{-2} \simeq d_0^4c_0^{-2}$ were calculated by using the expressions

$$H = -d_0 - 2c_0 - 6B$$

and

$$hc_0d_0^{-1} = K_{a2} = 10^{-9.63}$$

Measurements of this type are time consuming due to the very slow disproportionation equilibrium of U(V). Thus, only a few test solutions were studied. The data $Z(\log x, R)$ are given in Table I.

Experimental Section

Reagents and Analysis. Uranium(VI) perchlorate, perchloric acid, sodium hydrogen carbonate, sodium perchlorate, and **silver perchlorate** solutions were prepared as described previously.[2] **Sodium carbonate** solutions made from the Merck p.a. product were analyzed with standard $HClO_4$. The preparation of **mercury perchlorate** solutions is described elsewhere.[7]

Measurements. All the emf measurements were performed in a paraffin oil bath at 25.00 ± 0.02 °C. The bath was placed in a thermostated room kept at 25.0 ± 0.3 °C. The experimental apparatus and the measuring equipment are described in a previous paper.[1] Metrohm EA 109 glass electrodes were used. By comparison with a hydrogen electrode, calibration curves were constructed for the correction of the alkali error. This became important at $h < 10^{-10}$ M and attained a maximum level of 0.07 log h unit. We believe that the corrected log h values have an uncertainty not larger than 0.01 unit.

Treatment of the Experimental Data

The experimental data were divided into two parts. The $Z(\log x)$ data collected at $h < 10^{-11}$ M were analyzed with a mathematical procedure similar to that adopted in part 4[1] of this series.

The data collected at $h > 10^{-11}$ M were treated separately in a second stage.

For simplicity, the number and the oxidation state of uranium atoms in the complexes were determined first. Then the dependence of the $Z(\log x)$ data on c[8] and h was analyzed to determine the number of CO_3^{2-} and OH^- groups in the complexes.

At constant h and c, the complexes may generally be written $U_p(i)$, with formal charge $i/p < +6$.

The complexes $U_p(i)$ are formed by cathodic reduction of U(VI) according to the semireaction

$$p\mathrm{U(VI)} + (6p - i)\mathrm{e^-} \rightleftarrows \mathrm{U}_p(i) \qquad (1)$$

of which $K_{6,i}$ is the equilibrium constant. Z may then be written

$$Z = \frac{\sum(6p - i)K_{6,i}[\mathrm{U(VI)}]^{p-1}x^{6p-i}}{1 + \sum pK_{6,i}[\mathrm{U(VI)}]^{p-1}x^{6p-i}} \qquad (2)$$

The $Z(\log x)_{c,h}$ data, for different values of B, yield a single curve. This means that only mononuclear complexes are formed. Thus, p in (1) and (2) is equal to 1. Additionally, the $Z(\log x)$ data indicate that $Z \rightarrow 1$ as $\log x \rightarrow \infty$. This suggests that the lowest value of i is +5.

From previous studies,[2,3] we know that U(VI) at the low acidities encountered in this study is present as $UO_2(CO_3)_3^{4-}$.

Now we can write (1) for the data at different h and c as

$$\mathrm{UO_2(CO_3)_3^{4-}} + \mathrm{e^-} + (r-3)\mathrm{CO_3^{2-}} + q\mathrm{H_2O} \rightleftarrows \mathrm{UO_2(CO_3)}_r\mathrm{(OH)}_q^{1-2r-q} + q\mathrm{H^+} \qquad (3)$$

for which $\beta_{1,r,q}$ is the equilibrium constant related to $K_{6,5}$ by

$$K_{6,5} = \sum\beta_{1,r,q}c^{r-3}h^{-q}$$

Z is then defined by

$$Z = \frac{\sum\beta_{1,r,q}xc^{r-3}h^{-q}}{1 + \sum\beta_{1,r,q}xc^{r-3}h^{-q}} \qquad (4)$$

The $Z(\log x)$ data for different values of h and c, reported in Figure 1, fall on a single curve, indicating that both q and $(r - 3)$ in (3) and (4) are equal to zero. Thus, (3) can be written as a one-electron reaction

$$\mathrm{UO_2(CO_3)_3^{4-}} + \mathrm{e^-} \rightleftarrows \mathrm{UO_2(CO_3)_3^{5-}} \qquad (5)$$

with equilibrium constant $\beta_{1,3}$, and (4) takes the simple form

$$Z = \frac{\beta_{1,3}x}{1 + \beta_{1,3}x} \qquad (6)$$

In order to ensure that no oxidation states other than +6

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(7) G. Biedermann and D. Ferri, *Chem. Scr.*, **2**, 57 (1972).

(8) In the initial solution, containing uranium only as $UO_2(CO_3)_3^{4-}$, we calculated c_0 from the relation

$$H = h(1 - c_0K_{a2}^{-1}) - 2c_0 - 6B$$

We assumed as a first approximation that, in the course of the titration, c did not differ appreciably from c_0, since h never varied more than a few tenths of 1 mV.

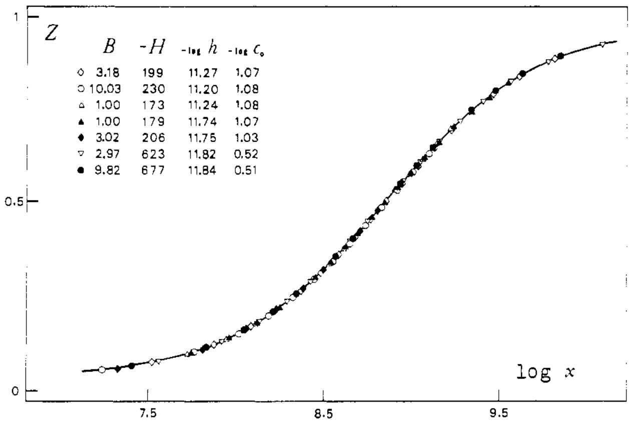

Figure 1. $Z(\log X)$ data. The full-drawn cruve has been calculated by assuming $\log \beta_{1,3} = -8.851$.

Table II. Survey of the Final Results

	$-\log \beta_{1,3}$	$-E°$, V
graphical method	8.850 ± 0.005	0.5236 ± 0.0003
from eq 7	8.851 ± 0.003	0.5236 ± 0.0002
proposed values	8.851 ± 0.005	0.5236 ± 0.0003

and +5 are to be assumed with the present data and to determine $\beta_{1,3}$, we compared the $Z(\log x)$ data with the normalized functions $Y(\log u)$ where

$$Y = u/(1 + u) \qquad \log u = \log x + \log \beta_{1,3}$$

The agreement between the experimental data and the theoretical curve calculated by assuming the redox equilibrium (5) is shown in Figure 1.

In the position of best fit, $\log \beta_{1,3}$ was obtained as the difference of the abscissas and is reported in Table II. The uncertainty represents the maximum deviation obtained from the limiting positions still giving an acceptable fit.

This value was then corroborated by the calculation of $\beta_{1,3}$ for each experimental point using the relation

$$\log \beta_{1,3} = \log \frac{Z}{1 - Z} - \log x \qquad (7)$$

The average value of $\beta_{1,3}$ and its standard deviation from the mean are shown in Table II.

From the definition of E

$$E = E° + 0.05916 \log \frac{[UO_2(CO_3)_3^{4-}]}{[UO_2(CO_3)_3^{5-}]}$$

we can calculate

$$E° = 0.05916 \log \beta_{1,3} = -0.5236 \pm 0.0003 \text{ V}$$

valid in 3 M $NaClO_4$.

At $h > 10^{-11}$ M, the functional dependence of Z on $\log x$ suggests that species containing uranium in the oxidation states +6, +5, and +4 coexist.

We thus attempted to explain the experimental data by assuming that the predominant equilibria are represented by (5) and

$$UO_2(CO_3)_3^{4-} + 2e^- + 4HCO_3^- \rightleftarrows U(CO_3)_5^{6-} + 2CO_3^{2-} \qquad (8)$$

with the constant $\beta_{1,5}$ deduced from the results of a previous study.[1]

This means

$$Z = \frac{\beta_{1,3}x + 2\beta_{1,5}Rx^2}{1 + \beta_{1,3}x + \beta_{1,5}Rx^2} \qquad (9)$$

To test this hypothesis, we compared the $Z(\log x, R)_B$ data with the normalized function $F(\log v)_L$ where

$$F = \frac{v + 2Lv^2}{1 + v + Lv^2} \qquad \log v = \log \beta_{1,3} + \log x$$

$$L = \frac{\beta_{1,5}}{\beta_{1,3}^{\,2}}R$$

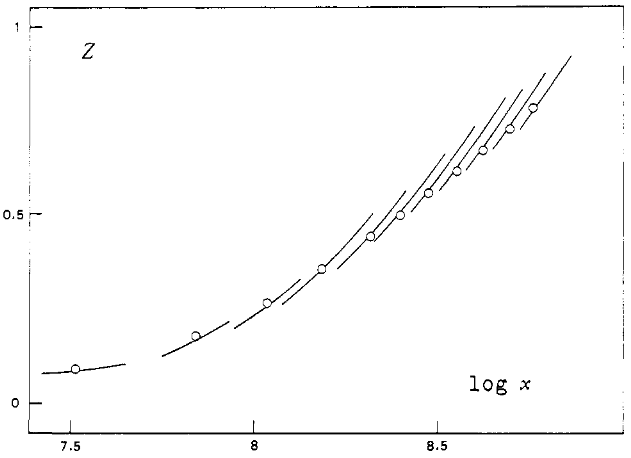

Figure 2. The $Z(\log x, R)$ data collected at $h = 10^{-10}$ M. The curves have been calculated by assuming the equilibria (5) and (8) with the values of $\beta_{1,3}$ given in Table II, $\log \beta_{1,5} = -12.72$, and the following experimental values of 10^5R (from left to right): 5.68, 4.47, 3.50, 2.72, 2.13, 1.80, 1.52, 1.29, 1.08, 0.91, 0.75.

Each theoretical $F(\log v)$ curve was constructed with the value of L calculated from the experimental R ratios, from the value of $\beta_{1,3}$ of Table II, and from $\beta_{1,5} = 10^{-12.72}$. The satisfactory agreement between the experimental data and the theoretical map, shown in Figure 2, indicates that no additional uranium(V) and uranium(IV) carbonate species are formed in appreciable amounts at $h > 10^{-11}$ M.

Discussion

Equilibrium data given in the literature have seldom been collected at the same ionic strength. In order to be able to compare our data on the uranium–carbonate system with information previously published, we need a method for recalculation of thermodynamic data to a common reference state. We have used the specific-ion-interaction theory[9-11] for this purpose.

All data have been referred to a 3 M $NaClO_4$ medium by using the interaction coefficients listed in Table III. The errors in the interaction coefficients are in some cases fairly large. This results in an increased error in the recalculated constants as compared to the experimental error. We are presently devoting much effort to the improvement of interaction coefficients in the uranium(IV, V, VI)–CO_3^{2-} systems, data which may be used also for other actinoid–carbonate equilibria.

The equilibrium constant $\log \beta_3^{U(V)} = 13.3 \pm 0.4$, for the reaction

$$UO_2^+ + 3CO_3^{2-} \rightleftarrows UO_2(CO_3)_3^{5-} \qquad (10)$$

in 3 M $NaClO_4$, has been evaluated by combining (5) with the equilibria

$$UO_2^{2}+ \; + 3CO_3^{2-} \rightleftarrows UO_2(CO_3)_3^{4-} \qquad (11)$$

$$UO_2^{2+} + e^- \rightleftarrows UO_2^+ \qquad (12)$$

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(9) (a) E. A. Guggenheim, "Applications of Statistical Mechanics", Clarendon Press, Oxford, 1966; (b) G. Scatchard, *Chem. Rev.*, **19**, 309 (1936).

(10) G. Biedermann, "On the Nature of Sea Water", Dahlem Konferenzen, Berlin, 1975.

(11) G. Biedermann, J. Bruno, D. Ferri, I. Grenthe, F. Salvatore, and K. Spahiu, *Mater. Res. Soc. Symp. Proc.*, **12** (1982).

Table III. Survey of Interaction Coefficients, $\epsilon(i,K)$, between Species i and K[a]

i, K	j, L	ϵ, Kg mol^{-1}	ref
UO_2^{2+}, ClO_4^-		0.47 ± 0.02	15
NpO_2^+, ClO_4^-		0.5 ± 0.1	16-19
AmO_2^+, ClO_4^-		0.5 ± 0.1	14
UO_2^+, ClO_4^-	NpO_2^+, ClO_4^-; AmO_2^+, ClO_4^-		
H^+, ClO_4^-		0.14 ± 0.02	15
AmO_2^{2+}, ClO_4^-	UO_2^{2+}, ClO_4^-		
Na^+, $AmO_2(CO_3)_3^{4-}$	K^+, $W(CN)_8^{4-}$; K^+, $Fe(CN)_6^{4-}$; $(CH_3)_4N^+$, $Mo(CN)_8^{4-}$	−0.13 ± 0.05	11
H^+, HCO_3^-	Li^+, NO_3^-; Li^+, Cl^-; Li^+, Br^-; H^+, NO_3^-; H^+, Cl^-	0.10 ± 0.05	20
H^+, CO_3^{2-}	Na^+, CO_3^{2-}; K^+, CO_3^{2-}; Li^+, SO_4^{2-}	−0.05 ± 0.05	20
Na^+, $AmO_2(CO_3)_3^{5-}$		−0.2 ± 0.1	rough est

[a] ϵ is assumed constant in the ionic strength range between 0 and 3.5 *m*. Unknown $\epsilon(i,K)$ values have been approximated with the interaction coefficients between the ions j and L in the second column.

The constant for (11) is $\log \beta_3^{U(VI)} = 22.6 \pm 0.1$, which we have determined in a separate study that will be reported soon. This value differs slightly from the estimate $\log \beta_3^{U(VI)} \simeq 24$ given in ref 1. The constant for (12) is $\log \beta^{U(VI,V)} = 0.4_4 \pm 0.3$, which has been extrapolated from Kern and Orlemann's[12] accurate determination of the normal potential of the semireaction (12) in 0.5 M $NaClO_4$.

The limiting carbonate complexes of both uranium(V) and uranium(VI) have the same stoichiometry and probably the same geometry. However, the uranium(V) complex is very much weaker.

It would be of interest to find out whether a trinuclear carbonate complex, $(UO_2)_3(CO_3)_6^{9-}$, analogous to the corresponding uranium(VI) complex, is formed. However, the disproportionation of U(V) does not allow measurements to be made in a carbonate concentration range where such a complex might be formed. The interesting question may be settled by studying the pentavalent oxidation state of another actinide that has a broader range of existence, e.g. Np(V).

A study of the NpO_2^+–CO_3^{2-} system is presently being carried out in cooperation with Dr. Billon's group at the CEA Laboratories, Fontenay-aux-Roses, France.

The relatively high U(V) and U(IV) concentrations encountered in the present study are not compatible with the low solubility product of $UO_2(s)$. We also observed this phenomenon at higher acidities and in solutions of U(IV),[1] and we explained it with the formation of supersaturated solutions.

The electrochemical properties of americium(III, IV, V, VI) in carbonate solutions have recently been studied.[13] The redox potential Am(VI)/Am(V) has been determined and found to be independent of the carbonate ion concentration at high ratios $[CO_3^{2-}]/([Am(VI)] + [Am(V)])$. The actinoids have, in a given oxidation state, very similar properties. Hence, the observations of Bourges et al.[13] on the Am(VI)/Am(V) redox couple can be explained by the equilibrium reaction (13), analogous to (5).

$$AmO_2(CO_3)_3^{4-} + e^- \rightleftarrows AmO_2(CO_3)_3^{5-} \qquad (13)$$

The normal potential of this semireaction extrapolated to the 3 M $NaClO_4$ medium equals 968 ± 25 mV; thus, $\log \beta_{1,3}^{Am} = 16.4 \pm 0.4$.

If we assume for the species $AmO_2(CO_3)_3^{5-}$ and $AmO_2(CO_3)_3^{4-}$ the same formation constants found for the corresponding uranium species (see (10) and (11)), we can calculate the normal potential for the semireaction

$$AmO_2^{2+} + e^- \rightleftarrows AmO_2^+ \qquad (14)$$

We find $E° = 1.52 \pm 0.05$ V.

From the measurements of Penneman and Asprey[14] in 0.3 and 1 M $HClO_4$, we have obtained $E° = 1.57 \pm 0.03$ V valid in 3 M $NaClO_4$. The agreement between the experimental and the calculated potentials is well within the experimental uncertainties. It corroborates satisfactorily our assumption that the formation constants of the carbonate species do not depend appreciably on the particular actinoid, but it is rather a property of the given oxidation state.

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Registry No. $UO_2(CO_3)_3^{5-}$, 86953-33-5; $AmO_2(CO_3)_3^{5-}$, 86953-34-6; U, 7440-61-1.

Supplementary Material Available: Table I, listing primary experimental data in the form of $Z(\log x)$ at various B, h, and c levels (2 pages). Ordering information is given on any current masthead page.

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(12) D. M. H. Kern and E. F. Orlemann, *J. Am. Chem. Soc.*, **71**, 2102 (1949).

(13) J. Y. Bourges, B. Guillaume, G. Koehly, and D. E. Hobart, *Inorg. Chem.*, **22**, 1179 (1983).

(14) R. A. Penneman and L. B. Asprey, Abstracts, 118th National Meeting of the American Chemical Society, Chicago, IL, 1950, p 28Q.

(15) R. A. Robinson and R. M. Stokes, "Electrolyte Solutions", 2nd ed., Butterworths, London, 1965.

(16) D. Cohen, and J. C. Hindman, *J. Am. Chem. Soc.*, **74**, 4679 (1952).

(17) R. W. Stromatt, R. M. Peekema, and F. A. Scott, Report HW-58212, Hanford Works, 1958.

(18) J. C. Sullivan, J. C. Hindman, and A. J. Zielen, *J. Am. Chem. Soc.*, **83**, 3373 (1961).

(19) A. J. Zielen and J. C. Sullivan, *J. Phys. Chem.*, **66**, 1065 (1962).

(20) L. Ciavatta, *Ann. Chim.* (*Rome*), **70**, 551 (1980).