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# Studies of Metal Carbonate Equilibria.
# 20. Formation of Tetra(carbonato)uranium(IV) Ion, $U(CO_3)_4^{4-}$, in Hydrogen Carbonate Solutions

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## Abstract

The equilibrium between the tetracarbonate and pentacarbonate complexes of the U(IV) ion has been studied at 25 °C in $CO_2/HCO_3^-$ solutions of different ionic strength ($I = 0.5; 1.0; 2.0; 3.0$ M $NaClO_4$), using Vis–UV spectrophotometry. The data have been explained by assuming the equilibrium

$$U(CO_3)_4^{4-} + CO_3^{2-} \rightleftharpoons U(CO_3)_5^{6-}$$

where $K_5$ is the (ionic strength dependent) equilibrium constant. The molar absorptivities for the penta- and tetracarbonate at 660 nm were constant and equal to $\epsilon_1 = 17.2 \pm 0.2$ and $\epsilon_2 = 35.5 \pm 0.5$, respectively. By using the specific ion interaction theory (S.I.T.), and the equilibrium constants at different ionic strength, the equilibrium at zero ionic strength: $\lg K_5(0) = -1.12 \pm 0.25$, was obtained. This stepwise equilibrium constant is small and the formation of $U(CO_3)_5^{6-}$ seems to be mainly an ionic strength effect. Hence, very small amounts of $U(CO_3)_5^{6-}$ (and possibly also similar complexes of the other tetravalent actinides) can form in natural waters.

## Introduction

Uranium is the major constituent of spent nuclear fuel (98%). In order to be able to assess the effects of a release of actinides into the geosphere, it is necessary to understand their chemistry under the conditions encountered in nature. Most ground water systems contain $OH^-$, $HCO_3^-$ and $CO_3^{2-}$ as predominant inorganic ligands. Their redox condition is highly variable, but is often reducing in deep crystalline bedrock systems. Hence, knowledge of the U(IV)–$H_2O$–$CO_2$ system is of particular interest, both for the understanding of the mobility of uranium in nature and as a model for the other tetravalent actinides.

In part 4 of this series [1], the formation constant of the limiting complex $U(CO_3)_5^{6-}$ has been determined using potentiometric and spectrophotometric data; this paper also reviews the older literature. Kim *et al.* [2] made solubility studies of the Pu(IV)–$CO_3^{2-}$ system and interpreted their results assuming the formation of $Pu(CO_3)_i^{(4-2i)+}$ ($i = 1$–$5$) complexes. The coexistence of americium (III, IV, V, VI) in concentrated carbonate media has been demonstrated using potentiometric data [3]. These data have been reinterpreted by Robouch and Vitorge [4] who calculated the formation constant of $Am(CO_3)_5^{6-}$. Two studies of the Th(IV)–$H_2O$–$CO_2$ system are under way in our laboratory: (i) e.m.f. data obtained by using a coulometric technique show the existence of $Th(CO_3)_5^{6-}$; (ii) solubility measurements indicate the formation of a mixed hydroxo–carbonate species with charge −1, the composition of which has to be determined.

It seems quite clear that in the An(IV)–$H_2O$–carbonate system, species other than the hydroxides and the limiting carbonate complex are formed. The transition from metal hydroxo to metal carbonato complexes normally occurs through the formation of mixed hydroxo–carbonato complexes [5]. This is particularly true in the case of highly hydrolyzed metal ions, such as the tetravalent actinides. The aim of this study is to obtain quantitative information on the stoichiometry and stability constants of the species found in the carbonate concentration range preceding the formation of $U(CO_3)_5^{6-}$. At lower carbonate concentrations one easily obtains the formation of $UO_2(s)$ [1], hence the experimental study should be made at the lowest possible total concentrations of U(IV). Under these conditions spectrophotometry is a very practical experimental method [1].

## Experimental

### *Reagents and Analysis*

Uranium(VI) perchlorate, sodium hydrogen carbonate and sodium perchlorate were prepared as

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described in ref. 6. The preparation of the Pd catalyst on the Pt net has been described elsewhere [1].

$H_2(g)$ (100 ± 0.4%) and $CO_2$–$H_2$ gas mixtures (with $CO_2/(CO_2 + H_2) = 100 \pm 0.6\%$; $50 \pm 0.3\%$; $10 \pm 0.2\%$ and $1 \pm 0.05\%$) were prepared and analyzed by AGA. These gases were purified from oxygen by passing them through two washing bottles containing a Cr(II) solution and zinc amalgam, and finally through a $NaClO_4$ solution of the same ionic strength as the test solution.

### *Methodology*

The experimental study was made in $HCO_3^-$/($CO_2$,$H_2$) solutions using spectrophotometry. In order to avoid the oxidation of U(IV) by air, an *in situ* reduction of the test solution was performed, as described previously [1]. Two different experimental procedures were used. In the first the test solution was circulated continuously between the reaction vessel and the cuvette by using a peristaltic pump. There seemed to be a continuous leakage of air into the system, resulting in incomplete and slow reduction. In the second method the reduction was performed in a closed cell; at equilibrium, the solution was pumped into the cuvette, the spectrum was recorded and the solution was them pumped back to the main cell. The test solution (of known ionic strength, total metal and bicarbonate concentrations) was reduced overnight with pure $H_2$, by using palladium sponge deposited on a platinum net. After recording the absorbance spectrum, a new gas mixture was bubbled through the solution. Equilibrium was reached within four hours, the new spectrum was recorded and the $CO_2$ partial pressure increased again. The measured absorptivities at 660 nm as a function of free carbonate concentration form the basis of the mathematical analysis of the data.

### *Measurements*

All the measurements were performed in a thermostated room at 25.0 ± 0.2 °C. The absorption spectra were measured in a Helma 10 cm cylindrical quartz cuvette by using a Cary 19 double beam spectrophotometer. A solution of the same bicarbonate and $NaClO_4$ concentrations as the test solution was used as a reference. The whole absorption spectrum, between 350 and 750 nm, was recorded, but only the absorptivity at 660 nm, where the optical changes were the largest, was used for the calculations. The test solution was circulated between the main cell and the cuvette by means of a Masterflex peristaltic pump; tygon (R-3603) tubings from Masterflex were used. The reduction efficiency of U(VI) to U(IV) in carbonate media is strongly dependent on the total metal concentration and the ionic strength. Table 1 presents the percentual reduction after a given period of contact with pure $H_2$ gas. Typical values for an overnight reduction (16 h) of a bicarbonate solution with $[U(IV)]_t = 0.4$ mM were 55, 75, 90 and 100%, in 0.5, 1, 2 and 3 M $NaClO_4$ media. This rate is much smaller than the one observed in acidic media (pH = 1 or 2), where more than 95% reduction was obtained in less than 4 h, for a solution at $I = 0.5$ M, $[U(IV)]_t = 0.4$ mM. The molar absorptivities were calculated by using the known degree of reduction of the test solutions, *cf.* Table 1.

## Treatment of Data

### *Free Carbonate Concentration*

In a $CO_2(g)/HCO_3^-$ medium of a given ionic strength the free carbonate concentration is given by

$$[CO_3^{2-}] = [HCO_3^-]^2/(K_{p1}(I) \times K_1(I) \times p(CO_2) \qquad (1)$$

### *Absorptivity Data*

The occurrence of an isosbestic point (Fig. 1) is consistent with the presence of two different complexes. The fact that the molar absorptivity, at a given value of $[CO_3^{2-}]$, does not depend on $pCO_2$ and $[HCO_3^-]$ (Table 1), shows that the complexes formed only contain carbonate as a ligand. When the reduction is complete, $[U(IV)]_t = C_1 + C_2$, where $C_1$ and $C_2$ are the concentrations of $U(CO_3)_5^{6-}$ and $U(CO_3)_4^{6-}$, respectively. The total absorptivity is: $A_\lambda = \epsilon_1 C_1 + \epsilon_2 C_2$. Substituting $[U(IV)]_t$ and $K_5$ by their analytical expressions one obtains

$$A_\lambda\text{norm.} = [K_5 \times [CO_3^{2-}] \times (\epsilon_1 + \epsilon_2)]/(K_5 \times [CO_3^{2-}] + 1) \qquad (2)$$

which is equivalent to

$$1/(A_\lambda\text{norm.} - \epsilon_1) = (K_5 \times [CO_3^{2-}] + 1)/(\epsilon_2 - \epsilon_1) \quad (3)$$

$\epsilon_1$ is obtained directly from the experimental data at the highest carbonate concentrations, in 3.5 m $NaClO_4$ medium (the experimental uncertainty on $\epsilon_1$ was estimated to be ±0.2). At other ionic strengths, the measured $A_\lambda$ at the highest $[CO_3^{2-}]$ and the value of $\epsilon_1$ gave the reduction efficiency from which $A_\lambda$norm. was deduced. $K_5$(0.5 M) and $\epsilon_2$ were obtained through a linear regression (eqn. (3)) of the experimental data. The equilibrium constants and their uncertainties (maximum deviation) at the other ionic strengths were determined graphically with the normalized curve, using eqn. (2) and the previously determined $\epsilon_1$ and $\epsilon_2$.

### *Ionic Strength Influence*

In order to compare the results obtained at different $I$, we have used the specific ion interaction theory (S.I.T.), as described elsewhere [7]. For the equilibrium $U(CO_3)_4^{4-} + CO_3^{2-} \rightleftharpoons U(CO_3)_5^{6-} (K_5)$, we obtain

$$\lg K_5(I) = \lg K_5(0) + \Delta Z^2 D - \Delta\epsilon I \qquad (4)$$

TABLE 1. Survey of the Experimental Data[a]

| $I$ (M) | $[U(IV)]_t$ (mM) | Reduction efficiency | $[HCO_3^-]$ (M) | $pCO_2$ (%) | pH | $\lg[CO_3^{2-}]$ | $A_\lambda$ norm. |
|---|---|---|---|---|---|---|---|
| 0.1 | 0.39 | | 0.1 | 0 | | $\geqslant -2.2$ | (s) |
| 0.5 | 2.16 | 48% | 0.2 | 0 | | $\geqslant -1.3$ | 20.00 |
| | | (5 h) | | 1 | 8.87 | −1.40 | 21.40 |
| | | | | 10 | 7.87 | −2.40 | 30.00 |
| | | | | 50 | 7.17 | −3.11 | (s) |
| | 0.39 | 55% | 0.5 | 1 | 9.27 | −0.61 | 17.28 |
| | | (16 h) | | 10 | 8.27 | −1.61 | 22.86 |
| | | | | 50 | 7.57 | −2.31 | 30.65 |
| | | | | 100 | 7.27 | −2.61 | 32.33 |
| | 0.39 | 55% | 0.4 | 0 | | $\geqslant -0.7$ | 19.33 |
| | | (16 h) | | 10 | 8.17 | −1.81 | 25.83 |
| | | | | 50 | 7.47 | −2.51 | 31.03 |
| | | | | 100 | 7.17 | −2.81 | 33.44 |
| 1.0 | 0.39 | 75% | 0.5 | 0 | | $\geqslant -0.4$ | 17.20 |
| | | (16 h) | | 1 | 9.31 | −0.51 | 17.50 |
| | | | | 10 | 8.31 | −1.51 | 20.01 |
| | | | | 50 | 7.61 | −2.21 | 27.68 |
| | | | | 100 | 7.31 | −2.51 | 29.89 |
| | 0.44 | 73% | 0.4 | 0 | | $\geqslant -0.6$ | 17.40 |
| | | (16 h) | | 1 | −9.21 | −0.71 | 18.00 |
| | | | | 10 | −8.21 | −1.71 | 21.87 |
| | | | | 50 | −7.51 | −2.41 | 29.23 |
| | | | | 100 | −7.21 | −2.71 | 31.85 |
| 2.0 | 0.39 | 89% | 0.15 | 0 | | $\geqslant -1.3$ | 17.20 |
| | | (16 h) | | 1 | 8.86 | −1.42 | 18.10 |
| | | | | 10 | 7.86 | −2.42 | 21.71 |
| | | | | 50 | 7.16 | −3.12 | 28.25 |
| | | | | 100 | 6.86 | −3.42 | 30.74 |
| | 0.44 | 87% | 0.2 | 0 | | $\geqslant -1.1$ | 17.50 |
| | | (16 h) | | 10 | 9.07 | −1.17 | 17.80 |
| | | | | 50 | 7.37 | −2.87 | 24.30 |
| | | | | 100 | 7.07 | −3.17 | 28.27 |
| 3.0 | 0.39 | 78% | 0.1 | 1 | 8.99 | −1.65 | 17.20 |
| | | (7 h) | | 10 | 7.99 | −2.65 | 20.16 |
| | | | | 50 | 7.29 | −3.35 | 24.56 |
| | | | | 100 | 6.99 | −3.65 | (s) |
| | 0.39 | 94% | 0.1 | 0 | | $\geqslant -1.5$ | 17.20 |
| | | (16 h) | | 1 | 8.99 | −1.65 | 17.20 |
| | | | | 10 | 7.99 | −2.65 | 20.66 |
| | | | | 50 | 7.29 | −3.35 | 25.60 |
| | | | | 100 | 6.99 | −3.65 | 15 (s) |
| | 0.43 | ≃100% | 0.2 | 0 | | $\geqslant -0.8$ | 17.20 |
| | | (48 h) | | 1 | 9.30 | −1.05 | 17.20 |
| | | | | 10 | 8.30 | −2.05 | 18.10 |
| | | | | 50 | 7.60 | −2.75 | 19.61 |
| | | | | 100 | 7.30 | −3.05 | 20.70 |

[a] (s): A solid precipitate was formed.

where $K_5$ and $I$ are expressed in molal units; $D$, the Debye–Huckel term, is: $D = 0.5107\sqrt{I}/(1 + 1.5\sqrt{I})$; $\Delta Z^2 = 16$; and

$$\Delta\epsilon = \epsilon(U(CO_3)_5^{6-},Na^+) - \epsilon(CO_3^{2-},Na^+) - \epsilon(U(CO_3)_4^{4-},Na^+) \qquad (5)$$

By plotting $(\lg K_5(I) - 16D)$ *versus* $I$, one obtains the equilibrium constant $K_5(0)$ (at zero ionic strength) and the interaction coefficient term $\Delta\epsilon$. The same kind of calculations have been performed to obtain $K_1$ and $K_{\mathrm{pl}}$ in different ionic media. Table 2 presents these constants in molar and molal units.

TABLE 2. Influence of the Conversion Factor of Molarity to Molality in $NaClO_4$ Media on the Equilibrium Constants of the $H_2O-CO_2$ System

| $C$ (M) | 0.100 | 0.200 | 0.500 | 1.000 | 1.500 | 2.000 | 3.000 |
|---|---|---|---|---|---|---|---|
| $m/C$[a] | 1.0073 | 1.0118 | 1.0256 | 1.0449 | 1.0759 | 1.1037 | 1.1652 |
| $m$ (m) | 0.101 | 0.202 | 0.513 | 1.045 | 1.614 | 2.207 | 3.496 |
| lg $K_1$ ($m^{-1}$) | 9.794 | 9.70 | 9.57[b] | 9.50 | 9.49 | 9.50 | 9.56[b] |
| lg $K_1$ ($M^{-1}$) | 9.80 | 9.70 | 9.58[b] | 9.52 | 9.52 | 9.54 | 9.63[b] |
| lg $K_{p1}$ ($m^2$/atm) | −7.62 | −7.58 | −7.55[b] | −7.57 | −7.62 | −7.69 | −7.85[c, d] |
| lg $K_{p1}$ ($M^2$/atm) | −7.63 | −7.59 | −7.57[b] | −7.61 | −7.69 | −7.77 | −7.98[c, d] |
| lg($K_1K_{p1}$) (M/atm) | 2.17 | 2.11 | 2.01 | 1.91 | 1.83 | 1.77 | 1.65 |

[a]Ref. 8. [b]Ref. 9. [c]Ref. 10. [d]Ref. 11.

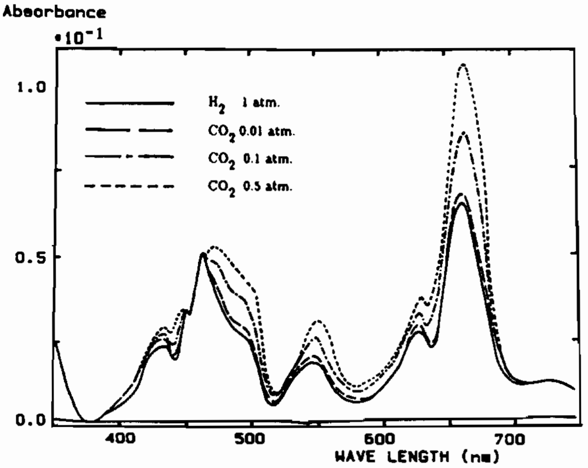

Fig. 1. Formation of the tetracarbonate complex as followed in the visible spectrum ($[U(IV)]_t = 0.39$ mM; $[HCO_3^-] = 0.15$ M; $I = 2.21$ m). An isosbestic point occurs at 463 nm. The absorbance increases in the 480 nm region and at 662 nm on the formation of $U(CO_3)_4^{4-}$.

## Results

For a given experiment (at fixed $I$, $[HCO_3^-]$ and $[U(IV)]_t$) the spectra recorded at different $pCO_2$ (Fig. 1) show the existence of an isosbestic point at 463 nm, indicating the presence of only two different complexes. The initial spectra (at highest pH) were similar to the one reported earlier in 1 M $NaHCO_3$ [12]. This was attributed to the $U(CO_3)_5^{6-}$ complex [1]. By increasing the partial pressure of $CO_2(g)$ one observes the formation of a shoulder at 480 nm and an increase of the peak at 660 nm, as compared to the initial spectrum. The experiments at 0.5 M (and 3 M) ionic strength were performed at different bicarbonate concentrations and $CO_2$ partial pressures. Figure 2 shows that the absorptivity depends only on the free carbonate concentration. The results are then interpreted by the following equilibrium: $U(CO_3)_4^{4-} + CO_3^{2-} \rightleftharpoons U(CO_3)_5^{6-}$. As described previously, we obtained the following molar absorptivities: $\epsilon_1 = 17.2 \pm 0.2$, $\epsilon_2 = 35.5 \pm 0.5$, and the equilibrium constants presented in Table 3. The graphically estimated maximum errors are smaller for the data at $I = 0.5$, 1 and 2 M than for the experiments made at $I = 3$ M. There seems to be no experimental reason for this. We have therefore assigned the same uncertainties ± 0.15 units in lg $K_5$ at all ionic strengths. The determination of lg $K_5(0)$ and $\Delta\epsilon$ from eqn. (4) was made by using a standard least-squares method using the same uncertainty and weight for all experimental lg $K_5$ values. The S.I.T. plot (Fig. 3) gives: lg $K_5(0) = -1.12 \pm 0.22$ and $\Delta\epsilon = -0.13 \pm 0.11$.

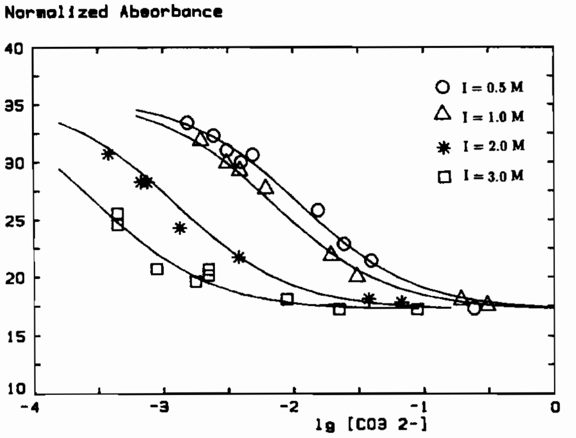

Fig. 2. Review of all our experimental data (*cf.* Table 1) obtained at different ionic strength *vs.* lg$[CO_3^{2-}]$. The full drawn curves are the calculated normalized function with $\epsilon_1 = 17.2$ and $\epsilon_2 = 35.5$.

## Discussion

In the previous uranium(IV) carbonate study [1] only the limiting complex $U(CO_3)_5^{6-}$ was identified. By using the value of lg $K_5$ determined in the present study one finds that at most a few percent of $U(CO_3)_4^{4-}$ was present under the experimental conditions used in ref. 1. Hence there is no contradiction between the two studies. However, the value of lg $\epsilon_1 = 1.29$ proposed by Ciavatta *et al.* [1] seems to

TABLE 3. Survey of the Final Results of lg $K_5(I)$

| $I$ (m) | 3.50 | 2.21 | 1.05 | 0.51 | 0.00 |
|---|---|---|---|---|---|
| lg $K_5$ ($M^{-1}$) | 3.50 ± 0.20 | 2.90 ± 0.15 | 2.15 ± 0.15 | 1.95 ± 0.15 | |
| lg $K_5$ ($m^{-1}$) | 3.43 ± 0.20 | 2.80 ± 0.15 | 2.15 ± 0.15 | 1.95 ± 0.15 | |
| lg $K_5 - 16D$ | −0.59 | −0.96 | −1.16 | −0.86 | |
| lg $K_5(0)$ | | | | | −1.12 ± 0.2 |

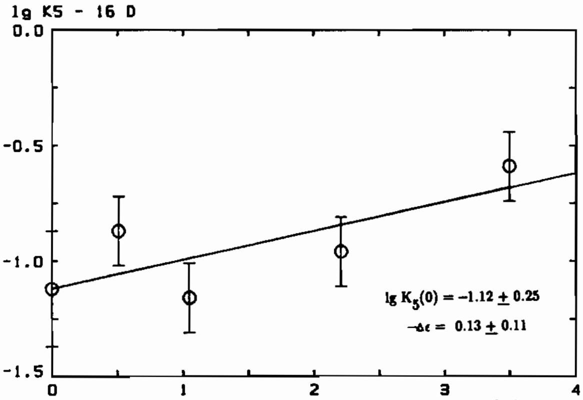

Fig. 3. Extrapolation of the equilibrium constant ($K_5$) to zero ionic strength, using S.I.T. (eqn. (4)).

be too large. As judged by their own experimental observations, lg $\epsilon_1 = 1.25 \pm 0.02$, the latter value is in good agreement with our own experimental determination, lg $\epsilon_1 = 1.24 \pm 0.01$.

The carbonate complexes of uranium(IV) are very strong, lg $\beta_5 = 38.6$ in 3 M $NaClO_4$. This value is obtained from the data in ref. 1 and a more recent and precise value of lg $\beta_3$ for the formation of $UO_2(CO_3)_3^{4-}$ given by Grenthe *et al.* [13]. The value of lg $K_5 = 3.50 \pm 0.15$ (in 3 M $NaClO_4$) is surprisingly small, however, Kim *et al.* [2] observed low values of both lg $K_5$ and lg $K_4$ for the plutonium(IV) carbonate complexes. The values of lg $K_5$ decrease with decreasing ionic strength and it is obvious that $U(CO_3)_5^{6-}$ is not the predominant uranium(IV) carbonate complex under the conditions encountered in most ground water systems. The situation is probably the same for other actinoid(IV) carbonates, *cf.* ref. 2.

One might ask whether $U(CO_3)_5^{6-}$ is stabilized by ionic-pairing with $Na^+$, or not. An indication is provided by the value of $\epsilon(U(CO_3)_5^{6-}, Na^+)$. From the value of $\Delta\epsilon = -0.13 \pm 0.11$ we obtain $\epsilon(U(CO_3)_5^{6-}, Na^+) - \epsilon(U(CO_3)_4^{4-}, Na^+) = -0.22 \pm 0.11$. If we assume $\epsilon(U(CO_3)_4^{4-}, Na^+) \simeq \epsilon(UO_2(CO_3)_3^{4-}, Na^+) = -0.02$ [13,14] we obtain $\epsilon(U(CO_3)_5^{6-}, Na^+) = -0.20 \pm 0.11$. This value is much lower than the value $\epsilon((UO_2)_3(CO_3)_6^{6-}, Na^+) = 0.39$ indicating a much larger degree of ionic-pairing with $Na^+$ for $U(CO_3)_5^{6-}$ than for $(UCO_2)_3(CO_3)_6^{6-}$. The data used in the S.I.T. plot scatter quite a lot around the regression line. We have no reasons to believe that the experimental uncertainties have been underestimated. Hence, the experimental findings might indicate that the S.I.T. theory is less satisfactory for equilibria involving complexes with very high negative charges where ionic pairing with the cation of the ionic medium may occur.

Both the degree and the rate of reduction of uranium(VI) were found to decrease with decreasing ionic strength. This observation is not a result of a change of chemical equilibrium for the reaction $UO_2(CO_3)_3^{4-} + 2CO_2(g) + H_2(g) \rightleftharpoons U(CO_3)_5^{6-} + 2H^+$ which is strongly displaced to the right under all the conditions encountered in the present study, *cf.* ref. 1 for the relevant equilibrium constant.

The chemical model for the uranium(IV)–$H_2O$–$CO_2(g)$ system is far from complete. The extreme ease of oxidation of uranium(IV) and of precipitation of $UO_2(s)$ complicates the experimental investigations. We are presently engaged in a study of the corresponding thorium system which offers some experimental simplifications. We hope that this system will provide us with some additional evidence also for the speciation of uranium(IV) carbonates.

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## Notation

| | |
|---|---|
| $A_\lambda$ | absorbance referred to a 10 cm optical path length |
| $[CO_3^{2-}]$ | concentration of $CO_3^{2-}$ (mol/l) |
| $[HCO_3^-]$ | concentration of $HCO_3^-$ (mol/l) |
| $I$ | ionic strength of the solution (m: molal; M: molar) |
| $K_1$ | equilibrium constant for $H^+ + CO_3^{2-} \rightleftharpoons HCO_3^-$ |
| $K_5$ | concentration equilibrium constant for $U(CO_3)_4^{4-} + CO_3^{2-} \rightleftharpoons U(CO_3)_5^{6-}$ |
| $K_5(0)$ | equilibrium constant at $I = 0$ m |
| $K_{p1}$ | equilibrium constant for $CO_2(g) + H_2O \rightleftharpoons H^+ + HCO_3^-$ |
| $pCO_2$ | partial pressure of $CO_2$ (atm) |
| $[U(IV)]_t$ | total concentration of uranium (mol/l) |
| $\epsilon_1, \epsilon_2$ | molar absorptivities at 660 nm of the penta- and tetracarbonate complexes, respectively (l/mol cm) |
| $\epsilon(i,Na^+)$ | specific interaction coefficient of the species $i$ (negatively charged) and $Na^+$ (l/mol). |