Studies on Metal Carbonate Equilibria. Part 10.† A Solubility Study of the Complex Formation in the Uranium(VI)–Water–Carbon Dioxide (g) System at 25 °C ‡

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The complex formation in the system $U^{VI}–H_2O–CO_2(g)$ was studied by measuring the solubility of $UO_2(CO_3)$ (s) as a function of the CO_2 pressure and the hydrogen-ion concentration. The measurements were made at 25 °C, by using two different ionic media, 0.5 and 3 mol dm^{-3} $NaClO_4$, respectively. The equilibrium constants for the following reactions were determined. Interaction

$$UO_2(CO_3)\text{ (s)} \rightleftharpoons UO_2^{2+} + CO_3^{2-} \qquad K_{s,0}$$

$$UO_2^{2+} + tCO_3^{2-} \rightleftharpoons UO_2(CO_3)_t,\ t = 1\text{—}3 \qquad \beta_{t,1}$$

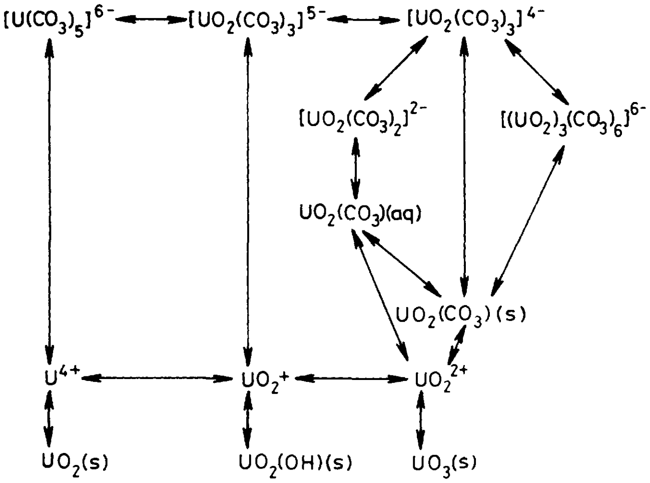
$$3UO_2^{2+} + 6CO_3^{2-} \rightleftharpoons [(UO_2)_3(CO_3)_6]^{6-} \qquad \beta_{6,3}$$

coefficients $\varepsilon(i,j)$ for the various uranium species with ClO_4^- (or Na^+) were determined by using the Brønsted, Guggenheim, Scatchard specific ion-interaction theory. By using these and equilibrium data from the literature, we propose the following set of 'best' estimates of equilibrium constants, referred to the pure water reference state: $\log K_{s,0} = -14.4 \pm 0.1$, $\log \beta_{1,1} = 9.5 \pm 0.2$, $\log \beta_{2,1} = 16.6 \pm 0.2$, $\log \beta_{3,1} = 21.3 \pm 0.2$, and $\log \beta_{6,3} = 53.4 \pm 0.8$.

In previous publications we have studied the uranium-(IV),[1] -(V),[2] and -(VI) [3-5] carbonate systems. These studies were made in carbonate concentration ranges where the concentration of free metal ion, *viz.* U^{4+}, UO_2^+, and UO_2^{2+}, is negligible in comparison with the total concentration of uranium. Hence, it was not possible to obtain numerical values for the overall stability constants for the complexes formed. The most direct way to obtain information of this kind seems to be to select a suitable thermodynamic cycle from the equilibria depicted in the Scheme. Hence, we have chosen to extend the solubility measurements described by Pirozhkov and Nikolaeva [6] and Sergeyeva *et al.*,[7] in order to evaluate the overall formation constants for the equilibria in the uranium(VI)-water-carbon dioxide (g) system. From these data, it is also possible to calculate the overall equilibrium constants for the formation of $[UO_2(CO_3)_3]^{5-}$ and $[U(CO_3)_5]^{6-}$ by combination with the previously obtained redox data.[1,2]

Solubility measurements do not in general provide sufficient information to establish a unique chemical equilibrium model for the system under study.[8,9] However, this is no drawback in the present case since a proper chemical equilibrium model has already been established by using e.m.f.[3] and spectrophotometric [4] measurements.

A prerequisite for the solubility method is that the composition of the solid phase is known and preferably constant. Several papers have been published on the relative stability of $UO_2(OH)_2$ (s) and $UO_2(CO_3)$ (s).[6,7,10] It is evident from these studies (*e.g.* ref. 7, p. 900) that $UO_2(CO_3)$ (s) is the thermodynamically stable phase in the system uranium(VI)–carbon dioxide (g)–water, provided the partial pressure of $CO_2(g)$ is not too low ($>10^{-3.5}$ atm). Hence, we decided to base our investigation on measurements of the solubility of $UO_2(CO_3)$ (s) as a function of the partial pressure of $CO_2(g)$ and the hydrogen-ion concentration as described previously.[11]



Scheme. Thermodynamic cycles for the uranium(IV,V,VI)–water–carbonate systems

The equilibria (1) were studied. In one of our previous

$$pUO_2(CO_3)\text{ (s)} + qCO_2(\text{g}, a\text{ atm}) + pH_2O \xrightleftharpoons{K_{(p+q),p}} [(UO_2)_p(CO_3)_{p+q}]^{-2q} + 2qH^+ \quad (1)$$

communications[3] we have proved the existence of a polynuclear uranium(VI)–carbonate complex, $[(UO_2)_3(CO_3)_6]^{6-}$, the structure of which has been reported.[12] The solubility method, where the total concentration of uranium in solution is much lower than in the previous experiments, offers an opportunity to test the possible formation of the mononuclear $[UO_2(CO_3)_2]^{2-}$ species reported by several other investigators.[7,13,14]

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† Part 9 is ref. 5.

‡ *Non-S.I. unit employed:* atm = 101 325 Pa.

In order to compare experimental equilibrium data obtained at different ionic strengths, or in different ionic media, it is necessary to be able to calculate the activity coefficients of the species participating in the reactions. In many practical applications it is also necessary to recalculate tabulated equilibrium constants so they are numerically correct under the conditions studied. In our previous papers we used the Brønsted,[15] Guggenheim,[16] Scatchard[17] specific ion-interaction theory for this purpose. The interaction coefficients $\varepsilon(i,j)$ may be determined from osmotic coefficients or mean activity factors of electrolytes. However, for complexes this method cannot in general be used. The interaction coefficients may instead be estimated by using size and charge considerations,[18] or determined experimentally by measuring the equilibrium constants as a function of the ionic strength.[19,20] In view of the very great practical need of precise equilibrium constants at different (usually low) ionic strengths for the actinoid–carbonate complexes, *e.g.* for the modelling of uranium ore formation and for the speciation/migration of actinoids in ground water, we have determined experimentally some interaction coefficients of uranium(VI) carbonate complexes with Na^+ or ClO_4^- from equilibrium constants at two different ionic strengths, 0.5 and 3 mol dm^{-3} $NaClO_4$.

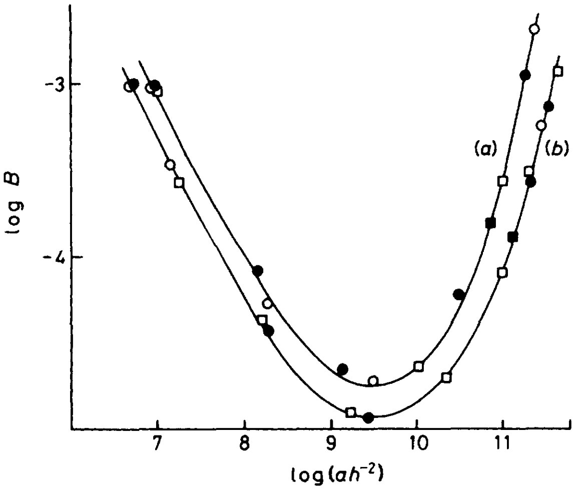

Figure. Experimental solubility data at 25 °C for the system $UO_2(CO_3)$ (s)–H_2O—CO_2 (g) in 0.5 (*a*) and 3 mol dm^{-3} $NaClO_4$ (*b*). The full curves have been calculated from the equilibrium constant given in Table 2. a = 0.97 (□), 0.29 (●), 0.098 (○), or 0.051 atm (■)

Experimental

Method.—The experimental method used was similar to that described in ref. 11. The solubility of $UO_2(CO_3)$ (s) was measured as a function of the hydrogen-ion concentration in solutions of acidity $10^{-6.3} < h < 10^{-3.5}$, saturated with CO_2–N_2 gas mixtures of known composition. The test solutions had the following analytical composition: H mol dm^{-3} H^+, $(C - H)$ mol dm^{-3} Na^+, C mol dm^{-3} ClO_4^-, saturated with $UO_2(CO_3)$ (s) and CO_2 (g) of partial pressure a atm.

The partial pressure of CO_2 (g) ($0.0477 \leqslant a \leqslant 0.9797$ atm) was calculated from the known analytical composition of the gas mixture, the measured atmospheric pressure, and the vapour pressure of water over C mol dm^{-3} $NaClO_4$. The determination of the free hydrogen-ion concentration, h, has been described before.[3] The Nernst equation takes in this case the simplified form (2) since the variations of the activity

$$E = E_0 - 59.16 \log h \qquad (2)$$

coefficient of H^+ and of the liquid-junction potential can be neglected.

The total concentration of uranium was determined spectrophotometrically using the thiocyanate method described by Ahrland.[21]

Preparation of the Test Solutions.—A typical solubility experiment started with V_0 cm^3 of a solution S_0 of composition H_0 mol dm^{-3} H^+, $(C - H_0)$ mol dm^{-3} Na^+, and C mol dm^{-3} ClO_4^- in a glass vessel. H_0 was determined by a Gran diagram[22] by using the coulometric technique described elsewhere;[23] E_0 was determined simultaneously, with a precision of 0.05 mV. A stream of a CO_2–N_2 gas mixture was then introduced into the titration vessel and the selected value of H was achieved by coulometric generation of OH^-, or in some cases, H^+. Finally, $UO_2(CO_3)$ (s) was added and the solubility equilibrium attained under continuous stirring. This could take a few days. The attainment of true equilibrium was indicated when the potential of the glass electrode remained constant within 0.2 mV during several days. At this point the experiment was discontinued and the total concentration of uranium, B, was determined. The value of E_0 was checked after each experiment by immersing the glass electrode in a fresh C mol dm^{-3} $NaClO_4$ solution, and then repeating the E_0 titrations. The changes in E_0 were less than 0.1 mV. The composition of the solid phase in equilibrium with the test solution was checked by *X*-ray powder photography. No changes in composition of the solid were detected.

All measurements were made at 25.00 ± 0.02 °C by using equipment described before.[1] The pressure was measured with a precision of 5×10^{-4} atm by using a piezoresistive transducer. The glass electrode was of type Metrohm EA 109.

Chemicals.—Uranium(VI) carbonate was precipitated from a $UO_2(NO_3)_2$ solution, saturated with CO_2 (g), by dropwise addition of a $NaHCO_3$ solution. The solid was stored under the mother-liquor in a CO_2 (g) atmosphere in order to avoid losses of CO_2. It was centrifuged and washed with C mol dm^{-3} $NaClO_4$ saturated with CO_2 (g) before adding to the test solution. Elemental analyses and *X*-ray powder diffraction spectra confirmed the composition $UO_2(CO_3)$. All other chemicals were prepared and analyzed as described before.[3]

Results

Treatment of Experimental Data.—The experimental data are given in Table 1 and plotted in the form log B *vs.* log (ah^{-2}) in the Figure. At the lowest values of log (ah^{-2}) a small correction (at most 5% of B) for the hydrolysis reaction (3)

$$UO_2^{2+} + 2H_2O \rightleftharpoons UO_2(OH)_2 + 2H^+ \qquad (3)$$

was made. The corresponding equilibrium constant was taken from the compilation of Baes and Mesmer.[24]

It appears that log B is a continuous function of log (ah^{-2}), *i.e.* B is independent of a at a given value of h. This, in turn, means that the complexes formed on dissolution of $UO_2(CO_3)$ (s) must have the general composition $(UO_2)_p(CO_3)_{p+q}^{-2q}$ as indicated by equation (1). The mass balance equation for uranium then takes the form (4). The activity of $UO_2(CO_3)$ (s)

$$B = \sum_p \sum_q pK_{(p+q),p}(ah^{-2})^q \qquad (4)$$

is constant throughout the experiment and the concentrations of UO_2^{2+} and CO_3^{2-} thus cannot be varied independently of

Table 1. Summary of solubility data ($-\log B$, $-\log h,a$) for the U^{VI}–$CO_2(g)$–H_2O system at $I = 3$ and 0.5 mol dm^{-3}

(*a*) 3 mol dm^{-3} $NaClO_4$

3.234, 6.215, 0.0970; 4.084, 3.568, 0.9768; 3.554, 5.916, 0.2887; 3.505, 5.652, 0.9758; 3.122, 6.014, 0.2917; 2.921, 6.303, 0.0978; 2.987, 3.621, 0.2909; 2.976, 3.841, 0.0975; 3.570, 3.621, 0.9713; 3.458, 4.066, 0.0984; 4.372, 4.113, 0.9658; 4.427, 4.406, 0.2863; 4.893, 4.625, 0.9577; 4.928, 4.981, 0.2910; 4.073, 5.180, 0.9599; 3.887, 6.210, 0.477

(*b*) 0.5 mol dm^{-3} $NaClO_4$

2.976, 3.753, 0.2900; 2.938, 3.980, 0.0983; 3.015, 3.491, 0.9797; 4.042, 4.349, 0.2844; 4.181, 4.629, 0.0974; 4.638, 5.008, 0.9666; 4.224, 5.501, 0.2932; 3.807, 5.918, 0.0981; 3.560, 5.496, 0.9742; 2.937, 5.885, 0.2917; 2.676, 6.175, 0.0987; 4.653, 4.826, 0.2932; 4.724, 5.246, 0.0982

Table 2. Equilibrium constants $K_{(p+q),p} = K_q/p$ for the uranium(VI)–carbonate system at $I = 0.5$ and 3 mol dm^{-3}. The deviations are estimated maximum errors. The deviations in the corresponding constants referred to the pure water reference state have been evaluated by adding the experimental and estimated errors in the various $\varepsilon(i,j)$ values

		$K_{(p+q),p}$		
q	$(p+q),p$	3 mol dm^{-3} $NaClO_4$	0.5 mol dm^{-3} $NaClO_4$	Pure water
−1	0,1	3.67 ± 0.03	3.94 ± 0.003	3.66 ± 0.05
0	1,1	−5.05 ± 0.05	−4.92 ± 0.05	−5.0 ± 0.2
1	2,1	−15.35 ± 0.05	−15.00 ± 0.05	−15.9 ± 0.1
2	3,1	−26.55 ± 0.05	−26.05 ± 0.05	−29.2 ± 0.2
3	6,3	−38.42 ± 0.05	−37.35 ± 0.05	−44.0 ± 0.5

one another. Hence, we can only obtain information on the constants $K_q = \sum_p pK_{(p+q),p}$ which are obtained by rewriting equation (4) as (5). The values of q and K_q in the polynomial

$$B = \sum_q K_q(ah^{-2})^q \qquad (5)$$

(5) are deduced directly from the data given in Table 1 by using standard graphical or least-squares methods. The data are satisfactorily explained by assuming $q = -1,0,1,2$, or 3. The corresponding K_q values are given in Table 2. The full curves in the Figure indicate the agreement between the experimental data and the proposed model.

The values of p and hence the individual constants $K_{(p+q),p}$ may be deduced by using additional chemical information from the previous study of homogeneous equilibria in the U^{VI}–CO_2 (g)–H_2O system.[3,4] In these studies, we established that only mononuclear and trinuclear complexes were formed, *i.e.* $p = 1$ or 3. We can now identify $K_2 = K_{3,1}$ {from the known formation of $[UO_2(CO_3)_3]^{4-}$}, $K_3 = K_{6,3}$ {from the known formation of $[(UO_2)_3(CO_3)_6]^{6-}$ and the fact that no complex $[UO_2(CO_3)_4]^{6-}$ is formed in the uranium carbonate system}, $K_{-1} = K_{0,1}$ and $K_0 = K_{1,1}$ which refer to the formation of UO_2^{2+} and $UO_2(CO_3)$ (aq). The remaining constant $K_1 = K_{2,1}$ refers to the formation of the mononuclear complex $[UO_2(CO_3)_2]^{2-}$. This interpretation can be quantitatively

$$3[UO_2(CO_3)_3]^{4-} + 6H^+ \rightleftharpoons [(UO_2)_3(CO_3)_6]^{6-} + 3CO_2\,(g) + 3H_2O \qquad (6)$$

checked by comparing the value of the equilibrium constant, K, for the reaction (6) calculated from solubility data ($K = K_{6,3}K_{3,1}^{-3}$) with the direct determination using e.m.f.[3] or spectrophotometric[4] techniques. The value obtained from the solubility data $\log K$ (solub.) $= 41.2 \pm 0.2$ agrees within experimental error with the corresponding values $\log K$(e.m.f.) $= \log K$ (spectrophot.) $= 41.5 \pm 0.1$ obtained previously.

By combining the equilibrium constants given in Table 2 with the protonation constants of the carbonate ion, we have calculated the formation constants $\beta_{t,p}$ for reactions of the type (7). These constants are given in Table 3.

$$pUO_2^{2+} + tCO_3^{2-} \rightleftharpoons [(UO_2)_p(CO_3)_t]^{2(p-t)} \qquad (7)$$

Extrapolation of Equilibrium Constants to the Pure Water Reference State.—The equilibrium constants have all been determined in the presence of a large excess of $NaClO_4$. The standard state of the participating species has been chosen so that the activity coefficients tend to unity in the pure solvent (0.5 or 3 mol dm^{-3} $NaClO_4$). We have previously used the specific interaction theory for comparison of data at different ionic strengths and also for the recalculation of equilibrium constants to the pure water reference state.[2,25] By following the same procedure we obtain expressions (8)—(11). Here

$$\log K_{0,1}^0 = \log K_{0,1} + \log(\delta - 0.12244C) - 2D(I) + [\varepsilon(UO_2^{2+}, ClO_4^-) - 2\varepsilon(H^+, ClO_4^-)]m_{NaClO_4} + \log a_{H_2O}(I) \qquad (8)$$

$$\log K_{2,1}^0 = \log K_{2,1} - 3\log(\delta - 0.12244C) - 6D(I) + \{\varepsilon[UO_2(CO_3)_2^{2-}, Na^+] + 2\varepsilon(H^+, ClO_4^-)\}m_{NaClO_4} - \log a_{H_2O}(I) \qquad (9)$$

$$\log K_{3,1}^0 = \log K_{3,1} - 5\log(\delta - 0.12244C) - 20D(I) + \{\varepsilon[UO_2(CO_3)_3^{4-}, Na^+] + 4\varepsilon(H^+, ClO_4^-)\}m_{NaClO_4} - 2\log a_{H_2O}(I) \qquad (10)$$

$$\log K_{6,3}^0 = \log K_{6,3} - 7\log(\delta - 0.12244C) - 42D(I) + \{\varepsilon[(UO_2)_3(CO_3)_6^{6-}, Na^+] + 6\varepsilon(H^+, ClO_4^-)\}\text{-}m_{NaClO_4} - 3\log a_{H_2O}(I) \qquad (11)$$

$D(I) = 0.5107\sqrt{I}/(1 + 1.5\sqrt{I})$ is the Debye–Hückel term at ionic strength I, a_{H_2O} is the activity of water, 0.9837 and 0.8876 at $I = 0.5$ and 3 mol dm^{-3}, respectively, and δ is the density at 25 °C of C mol dm^{-3} $NaClO_4$ (equal to 1.0381 and 1.2236 g cm^{-3} at $C = 0.5$ and 3 mol dm^{-3} respectively). The interaction coefficient $\varepsilon(H^+, ClO_4^-) = 0.14$ kg mol^{-1} was obtained from the literature.[18] The unknown interaction coefficients and the values of $K_{(p+q),p}{}^0$ were calculated from equations (8)—(11) using the experimental $K_{(p+q),p}$ constants (Table 2): $\varepsilon(UO_2^{2+}, ClO_4^-) = 0.45$, $\varepsilon[UO_2(CO_3)_2^{2-}, Na^+] = -0.09$, $\varepsilon[UO_2(CO_3)_3^{4-}, Na^+] = -0.02$, and $\varepsilon[(UO_2)_3(CO_3)_6^{6-}, Na^+] = 0.39$ kg mol^{-1}.

It is difficult to estimate the errors in the interaction coefficients because we have used experimental data at two ionic strengths only. Furthermore, for species with high charge the change of the equilibrium constant with the ionic strength is mainly due to the Debye–Hückel term $D(I)$. Hence, the interaction coefficient comes out as a small difference between large numbers and will be rather uncertain. The first two interaction coefficients should be rather precise as indicated by the fact that the values agree well with interaction coefficients evaluated from mean activity coefficient data from $UO_2(ClO_4)_2$ solutions[18] [$\varepsilon(UO_2^{2+}, ClO_4^-) = 0.46 \pm 0.02$ kg mol^{-1}] and other electrolytes containing anions of charge 2− [*e.g.* Na_2CrO_4 with $\varepsilon(CrO_4^{2-}, Na^+) = -0.09 \pm 0.02$ kg mol^{-1}], respectively. The value of $\varepsilon[UO_2(CO_3)_3^{4-}, Na^+]$ agrees within

Table 3. The solubility product of $UO_2(CO_3)$ (s) and overall stability constants for the complexes formed in the U^{VI}–H_2O–CO_2 (g) system at 25 °C. Equilibrium constants are given at two different ionic strengths; these data have been used to calculate the corresponding equilibrium constants in the pure water reference state by using specific ion-interaction theory

Reaction	3 mol dm^{-3} NaClO$_4$	0.5 mol dm^{-3} NaClO$_4$	Pure water
CO_2 (g) + $H_2O \rightleftharpoons CO_3^{2-}$ + 2 H^+, log K_{a2}	-17.61 ± 0.03	-17.15 ± 0.03	-18.10 ± 0.05
$UO_2(CO_3)$ (s) $\rightleftharpoons UO_2^{2+} + CO_3^{2-}$, log K_s	-13.94 ± 0.06	-13.21 ± 0.06	-14.4 ± 0.1
$UO_2^{2+} + CO_3^{2-} \rightleftharpoons UO_2(CO_3)$ (aq), log $\beta_{1,1}$	8.3 ± 0.1	8.3 ± 0.1	9.5 ± 0.2
$UO_2^{2+} + 2CO_3^{2-} \rightleftharpoons [UO_2(CO_3)_2]^{2-}$, log $\beta_{2,1}$	16.20 ± 0.15	15.36 ± 0.15	16.6 ± 0.2
$UO_2^{2+} + 3CO_3^{2-} \rightleftharpoons [UO_2(CO_3)_3]^{4-}$, log $\beta_{3,1}$	22.61 ± 0.15	21.46 ± 0.15	21.3 ± 0.2
$3UO_2^{2+} + 6CO_3^{2-} \rightleftharpoons [(UO_2)_3(CO_3)_6]^{6-}$, log $\beta_{6,3}$	56.2 ± 0.3	53.7 ± 0.3	53.4 ± 0.8

Table 4. Summary of some equilibrium constants in the system U^{VI}–CO_2 (g)–H_2O. Published data have been recalculated to the pure water reference state

	Experimental conditions			log *K* at		
Reaction	*I*/mol dm^{-3}	θ_c/°C	log *K*	*I* = 0	Ref.	Comments
$UO_2(CO_3)$ (s) $\rightleftharpoons UO_2^{2+} + CO_3^{2-}$	<0.03	25	−14.26	−14.26	7	*a*
				−14.4		This study
$UO_2(CO_3)$ (s) + $2HCO_3^- \rightleftharpoons [UO_2(CO_3)_2]^{2-} + CO_2$ (g) + H_2O	*ca.* 0	25	1.42	1.42	26	This value differs significantly from other published data and has been discarded, *cf.* ref. 7
				−0.2		Calculated from data in this study
$UO_2(CO_3)$ (s) + $HCO_3^- \rightleftharpoons [UO_2(CO_3)_2]^{2-} + H^+$	*ca.* 0	26	*b*	−8.3	27	
				−8.3		Calculated from data in this study
$UO_2^{2+} + CO_3^{2-} \rightleftharpoons UO_2(CO_3)$ (aq)	<0.03	25	9.9 ± 0.3	9.9	7	
	3	25	8.60 ± 0.03	9.2	28	
				9.5		This study
$UO_2^{2+} + 2CO_3^{2-} \rightleftharpoons [UO_2(CO_3)_2]^{2-}$	<0.03	25	16.7 ± 0.3	16.7	7	Few experimental data
	ca. 0	26	*b*	16.3	*c*	Value probably influenced by polynuclear carbonate complex
	0.1	25	16.18 ± 0.05	17.1	13	Data may be influenced by the choice of chemical model
	0.1	25	16.2 ± 0.3	17.0	14	Fairly large uncertainty in measured e.m.f. values
	0.2	20	15.6 ± 0.3	16.7	*d*	Solid phase not properly characterized, *cf.* ref. 7
				16.6		This study
$UO_2^{2+} + 3CO_3^{2-} \rightleftharpoons [UO_2(CO_3)_3]^{4-}$	0.1	20	21.54 ± 0.03	21.1	27	Corrections for temperature by using data from ref. 5
	1	25	22.8 ± 0.4	22.8	*e*	Some evidence for the formation of $[UO_2(CO_3)_2]^{2-}$, neglected by the authors
	0.5	*ca.* 20	23.0	23.0	*f*	Doubtful experimental technique and calculation method
	0.2	*ca.* 20	20.7	20.7	*d*	See previous comments
	0.1	25	21.57 ± 0.03	21.6	13	See previous comments
	0.1	25	21.8 ± 0.1	21.8	14	See previous comments
				21.3		This work
$[UO_2(CO_3)_2]^{2-} + CO_3^{2-} \rightleftharpoons [UO_2(CO_3)_3]^{4-}$	*ca.* 2	25	3.5	1.9	*c*	No $[UO_2(CO_3)_2]^{2-}$ present at the *B* levels used
	varying	25	6.1	—	*g*	No $[UO_2(CO_3)_2]^{2-}$ present at the *B* levels used

[a] K. M. Krupka, E. A. Jenne, and W. J. Deutsch, 'Validation of the WATEQ4 Geochemical Model for Uranium,' Report PNL–4333, Pacific Northwest Laboratories, 1983. [b] Recalculated by Sergeyeva *et al.*[7] [c] C. A. Blake, C. F. Coleman, K. B. Brown, D. G. Hill, R. S. Sowrie, and J. M. Schmitt, *J. Am. Chem. Soc.*, 1956, **78**, 5978. [d] A. K. Babko and V. S. Kodenskaya, *Russ. J. Inorg. Chem.*, 1960, **5**, 1241. [e] A. E. Klygin and I. D. Smirnova, *Russ. J. Inorg. Chem.*, 1959, **4**, 16. [f] V. I. Paramonova and N. M. Nikolaeva, *Radiokhimiya*, 1962, **4**, 84. [g] C. A. Blake, R. S. Lowrie, K. B. Brown, and D. G. Hill, Report Y-794, U.S. Atomic Energy Commission, 1951.

experimental error with the interaction coefficients for other ions of charge 4− such as $\varepsilon[W(CN)_8^{4-}, K^+] = -0.1$ kg mol^{-1} and $\varepsilon[Mo(CN)_8^{4-}, N(CH_3)_4^+] = -0.07$ kg mol^{-1}. We suggest that the value −0.02 kg mol^{-1} is used tentatively for the interaction coefficient $\varepsilon[UO_2(CO_3)_3^{4-}, Na^+]$. The interaction coefficient $\varepsilon[(UO_2)_3(CO_3)_6^{6-}, Na^+]$ is very uncertain and there are no additional data with which to obtain a better estimate. However, the extrapolation of the equilibrium constants to the pure water reference state is mainly influenced by the $D(I)$ term. It is easy to verify that even a large uncertainty (*e.g.* 50%) in the ε terms will have only a small effect on the values of the extrapolated constants.

Discussion

A large number of experimental studies of the U^{VI}–H_2O–CO_3^{2-} system have been carried out, *cf.* Table 4. The chemical models proposed and the corresponding equilibrium constants often differ substantially from one investigator to another. These differences can in some cases be traced back to differences in the precision of the experimental method used, but they are also to some extent dependent on the composition and concentration of the ionic medium. In order to make a quantitative comparison of data from different experimental investigations it is necessary to recalculate them to a common reference state.

All investigators agree about the stoicheiometry of the limiting complex and its precursor, $[UO_2(CO_3)_3]^{4-}$ and $[UO_2(CO_3)_2]^{2-}$, respectively. The possible formation of polynuclear carbonate complexes, *e.g.* $[(UO_2)_3(CO_3)_6]^{6-}$, has not been tested, even though the experimental measurements have been performed at such high B levels (McClaine *et al.*[26] and Tsymbal[13]) that the latter complex ought to be present. Maya[14] has tested his experimental data with chemical models involving either $[UO_2(CO_3)_2]^{2-}$ or $[(UO_2)_3(CO_3)_6]^{6-}$ and suggests that a least-squares fitting of the data is better with the former model. However, the experimental data are rather imprecise (the error in the measured e.m.f. is $\geqslant 1$ mV) and may not allow the selection of a proper chemical model. A calculation of the average number of OH^- per uranium, Z (*cf.* ref. 3, p. 464 for notation), at different values of $-\log h$ from his published experimental data shows that $Z(-\log h)$ is a function of B. Hence, Maya's primary experimental data indicate the formation of polynuclear species.

Scanlan and co-workers[27] used an extraction method to determine a value of the overall equilibrium constant β_3 for the formation of $[UO_2(CO_3)_3]^{4-}$. This experimental study is precise and technically sound. Sergeyeva *et al.*[7] used the solubility technique. The number of experimental data is rather small but seems to be of good quality.

Table 4 also contains data from our own studies, recalculated to zero ionic strength in order to facilitate comparisons. We have found no evidence for the formation of mixed complexes of the type $(UO_2)_p(OH)_q(CO_3)_r$ in the p_{CO_2} and $-\log h$ ranges investigated. From the work of Ciavatta *et al.*[28] there is no doubt that such complexes are formed at lower values of $-\log h$ than those used in this study. Tsymbal[13] and Maya[14] also propose the formation of mixed complexes, and we will discuss their possible formation in a subsequent publication. However, it is quite clear that the concentration of these species is lower than those of the pure carbonate complexes in the concentration ranges studied here.

We propose the following set of 'best' estimates of the equilibrium constants in the U^{VI}–H_2O–CO_3^{2-} system at the pure water reference state given in the last column of Table 3: $\log K_{s,0} = -14.4 \pm 0.1$, $\log \beta_{1,1} = 9.5 \pm 0.2$, $\log \beta_{2,1} = 16.6 \pm 0.2$, $\log \beta_{3,1} = 21.3 \pm 0.2$, and $\log \beta_{6,3} = 53.4 \pm 0.8$. The equilibrium constant for the reaction $3[UO_2(CO_3)_2]^{2-} \rightleftharpoons [(UO_2)_3(CO_3)_6]^{6-}$ is *ca.* 5×10^7 and 5×10^3 at $I = 3$ and 0 mol dm^{-3}, respectively. The trinuclear complex thus seems to be stabilized at high ionic strength, perhaps due to ion pairing with Na^+. The fact that this complex is of relatively less importance at low ionic strength may be one reason why it was not detected in the previous studies.

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