

# REDOX POTENTIALS OF M(VI)/M(V) LIMITING CARBONATE COMPLEXES (M = U OR Pu) AT DIFFERENT IONIC STRENGTHS AND TEMPERATURES. ENTROPY AND HEAT CAPACITY.

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For waste disposal programs, actinide aqua ions and limiting complexes had been studied by cyclic voltametry. Measured redox potentials in non complexing media were modelled by using SIT and Taylor's series expansions to the second order for ionic strength  $I$ , and temperature  $T$ , influences. These data treatments give standard values for redox potential  $E^\circ$ , corresponding  $\Delta S^\circ$ ,  $\Delta H^\circ$  and  $\Delta C_p^\circ$  of reactions, and excess values (variations of  $E^\circ$ ,  $\Delta S$ ,  $\Delta H$  and  $\Delta C_p$  with  $I$ ) that can be deduced by using  $T$  influence on fitted SIT coefficients  $\Delta\epsilon$ . This methodology is used here at 5 to 70°C in 0.3 to 1.5 M  $\text{Na}_2\text{CO}_3$  media ( $I = 0.9$  to 4.5 M).  $E^\circ = 0.191 \pm 0.015$  (-0.779  $\pm$  0.010) V/SHE,  $\Delta S^\circ = -178 \pm 37$  (-174  $\pm$  5) J.  $\text{K}^{-1} \cdot \text{mol}^{-1}$ ,  $\Delta C_p^\circ = -516 \pm 744$  (-414  $\pm$  176) J.  $\text{K}^{-1} \cdot \text{mol}^{-1}$  and  $\Delta\epsilon = -0.175 \pm 0.04 + (2.1 \pm 2.0)10^{-3} \Delta T - (2.4 \pm 7.7)10^{-5} (\Delta T)^2 / 2 - (0.91 \pm 0.10 + (7.0 \pm 1.9)10^{-3} \Delta T - (5.8 \pm 0.11)10^{-5} (\Delta T)^2 / 2)$  kg.mol<sup>-1</sup> are obtained at 25°C and  $I=0$  for the  $\text{MO}_2(\text{CO}_3)_3^{4-} + e^- \rightarrow \text{MO}_2(\text{CO}_3)_3^{5-}$  reaction where  $M = \text{Pu}$  (and  $\text{U}$  respectively).  $\lg(\beta_3^{\text{V}0}/\beta_3^{\text{VI}0}) = -12.6 \pm 0.3$  (-14.65  $\pm$  0.17) is deduced.  $\lg\beta_3^{\text{V}} = 3.1 \pm 1.4$  (6.95  $\pm$  0.18) is proposed using published  $\beta_3^{\text{VI}}$  values.

## 1 Introduction

Redox properties, hydrolysis, carbonate complexation are studied to understand geochemical behaviour of radioelements. Their migration in groundwaters can be modelled by coupling hydrodynamics, physico-chemical interactions with rock surfaces studied in batches [1] and aqueous chemistry. We typically checked experimentally such predictions by using column experiments with  $\text{Np(V)}$  in bicarbonate media [2]. Aqueous speciation was calculated with complexation constants obtained from our measurements and critical review [3], part of OECD program [4]. This bibliographic work pointed out contradictions and lack of published data. For this, actinide aqua ions and limiting carbonate complexes have been studied in our laboratory. Cyclic voltametry technique and data treatment were first validated with well-known  $\text{U}$  redox system, and mean activity coefficients of typically  $\text{HCl}$  and  $\text{NaCl}$  electrolytes: redox potentials of actinide couples had previously been measured in non complexing media as a function of  $T$  and  $I$ , to obtain thermodynamic data, activity coefficients,  $\gamma$ , and  $T$  influence on  $\gamma$  [5]. We are now reporting this type of measurements for  $\text{Pu}$ . We shall also reinterpret previous  $\text{U}$  data [6, 7] to compare the chemistry of analogue actinide ions.

## 2 Notations

$A(T)$        $A(T) = R T \ln(10) / F = 0.0591597 \text{ V}$  at 298.15 K  
 $a_i, m_i, [i]$  : activity (mol.kg<sup>-1</sup>), molality (mol.kg<sup>-1</sup>), molarity (mol.l<sup>-1</sup>) of ion  $i$   
 $z_i, \gamma_i$     charge, activity coefficient of ion  $i$   $\gamma_i = a_i / m_i$ ,  
 $\Delta z^2, \Delta\epsilon$     :  $z_{\text{Red}}^2 - z_{\text{Ox}}^2$ ,  $\epsilon(\text{Red}, \text{Na}^+) - \epsilon(\text{Ox}, \text{Na}^+)$ .  $\Delta\epsilon(T) = \Delta\epsilon$  value at  $T$   
 $\epsilon(i, j)(T)$  : value of the specific interaction coefficient between ions  $i$  and  $j$  at  $T$ ,  
 (kg.mol<sup>-1</sup>)

$$\begin{aligned}
 D(T,I) &= a(T)\sqrt{I} (1 + a_j b(T)\sqrt{I}) [8-10], a_j = 1.5/b(25^\circ\text{C}), a(25^\circ\text{C}) = 0.509 \text{ kg}^{0.5} \text{ mol}^{-0.5} \\
 F &= 96485.309 \text{ C.mol}^{-1} \\
 I, T, \Delta T &: \text{ionic strength (mol.kg}^{-1}), \text{ temperature (K), } \Delta T = T - T^\circ, T^\circ = 298.15 \text{ K} \\
 R, r &= 8.314510 \text{ J. K}^{-1} \text{ .mol}^{-1}, r = R \ln(10) = 19.144867 \text{ J. K}^{-1} \text{ .mol}^{-1} \\
 X(T,I), X^\circ &: X \text{ value at T and I, where X is E, S, C}_p, \text{ or D, } X^\circ = X(T^\circ, 0) \\
 X', X'', \sigma &: (\frac{\partial X}{\partial T})_p, X'(T,I) \text{ is } X' \text{ value at T and I. } X'' = (X')'. \sigma \text{ is standard deviation.} \\
 \Delta Z &= Z_{\text{Red}} + Z_{\text{H}^+} - 0.5 Z_{\text{H}_2} - Z_{\text{Ox}} \text{ for reaction } \text{Ox} + 1/2 \text{ H}_2 \rightarrow \text{Red} + \text{H}^+, Z \text{ is S, or C}_p \\
 \beta_3^{\text{VI}} (\beta_3^{\text{V}}) &= [\text{MO}_2(\text{CO}_3)_3]^{2+} / ([\text{MO}_2^{2+}] [\text{CO}_3^{2-}]^3), \text{ where } z^{\text{VI}} = -4 \text{ and } z^{\text{V}} = -5.
 \end{aligned}$$

### 3 Method

The Specific Interaction Theory (S. I. T.) was used to calculate activity coefficients  $\gamma_i$ ,

$$\lg \gamma_i = -z_i^2 D(T,I) + \epsilon(i, \text{Na}^+)(T) m_{\text{Na}^+} \quad (1)$$

[7-11], and then to extrapolate to the standard state ( $I = 0$ )

$$E_{\text{Ox/Red}}(T,I) = E_{\text{Ox/Red}}(T,0) + A(T) [\Delta z^2 D(T,I) - \Delta \epsilon(T) m_{\text{Na}^+}] \quad (2)$$

$E_{\text{Ox/Red}}(T,0)$  and  $\Delta \epsilon(T)$  were obtained (Eq. 2) by linear regression on ( $Y(T,I), m_{\text{Na}^+}$ ) data, where  $Y(T,I) = [E_{\text{Ox/Red}}(T,I) / A(T) - \Delta z^2 D(T,I)]$ .  $E(T^\circ, I)$ ,  $\Delta S(T^\circ, I)$  and  $\Delta C_p(T^\circ, I)$  were obtained (Fig. 1) by fitting experimental data  $E(T, I)$  (vs.  $T$  at constant  $I$ ), to Eq.(3)

$$E(T,I) = E(T^\circ, I) + [\Delta S(T^\circ, I) / F] \Delta T + [\Delta C_p(T^\circ, I) / 2T^\circ F] (\Delta T)^2 + \dots \quad (3)$$

$\Delta S$  and  $\Delta C_p$  are in first and second order terms, and the precision of the measurements is not enough to determine a third order term [5, 11]. Still  $\Delta C_p$  for solutes in aqueous solutions, usually vary with  $T$ ,  $\Delta C_p(T^\circ, I)$  obtained in this way, is rather a mean value slightly depending on the  $T^\circ$  and  $\Delta T$  values chosen. We obtained  $I$  influence by combining thermodynamic definitions with S. I. T. relation [11]:

$$\Delta H(T^\circ, I) = \Delta H^\circ + r T^{\circ 2} [\Delta z^2 D'(T^\circ, I) - m_{\text{Na}^+} \Delta \epsilon'(T^\circ)] \quad (4)$$

$$\Delta S(T^\circ, I) = \Delta S^\circ + r [\Delta z^2 (D(T^\circ, I) + T^\circ D'(T^\circ, I)) - m_{\text{Na}^+} (\Delta \epsilon(T^\circ) + T^\circ \Delta \epsilon'(T^\circ))] \quad (5)$$

$$\Delta C_p(T^\circ, I) = \Delta C_p^\circ + r T^\circ [\Delta z^2 (2 D''(T^\circ, I) + T^\circ D'''(T^\circ, I)) - m_{\text{Na}^+} (2 \Delta \epsilon''(T^\circ) + T^\circ \Delta \epsilon'''(T^\circ))] \quad (6)$$

$D(T, I)$  was calculated analytically.  $\Delta \epsilon(T)$  and  $D(T, I)$  derivatives were calculated from the first and second order terms of polynomial regressions vs.  $\Delta T$ .  $[2 \Delta \epsilon'(T^\circ) + T^\circ \Delta \epsilon''(T^\circ)]$  can also be determined as the slope of  $[\Delta C_p(T^\circ, I) / r - \Delta z^2 (2 D''(T^\circ, I) + T^\circ D'''(T^\circ, I))]$  vs.  $m$  (Eq. 6). Similar linear regressions can be performed based on Eq.(4 or 5).  $I$  influence is usually small on  $\Delta H(T^\circ, I)$  because it depends only on  $\gamma'$  ( $D'(T^\circ, I)$ ) and  $\Delta \epsilon'(T^\circ)$  in Eq.(4) and not on  $\gamma$  itself.

$$(E(\text{PuO}_2(\text{CO}_3)_3^{4-} / \text{PuO}_2(\text{CO}_3)_3^{5-}) - E(\text{PuO}_2^{2+} / \text{PuO}_2^+)) = A (\lg \beta_3^{\text{V}} - \lg \beta_3^{\text{VI}}) \quad (7)$$

equation was used for thermodynamic cycles:  $\lg \beta_3^{\text{V}}$  for  $\text{Pu(V)}$  that disproportionates in carbonate media, was deduced from  $\lg \beta_3^{\text{VI}} (3 \text{ M NaClO}_4) = 18.2 \pm 0.4$  we obtained from  $\text{PuO}_2\text{CO}_{3(s)}$  solubility measurements and  $\lg \beta_3^{\text{VI}} (I = 0) = 17.4 \pm 0.5$  was proposed [12]. We pointed out small inconsistency for  $\epsilon(\text{CO}_3^{2-}, \text{Na}^+)$  numerical value used for this type of extrapolation to  $I = 0$ , and this was corrected later [8]. Anyhow we recently determined  $I$  correction for the  $\text{Np}$  system is slightly different from the  $\text{U}$  one. Using for  $\text{Pu}$ , the  $\text{Np}$  correction to  $I = 0$ , we obtain  $\lg \beta_3^{\text{VI}} (I = 0) = 15.7 \pm 1.3$  which is much less than the previous estimation, and needs confirmation. Experimental details were described elsewhere [6, 7].

#### 4 Results, Interpretation and Discussion

The difference between the two potential peaks of the voltammograms increased with the scanning speed, but the half sum was constant (within 1 mV). It was used as an estimate of the formal potential. This nearly reversible behaviour is often found for couples of ions of similar geometry. For potential measurements (Table 1),  $\sigma$  on T regressions (Eq. 3) was 3 to 7 mV (Table 2). The uncertainty is set to 10 mV, it includes systematic errors and junction potential. For extrapolation to  $I = 0$  (Eq. 2),  $\sigma$  was less than 10 mV (Table 1); the uncertainty is set to 15 mV, and the series at  $T = 5^\circ\text{C}$  is rejected because of the too low number of experimental points. Our data are in reasonable agreement with published ones (Table 3) considering junction potential, I effect and possible dissociation of the Pu(V) limiting complex in 0.1 M  $\text{K}_2\text{CO}_3$  as for Np(V) [3], that were not documented in published works. We performed similar measurements on the Np(VI)/Np(V) redox system [3, 13], and our formal potential measurements are in very good agreement with Simakin's study [14] when interpreting his data with the SIT [3].

Table 1. Experimental Results. Pu(VI)/Pu(V) redox potential  $E$  (mV/SHE), are Eq.(2) extrapolated to  $I = 0$ . The values in parenthesis are  $\sigma$ 's on these SIT linear regressions. Corresponding experimental results for Uranium were taken from Ref. [6, 7]. Data in 3.2 M  $\text{Na}^+$  were not taken into account in the extrapolation to  $I=0$ , for the reasons explained in the text.

0.3 M $\text{Na}_2\text{CO}_3$		0.5 M $\text{Na}_2\text{CO}_3$		1 M $\text{Na}_2\text{CO}_3$		1.5 M $\text{Na}_2\text{CO}_3$		I=0		
T	E	T	E	T	E	T	E	T	E	$\Delta\varepsilon$ (kg.mol <sup>-1</sup> )
9	325	15	327	4	360	5	389	5	196 (6)	0.41 (0.05)
16	320	20	329	10	356	10	383	10	216 (5)	0.21 (0.04)
20	314	25	318	15	350	10	383	15	207 (4)	0.20 (0.04)
21	311	25	313	20	344	15	375	20	201 (4)	0.18 (0.03)
25	297	25	315	25	340	15	376	25	188 (4)	0.18 (0.02)
25	307	30	307	25	336	20	368	30	183 (4)	0.16 (0.04)
30	299	35	298	25	337	20	369	35	171 (4)	0.20 (0.04)
31	299	35	306	25	336	25	362	40	164 (5)	0.12 (0.04)
35	294	40	290	34	326	25	356	45	151 (6)	0.11 (0.04)
35	286	45	280	35	324	25	362	50	143 (7)	0.12 (0.04)
40	285	45	280	40	315	30	353	55	124 (8)	0.15 (0.04)
40	287	55	264	43	313	35	340	60	102 (9)	0.20 (0.04)
45	279	60	256	45	307	35	345	65	112 (10)	0.08 (0.05)
45	279			50	298	40	338			
50	269			50	300	45	323			
50	271			52	297	45	330			
55	259			55	290	50	322			
65	246			60	278	50	330			
				64	277	55	308			
						55	320			
						55	315			
						60	307			
						60	310			
						60	299			
						65	298			

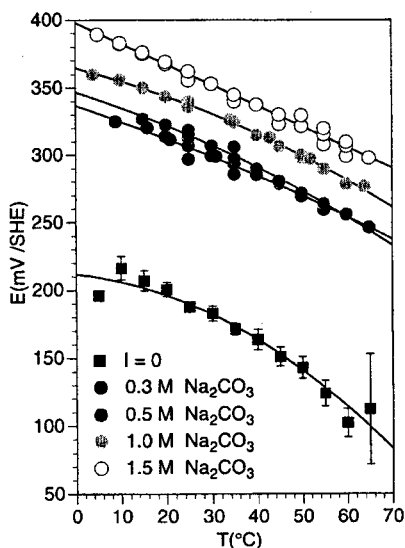


Fig. 1. Temperature influence on the formal potential of the  $\text{PuO}_2(\text{CO}_3)_3^{4-}/\text{PuO}_2(\text{CO}_3)_3^{5-}$  redox couple. Table 1 data are plotted. Curves are calculated by using (Eq. 3) with  $E(T^0)$ ,  $\Delta S(T^0)$  and  $\Delta C_p(T^0)$  fitted values (Table 2).

E variations with T are quite small and similar at each I (Fig. 1), hence (Eqs. 5 and 6),  $\Delta S$  and above all the  $\Delta C_p$  variations with I are small (Fig. 2 and 3).  $\Delta S$  variations vs. I might be compared with a line (Eq. 5) of slope  $[-r (\Delta\epsilon(T^0) + T^0 \Delta\epsilon'(T^0))]$  when  $I > 0.5 \text{ mol.kg}^{-1}$ . The uncertainty on  $\Delta C_p$ , is of the order of magnitude of the variations with I. But the  $\Delta C_p$  term is maintained to determine the uncertainty of  $\Delta S$ , and to perform the same treatment of data as in acidic media [5]. E decreases with T (Fig. 1): Pu(VI) becomes more stable than Pu(V).

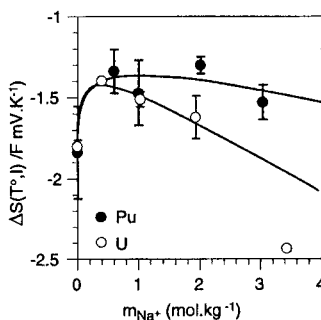


Fig. 2. Ionic strength influence on the entropy of the  $\text{MO}_2(\text{CO}_3)_3^{4-} + e^- \rightarrow \text{MO}_2(\text{CO}_3)_3^{5-}$  reaction. For  $M = \text{Pu}$ , Table 2 data are plotted, for  $M = \text{U}$ , similar treatment was used on data published in Ref.[6, 7] where only a first order approximation (Eq. 3) had been used excluding data in  $3.2 \text{ M Na}^+$  media for Uranium (see text). Curves are calculated by using (Eq. 5) with  $\Delta S^0$ ,  $\Delta\epsilon(T^0)$  and  $\Delta\epsilon'(T^0)$  fitted values (Table 2).

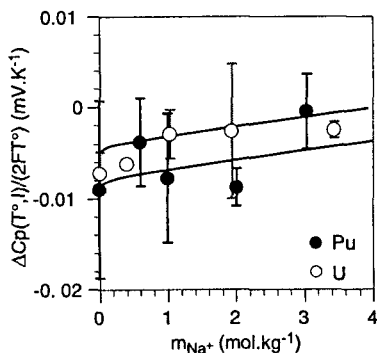


Fig. 3. Ionic strength influence on the heat capacity of the  $\text{MO}_2(\text{CO}_3)_3^{4-} + e^- \rightarrow \text{MO}_2(\text{CO}_3)_3^{5-}$  reaction. For  $M = \text{Pu}$ , Table 2 data are plotted, for  $M = \text{U}$ , similar treatment was used on data published in Ref.[6, 7] where only  $E^\circ$  and  $\Delta S$  (not  $\Delta C_p$ ) were estimated. Curves are calculated by using (Eq. 6) with  $\Delta C_p^\circ$ ,  $\Delta \epsilon'(T^\circ)$  and  $\Delta \epsilon''(T^\circ)$  fitted values (Table 2).

Table 2. Potentials, Entropies and Heat Capacities of Reaction for the Pu(VI)/Pu(V) Redox Couple. Results of the regressions vs. T (Eq. 3) from E and  $\Delta \epsilon$  data (Table 1). Values in parenthesis are  $\sigma$ 's.

$\text{Na}_2\text{CO}_3$ ( $\text{mol.l}^{-1}$ )	molality / molarity ( $\text{l.kg}^{-1}$ ) [8]	$E(T^\circ)$ (mV/SHE)	$\Delta S(T^\circ) / F$ ( $\text{mV. K}^{-1}$ )	$\Delta C_p(T^\circ) / (2 T^\circ F)$ ( $\mu\text{V } ^\circ\text{K}^{-2}$ )
0	1	191 (8)	-1.84 (0.19)	-9.0 (6.5)
0.3	1.0033	306 (3)	-1.34 (0.09)	-3.8 (3.2)
0.5	1.0043	315 (3)	-1.47 (0.13)	-7.7 (4.7)
1	1.0094	338 (2)	-1.30 (0.04)	-8.7 (1.4)
1.5	1.0170	360 (4)	-1.53 (0.07)	-0.4 (2.7)
		$\Delta \epsilon(T^\circ)$ ( $\text{kg.mol}^{-1}$ )	$\Delta \epsilon'(T^\circ)$ ( $\text{g.mol}^{-1}\text{K}^{-1}$ )	$\Delta \epsilon''(T^\circ)/2$ ( $\text{mg.mol}^{-1}\text{K}^{-2}$ )
		0.18 (0.05)	-2.1 (1.1)	24 (38)

This can be attributed to increase of ionic radii with T. This steric effect should be more dramatic on Pu(VI) ion because it is smaller than Pu(V) one, hence it can also explain  $\beta_3^{\text{VI}}$ ,  $\beta_3^{\text{V}}$ , and  $\beta_3^{\text{VI}}/\beta_3^{\text{V}}$  values (Table 4) decrease with atomic number (from U to Pu). I influence at high carbonate concentration is not the same for U and Pu limiting complexes. We already pointed out this type of difference between  $\text{NpO}_2(\text{CO}_3)_3^{5-}$  and  $\text{UO}_2(\text{CO}_3)_3^{5-}$  [15], and between  $\text{Pu}(\text{CO}_3)_3^{6-}$  and  $\text{U}(\text{CO}_3)_3^{6-}$  [16] activity coefficients: the numerical values of  $\Delta \epsilon$  are different. Anyhow the S. I. T. might not be accurate enough in this case because I was too high or the complexes too highly charged,. In addition ion pair formation between  $\text{Na}^+$  and  $\text{UO}_2(\text{CO}_3)_3^{5-}$  are suspected [15]. To obtain complexation constants in 1 M and 3 M  $\text{NaClO}_4$  media where some of them have already been measured, we calculated our data in this media with the S. I. T. coefficients measured in this work. From published [5-7, 9, 12] potential values in acidic media and  $\lg \beta_3^{\text{VI}}$  value, we deduced Eq.(7)  $\lg \beta_3^{\text{V}}$ , using Np(VI)-Pu(VI) analogy for I corrections: our  $\epsilon(\text{Na}^+, \text{NpO}_2(\text{CO}_3)_3^{5-})$  determination [3, 4] propagates (in thermodynamic cycles) to Pu values of  $\beta_3^{\text{VI}}$  and  $\beta_3^{\text{V}}$ , that are surprisingly low, this has to be confirmed.

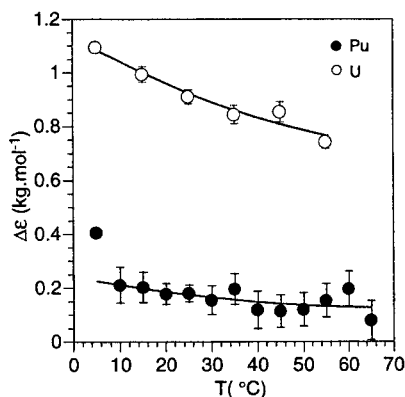


Fig. 4. Temperature influence on  $\varepsilon(\text{MO}_2(\text{CO}_3)_3^{4-}, \text{Na}^+) - \varepsilon(\text{MO}_2(\text{CO}_3)_3^{5-}, \text{Na}^+) = \Delta\varepsilon$  (points) values (Table 1) obtained (Eq. 2) at each T from I influence on the formal potential of the M(VI)/M(V) redox couple in carbonate media. Curves are second order polynomial regressions using  $\Delta\varepsilon(T^0)$ ,  $\Delta\varepsilon'(T^0)$  and  $\Delta\varepsilon''(T^0)$  fitted values (Table 2).

Table 3. Literature redox potential for the M(VI)/M(V) couples in carbonate media

Ref.	Medium	E (mV/SHE)	E (mV/SCE)	Ref.	Medium	E (mV/SHE)
[17]	1 M $\text{K}_2\text{CO}_3$	Pu $320 \pm 10$		[9]	I = 0	U $-752 \pm 16$
[17]	0.1 M $\text{K}_2\text{CO}_3$	Pu $300 \pm 10$		p.w.	I = 0	U $-779 \pm 15$
[18]	1 M $\text{Na}_2\text{CO}_3$	Pu $351 \pm 10$	$110 \pm 10$			
p.w.	1 M $\text{Na}_2\text{CO}_3$	Pu $337 \pm 10$				

p. w. = present work

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Table 4. Comparison of thermodynamic data for U and Pu at 25°C in 0.1 and 3 M NaClO<sub>4</sub>. Uncertainty is 1.5σ, or calculated using propagation rules.

		U <sup>m</sup>	Pu	U	Pu
		$\text{MO}_2(\text{CO}_3)_3^{4+} + e^- \rightarrow \text{MO}_2(\text{CO}_3)_3^{5-}$		$\text{MO}_2^{2+} + e^- \rightarrow \text{MO}_2^+$	
$E^\circ$	(mV/SHE)	-779 ± 10 <sup>a</sup>	191 ± 15 <sup>a</sup>	87.9 ± 1.3 <sup>b</sup>	938 ± 10 <sup>c</sup>
$E(1\text{M})^d$	(mV/SHE)	-613 ± 10	311 ± 10	63.8 ± 1.4	915 ± 5
$E(3\text{M})^d$	(mV/SHE)		360 ± 10	84.9 ± 2.4	939 ± 5
$\Delta\epsilon$	(kg.mol <sup>-1</sup> )	-0.91 ± 0.1 <sup>e</sup>	-0.17 <sub>5</sub> ± 0.04 <sup>e</sup>	-0.2 ± 0.01 <sup>b</sup>	-0.22 ± 0.05 <sup>c</sup>
$\Delta\epsilon'$	(g.mol <sup>-1</sup> . K <sup>-1</sup> )	7.0 ± 1.9 <sup>e</sup>	2.1 ± 2.0 <sup>e</sup>		1.48 ± 0.34 <sup>c</sup>
$\Delta\epsilon''/2$	(mg.mol <sup>-1</sup> . K <sup>-2</sup> )	-58.1 ± 1.1 <sup>e</sup>	-24 ± 77 <sup>e</sup>		-12.2 ± 13.0 <sup>c</sup>
$\Delta S^\circ/F$	(mV. K <sup>-1</sup> )	-1.80 ± 0.05 <sup>f</sup>	-1.84 ± 0.38 <sup>f</sup>	-0.06 ± 0.05 <sup>m</sup>	0.34 ± 0.04 <sup>c</sup>
$\Delta S(1\text{M})/F^d$	(mV. K <sup>-1</sup> )	-1.52 ± 0.2	-1.41 ± 0.40	-0.24 ± 0.02 <sup>m</sup>	0.16 ± 0.04
$\Delta S(3\text{M})/F^d$	(mV. K <sup>-1</sup> )		-1.52 ± 0.55		-0.02 ± 0.02
$\Delta C_p^\circ/2T^\circ F$	(μV. K <sup>-2</sup> )	-7.2 ± 3.1 <sup>f</sup>	-9 ± 13 <sup>f</sup>		-6.77 ± 1.62 <sup>c</sup>
$\Delta C_p(1\text{M})/2T^\circ F^d$	(μV. K <sup>-2</sup> )	-3.98	-7 ± 14		-7.29 ± 1.53
$\Delta C_p(3\text{M})/2T^\circ F^d$	(μV. K <sup>-2</sup> )		-4 ± 20		-4.86 ± 1.00
$\text{MO}_2^{2+} + \text{MO}_2(\text{CO}_3)_3^{5-} \rightarrow \text{MO}_2(\text{CO}_3)_3^{4+} + \text{MO}_2^+$					
$\lg(\beta_3^{\text{VI}0}/\beta_3^{\text{V}0})^g$		14.65 ± 0.17	12.63 ± 0.30		
$\lg(\beta_3^{\text{VI}(1\text{M})}/\beta_3^{\text{V}(1\text{M})})^g$		11.44 ± 0.17	10.21 ± 0.19		
$\lg(\beta_3^{\text{VI}(3\text{M})}/\beta_3^{\text{V}(3\text{M})})^g$			9.79 ± 0.19		
$\text{MO}_2^{2+} + 3 \text{CO}_3^{2-} \rightleftharpoons \text{MO}_2(\text{CO}_3)_3^{4-}$					
$\text{MO}_2^+ + 3 \text{CO}_3^{2-} \rightleftharpoons \text{MO}_2(\text{CO}_3)_3^{5-}$					
$\lg\beta_3^\circ$		21.60 ± 0.05 <sup>b</sup>	15.7 ± 1.3 <sup>h,1</sup>	6.95 ± 0.18 <sup>k</sup>	3.1 ± 1.4 <sup>k,1</sup>
$\lg\beta_3(1\text{M})$		21.90 ± 0.07 <sup>h</sup>	16.5 ± 1.2 <sup>h,1</sup>	10.46 ± 0.19 <sup>k</sup>	6.3 ± 1.2 <sup>k,1</sup>
$\lg\beta_3(3\text{M})$		22.60 ± 0.18 <sup>h</sup>	18.2 ± 0.4 <sup>i</sup>		8.4 ± 0.4 <sup>k</sup>

obtained (Eq. 2) from E data (Table 1 and [6, 7]). <sup>b</sup>[9]. <sup>c</sup>[5]. <sup>d</sup>calculated (Eq. 2) from other data of this table. <sup>e</sup>deduced (Eq. 3) from  $\Delta\epsilon(T)$  obtained<sup>a</sup> (Eq. 2) in this work. <sup>f</sup>deduced (Eq. 3) from  $E^\circ$  values obtained<sup>a</sup> (Eq. 2) in this work. <sup>g</sup>calculated (Eq. 7) from other data of this table. <sup>h</sup>calculated (Eq. 2) from data of Ref.[8, 9]. <sup>i</sup>[12]. <sup>j</sup>calculated (Eq. 2) from data of Ref.[12] and  $N_p \epsilon(\text{Na}^+, N_p\text{O}_2(\text{CO}_3)_3^{5-})$  value [3] for Pu. <sup>k</sup> $\beta_3^{\text{V}}$  values calculated from  $\beta_3^{\text{VI}}/\beta_3^{\text{V}}$  and  $\beta_3^{\text{VI}}$  data of this table. <sup>l</sup>Surprisingly low value due to  $\epsilon(\text{Na}^+, \text{PuO}_2(\text{CO}_3)_3^{5-})$  estimate<sup>j</sup> (see text). <sup>m</sup>From data in 0.2 M Na<sub>2</sub>CO<sub>3</sub> + 0.6 to 1.4 M NaClO<sub>4</sub> [6, 7]

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