Thermoelectric Properties of M^{4+}/M^{3+} and MO_2^{2+}/MO_2^{+} Redox Couples of Neptunium and Plutonium in Aqueous $HClO_4$ and HNO_3 Media

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The thermoelectric properties of redox couples of transuranium elements in aqueous $HClO_4$ and HNO_3 media have been considered. The thermoelectric power ϵ of M^{4+}/M^{3+} and MO_2^{2+}/MO_2^{+} of neptunium and plutonium is not temperature-dependent for the ΔT investigated, but obeys the approximation of the derivation of the Nernst equation vs. T:

$$\epsilon = \epsilon^\circ + \frac{R}{nF}\ln\frac{C_{Ox}}{C_{Red}} + A(Z^2{}_{Ox} - Z^2{}_{Red})\frac{I^{1/2}}{1 + I^{1/2}}$$

with $\epsilon^\circ = \Delta S^\circ/nF + (0.195\ mV\ K^{-1})$

The standard thermoelectric powers ϵ° are found in the range 2 to 2.25 mV K^{-1} for both Pu^{4+}/Pu^{3+} and Np^{4+}/Np^{3+}; 0.430 mV K^{-1} for NpO_2^{2+}/NpO_2^{+} and 0.850 mV K^{-1} for PuO_2^{2+}/PuO_2^{+} redox couples. The differences $S^\circ(Red) - S^\circ(Ox)$ are calculated for each couple and compared with published values.

Introduction

The thermoelectric properties of redox couples have hitherto been little investigated. More than twenty years ago, de Bethune *et al.* [1] developed a theoretical explanation of these phenomena and, in their basic paper, published calculated values of thermoelectric powers for more than 300 redox couples. More recently, Burrows [2] studied the thermoelectric properties of Fe^{3+}/Fe^{2+} and $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ systems, with the aim of designing regenerable thermogalvanic cells to convert heat into electricity. Since, according to de Bethune *et al.* [1], the M^{4+}/M^{3+} redox couples of the transuranium elements possess the highest thermoelectric powers among the 300 systems investigated, this study was undertaken with the following goals: i) confirm the theoretical prediction, ii) obtain new data on the chemistry of transuranium elements in aqueous solutions. The work was also extended to the study of the transuranium MO_2^{2+}/MO_2^{+} redox couples. For these elements, the redox systems susceptible to such investigation only correspond to the reversible M^{4+}/M^{3+} and MO_2^{2+}/MO_2^{+} couples. In the case of uranium and americium, such research is prevented by the instability of U^{3+}, UO_2^{+} and AmO_2^{2+} *vs.* oxidation by water, disproportionation reaction and reduction by water respectively. For neptunium and plutonium, both M^{4+}/M^{3+} and MO_2^{2+}/MO_2^{+} redox couples are suitable; their formal potentials are given in Table I.

After a short theoretical description of these phenomena and details of the experimental procedure, this paper describes the results obtained for Np^{4+}/Np^{3+}, Pu^{4+}/Pu^{3+}, NpO_2^{2+}/NpO_2^{+} and PuO_2^{2+}/PuO_2^{+} redox couples present in $HClO_4$ and HNO_3 aqueous media, and briefly discusses the chemical consequences.

TABLE I. Potentials of Reversible Redox Couples of Neptunium and Plutonium at 25 °C.

	Media		$E^\circ_{M^{4+}/M^{3+}}$ (V)	$E^\circ_{MO_2^{2+}/MO_2^{+}}$ (V)	Ref.
Np	$HClO_4$	*M*	0.155	1.137	[3]
	HNO_3	1.02 *M*	–	1.138	
Pu	$HClO_4$	*M*	0.982	0.916	[4]
	HNO_3	*M*	0.914	0.920	

Theoretical Approach (according to de Bethune *et al.* [1])

A chemical thermoelement is a redox couple and its thermoelectric power is expressed by the derivative of the e.m.f. of the thermal cell *vs.* temperature:

Electrode (T_1)/Electrolyte (T_1)/Electrolyte (T_2)/Electrode (T_2)

In these studies, the two species Ox, Red of the redox couple are dissolved in the electrolyte and the electrodes are inert.

The thermoelectric power ϵ is identical to the thermal temperature coefficient $(dE/dT)_{Th.}$ of de Bethune *et al.* [1].

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By means of the theory of thermodynamics of irreversible processes ϵ can be expressed by

$$\epsilon = \frac{dE}{dT} = \frac{S^*}{nF} \qquad (1)$$

where n and F possess their usual significance and S^* is the so-called entropy of transport, which corresponds to the entropy transported from the hot side to the cold side of the thermal cell by the transfer of n Faradays.

In fact S^* is not directly measurable; however it can be expressed according to

$$S^* = S^*_E + S^*_M \qquad (2)$$

where S^*_E, called the entropy of electrochemical transport, represents the entropy exchange at the electrodes, and S^*_M, called the entropy of migration transport, is the entropy transported through the cell by diffusion or electromigration. In practice, the standard entropy of electrochemical transport of the i species, $S^{*\circ}_{Ei}$, can be obtained by:

$$S^{*\circ}_{Ei} = S^\circ_i + zS^{*\circ}_E(H^+) \qquad (3)$$

where S°_i is the standard entropy of i, z its ionic charge and $S^\circ_E(H^+)$ the standard ionic entropy of H^+. $S^{*\circ}_E(H^+)$ was calculated as (-18.74 ± 2) J K^{-1} by de Bethune *et al.* [1]. Hence

$$S^{*\circ}_E = S^{*\circ}_E(\text{Red}) - S^{*\circ}_E(\text{Ox}) = [S^\circ(\text{Red}) - S^\circ(\text{Ox})] - nS^{*\circ}_E(H^+) \qquad (4)$$

On the other hand, the S^*_M term contribution to S^* is quite small and only observable after a long time interval [1, 5].

Thus for the initial period: $S^* = S^*_E$ and for the standard state:

$$\epsilon^\circ = \frac{dE^\circ}{dT} = \frac{S^{*\circ}}{nF} = \frac{S^\circ(\text{Red}) - S^\circ(\text{Ox})}{nF} - \frac{S^{*\circ}_E(H^+)}{F}$$

or

$$\epsilon^\circ = \frac{\Delta S^\circ}{nF} + (0.195 \text{ mV K}^{-1}) \qquad (5)$$

As the Nernst equation gives the potential:

$$E = E^\circ + \frac{RT}{nF} \ln \frac{a_{Ox}}{a_{Red}} = E^\circ + \frac{RT}{nF} \ln \frac{C_{Ox}}{C_{Red}} + \frac{RT}{nF} \ln \frac{\gamma_{Ox}}{\gamma_{Red}} \qquad (6)$$

where (a, C, γ) are respectively the activity, concentration and activity coefficient ϵ can be expressed by:

$$\epsilon = \frac{dE}{dT} = \frac{dE^\circ}{dT} + \frac{R}{nF} \ln \frac{C_{Ox}}{C_{Red}} + \frac{R}{nF} \ln \frac{\gamma_{Ox}}{\gamma_{Red}} \qquad (7)$$

According to de Bethune *et al.* [1], the contribution of $d(\ln C_{Ox}/C_{Red})/dt$ to ϵ is negligible. Hence the expression of ϵ contains two contributions, (i) an intrinsic property of the redox couple, the standard thermoelectric power $\epsilon^\circ = dE^\circ/dT$; (ii) the experimental conditions, *i.e.* concentration ratio in $(R/nF) \ln(C_{Ox}/C_{Red})$, ionic strength I in $(R/nF) \ln(\gamma_{Ox}/\gamma_{Red})$, which by the use of the first order Debye Huckel equation, becomes

$$\frac{RA}{nF} \ln_{10}(Z_{Ox}{}^2 - Z_{Red}{}^2) \frac{I^{1/2}}{1 + I^{1/2}} \qquad (8)$$

where A is the Debye–Huckel coefficient.

Experimental

Chemicals

The reagents HNO_3, $HClO_4$, $NaNO_3$ were Prolabo products (Normapur grade). The ^{237}Np and ^{239}Pu stock solutions were supplied by the Section des Transuraniens (Commissariat à l'Energie Atomique, Fontenay-aux-Roses, France).

Solutions

Np(III): A Np(V) solution was completely reduced to Np(III) with Zn amalgam. To prevent the oxidation of Np^{3+} ion by dissolved oxygen, the solution was purged and stored under inert nitrogen atmosphere.

Np(IV): Part of the corresponding Np(III) solution was oxidized to Np(IV) by air and then nitrogen purged.

Np(V): The neptunium(V) of the stock solution was precipitated as the hydroxide by the addition of NaOH. The precipitate was washed and then redissolved in the appropriate medium.

Np(VI): The corresponding Np(V) solution was oxidized electrochemically to Np(VI) on a platinum electrode at 1.300 V/N.H.E. using a conventional three electrode system.

Pu(III): A Pu(IV) solution was completely reduced to Pu(III) with Zn amalgam. Small amounts of NH_2SO_3H added prevent the oxidation of Pu^{3+} ion in HNO_3 medium.

Pu(IV): Pu(IV) of a stock solution was precipitated as hydroxide by the addition of NH_3. The hydroxide was washed and then redissolved in the appropriate medium.

Pu(V): To minimize the disproportionation reaction of $PuO_2{}^+$ ion, the solution must be adjusted and stored with a pH close to 3.5. Hence a solution of Pu(VI) was adjusted to a pH of (3.5 ± 0.2) and reduced electrochemically to Pu(V) on a platinum electrode at 0.790 V/N.H.E. The pH measurements were taken before and after each experiment with a Metrohm calomel glass combination electrode and a Tacussel Minissis 6000 digital pH meter.

Pu(VI): A stock solution of plutonium(IV) was completely oxidized to Pu(VI) by addition of AgO. Ag^+ ions were eliminated as AgCl. The Pu(VI) was then precipitated as barium plutonate by the addition of barium hydroxide solution. The precipitate was washed and then taken up in the appropriate medium.

For all the solutions, the completion of oxidation state adjustment was checked by spectrophotometry and the concentrations of the species were determined on aliquots by coulometry. The solutions used for thermoelectric measurements were obtained by mixing the stock solutions, except for the study of the influence of [Ox]/[Red] on ϵ, for which the species were generated electrochemically in the thermogalvanic cell.

Apparatus

Spectrometry

A Hewlett-Packard 8450 A rapid scanning spectrophotometer was used, and the solutions were placed in one cm path length quartz cells.

Electrochemistry

The apparatus used in this study was a Tacussel PRT 20-2 potentiostat/Servovit 12 pilot scanner/IG 6 N coulometer.

The electrochemical cells used for bulk electrolysis had separate compartments for reference electrode and counterelectrode. All potential measurements were taken *vs.* (mercury/Mg_2SO_4/saturated K_2SO_4) reference electrode.

Thermogalvanic cell (Fig. 1): this comprises i) a plexiglass block containing a working compartment equipped with two working electrodes (Pt disks) facing each other; ii) two screw-on blocks in which a thermostatted fluid flows along the back of the working electrode. Thus the temperature gradient was imposed by the use of two Haake units. The ΔE variations were recorded on a Sefram apparatus and the measurements were taken with an A.O.I.P. Multimeter MNK 177.

Measurements

The following procedure was used to determine the temperature gradient ΔT between the two Pt working electrodes:

The thermoelectric power of a known redox couple (*i.e.* $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$) was determined by the study of the variation of e.m.f. *vs.* ΔT (the ΔT values were calculated as the difference between the temperatures measured with a precision thermometer dipped in the thermostats). The ϵ values obtained were identical to those published by Burrows [2]. Thus for this study, the ΔT values correspond to the temperature difference measured by the presion thermometers. Hence the accuracy of the ΔT determination was about ±0.1 K.

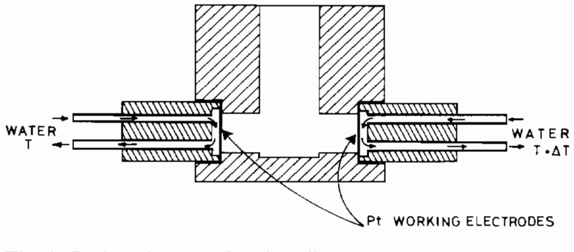

Fig. 1. Redox thermogalvanic cell.

The e.m.f. between the two Pt electrodes were recorded until a plateau was reached and the mean ΔE value corresponding to the plateau was measured with an accuracy of ±0.01 mV.

The constancy of the composition of the working solutions was checked by recording their absorption spectra before and after each experiment.

Results and Discussion

Figure 2 shows the variations of the e.m.f. ΔE *vs.* the temperature gradient between the two platinum electrodes (ΔT) for all the neptunium and plutonium redox couples investigated. All the plots are straight lines, implying that the thermoelectric powers of the redox couples M^{4+}/M^{3+} and MO_2^{2+}/MO_2^{+} of Pu and Np do not vary with temperature. The same observation was made in the studies of other redox couples in similar experimental conditions ($\Delta T < 100$ K) [2, 6].

The slope of the straight lines $\Delta E = f(\Delta T)$ corresponds to the thermoelectric power for the entire

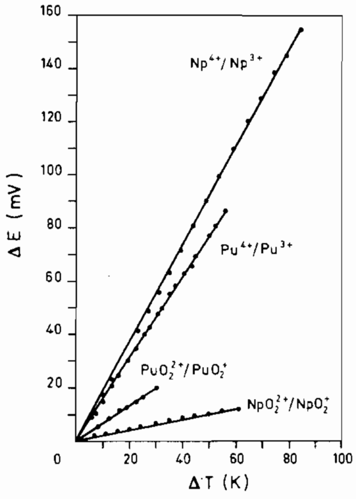

Fig. 2. E.m.f. of M^{4+}/M^{3+} and MO_2^{2+}/MO_2^{+} redox couples of plutonium and neptunium elements *vs.* temperature gradient.

Experimental conditions:

NpO_2^{2+}/NpO_2^{+}: $C_{Ox} = C_{Red} = 5 \times 10^{-2}$ *M*, $HClO_4$ 2 *N*

PuO_2^{2+}/PuO_2^{+}: $C_{Ox} = C_{Red} = 1.3 \times 10^{-3}$ *M*, $NaClO_4$ *M* pH = 3.5

Pu^{4+}/Pu^{3+}: $C_{Ox} = C_{Red} = 5 \times 10^{-3}$ *M*, $HClO_4$ *N*

Np^{4+}/Np^{3+}: $C_{Ox} = C_{Red} = 3 \times 10^{-2}$ *M*, $HClO_4$ *N* range of ΔT. The slopes of the straight lines presented in Fig. 2 are respectively equal to:

$$\epsilon = \begin{cases} 1.87\ \mathrm{mV\,K^{-1}}\ (Np^{4+}/Np^{3+}); \\ 1.53\ \mathrm{mV\,K^{-1}}\ (Pu^{4+}/Pu^{3+}); \\ 0.66\ \mathrm{mV\,K^{-1}}\ (PuO_2{}^{2+}/PuO_2{}^{+}); \\ 0.22\ \mathrm{mV\,K^{-1}}\ (NpO_2{}^{2+}/NpO_2{}^{+}). \end{cases}$$

These values are related to the experimental conditions shown in Fig. 2.

For both elements, the M^{4+}/M^{3+} couples display a high ϵ value and the $MO_2{}^{2+}/MO_2{}^{+}$ couples display a low ϵ value. No difference was observed for results obtained for perchloric and nitric media. For constant ΔT values, the effect of C_{Ox}/C_{Red} on the thermoelectric power was studied for all the systems with variations of the ratio equal to two orders of magnitude. Figures 3 and 4 show the results for (M^{4+}/M^{3+}) and ($MO_2{}^{2+}/MO_2{}^{+}$) systems respectively.

The experimental data fit straight lines in semi-logarithmic plots; this agrees with the theoretical prediction (see eqn. 7). The slopes of the straight lines are respectively equal to:

0.184 mV K^{-1} (Np^{4+}/Np^{3+});
0.182 mV K^{-1} (Pu^{4+}/Pu^{3+});
0.192 mV K^{-1} ($NpO_2{}^{2+}/NpO_2{}^{+}$);
0.197 mV K^{-1} ($PuO_2{}^{2+}/PuO_2{}^{+}$).

These results agree reasonably with the theoretical value of 0.198 mV K^{-1}.

The effect of ionic strength on the thermoelectric powers of all the couples is shown in Fig. 5. Large differences are observed for the M^{4+}/M^{3+} and $MO_2{}^{2+}/MO_2{}^{+}$ systems. For the $MO_2{}^{2+}/MO_2{}^{+}$ couples, ϵ increases with a decreasing ionic strength. However, ϵ increases with ionic strength for Pu^{4+}/Pu^{3+} or exhibits a maximum for the Np^{4+}/Np^{3+} couple. The difference of the behaviour of the M^{4+}/M^{3+} and $MO_2{}^{2+}/MO_2{}^{+}$ systems is certainly related to the highly acidic properties of the actinide M^{4+} ions.

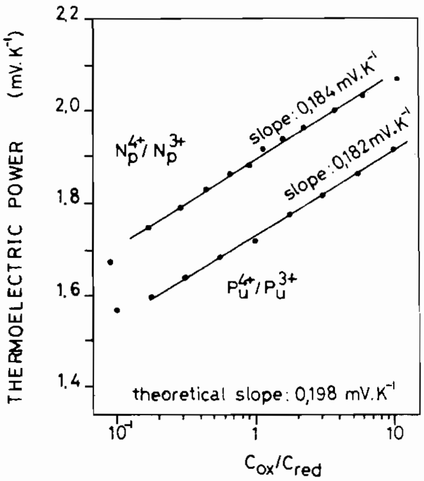

Fig. 3 Thermoelectric power of Np^{4+}/Np^{3+} and Pu^{4+}/Pu^{3+} couples *vs.* concentration ratio C_{Ox}/C_{Red}.
Experimental conditions:
Pu^{4+}/Pu^{3+}: $C_{Ox} + C_{Red} = 1.5 \times 10^{-2}\,M$, $HClO_4$ 2 N
Np^{4+}/Np^{3+}: $C_{Ox} + C_{Red} = 5 \times 10^{-2}\,M$, $HClO_4$ 1.1 N

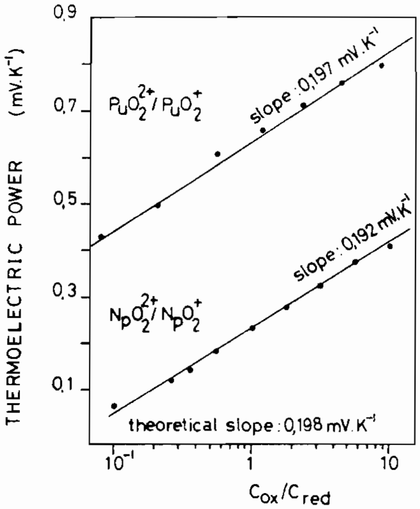

Fig. 4. Thermoelectric power of $NpO_2{}^{2+}/NpO_2{}^{+}$ and $PuO_2{}^{2+}/PuO_2{}^{+}$ couples *vs.* concentration ratio C_{Ox}/C_{Red}.
Experimental conditions:
$PuO_2{}^{2+}/PuO_2{}^{+}$: $C_{Ox} + C_{Red} = 2.5 \times 10^{-2}\,M$, pH = 3.5, $NaClO_4$ M
$NpO_2{}^{2+}/NpO_2{}^{+}$: $C_{Ox} + C_{Red} = 4.5 \times 10^{-2}\,M$, HNO_3 1.3 N

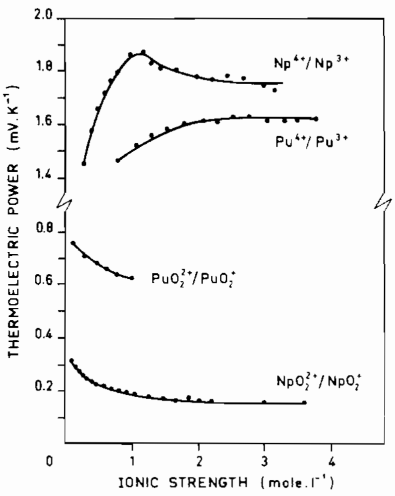

Fig. 5. Thermoelectric power of M^{4+}/M^{3+} and $MO_2{}^{2+}/MO_2{}^{+}$ redox couples of plutonium and neptunium elements *vs.* ionic strength.
Experimental conditions:
$NpO_2{}^{2+}/NpO_2{}^{+}$: $C_{Ox} = C_{Red} = 5 \times 10^{-3}\,M$, I = f($HClO_4$)
$PuO_2{}^{2+}/PuO_2{}^{+}$: $C_{Ox} = C_{Red} = 3.5 \times 10^{-3}\,M$, pH = 3.5, I = f($NaClO_4$)
Pu^{4+}/Pu^{3+}: $C_{Ox} = C_{Red} = 5 \times 10^{-3}\,M$, I = f($HClO_4$)
Np^{4+}/Np^{3+}: $C_{Ox} = C_{Red} = 7.5 \times 10^{-3}\,M$, I = f($HClO_4$)

TABLE II. Entropy Values.

Couples	S°(Ox) J mol^{-1} K^{-1}		S°(Red) J mol^{-1} K^{-1}		ΔS° J mol^{-1} K^{-1}		
	Latimer [7]	Fuger & Oetting [8]	Latimer [7]	Fuger & Oetting [8]	Latimer [7]	Fuger & Oetting [8]	This work
Np^{4+}/Np^{3+}	−326	−389	−130	−179	196	210 ± 27	195 ± 12
Pu^{4+}/Pu^{3+}	−363	−389	−163	−184	200	205 ± 27	195 ± 12
NpO_2^{2+}/NpO_2^+	−71	−92	50	−21	121	71 ± 16	23 ± 5
PuO_2^{2+}/PuO_2^+	−54	−88	79	−21	134	67 ± 16	63 ± 5

Calculated curves obtained for MO_2^{2+}/MO_2^+:

$$\text{Np: } \epsilon = \left[0.430 - 0.465\,\frac{I^{1/2}}{1 + I^{1/2}}\right] \text{mV K}^{-1}$$

$$\text{Pu: } \epsilon = \left[0.850 - 0.465\,\frac{I^{1/2}}{1 + I^{1/2}}\right] \text{mV K}^{-1}$$

Similar results were obtained in the study of the Fe^{3+}/Fe^{2+} system [6].

Thus for Np^{4+}/Np^{3+} at ionic strength higher than 1.2 mol l^{-1}, the variations of ϵ agree with the Debye–Huckel equation (see eqn. 8); for $I \leqslant 1.2$ mol l^{-1} the activity of Np^{4+} ion decreases due to the formation of Np(IV) hydroxo-complexes.

The same explanation accounts for the behavior of the Pu^{4+}/Pu^{3+} system, but as Pu^{4+} is shown to be more acidic than Np^{4+}, a deviation from the Debye–Huckel law appears for higher ionic strength. For the MO_2^{2+}/MO_2^+ systems, the experimental data fit fairly well the calculated curves obtained using eqns. 7 and 8 (see Fig. 5). This allows extrapolation at zero ionic strength to yield the following ϵ° values: 0.430 mV K^{-1} and 0.850 mV K^{-1} for neptunium and plutonium respectively.

For M^{4+}/M^{3+}, the extrapolations from data obtained at high acid concentration (*i.e.* high ionic strength), allow the estimation of ϵ°, which was found in the range 2.0 to 2.25 mV K^{-1} for neptunium and plutonium.

The ϵ° estimation for M^{4+}/M^{3+} couples is very close to the values computed by de Bethune *et al.* [1] (2.27 mV K^{-1} for Pu^{4+}/Pu^{3+} and 2.23 mV K^{-1} for Np^{4+}/Np^{3+}). In the case of MO_2^{2+}/MO_2^+ couples the published values (1.45 mV K^{-1} and 1.58 mV K^{-1} respectively for Np and Pu systems) are very different from those obtained.

For all the couples, the measurements confirmed the theoretical approach discussed above.

The extrapolations and estimations of the thermoelectric powers of the four couples allow the calculation of ΔS° for each couple using eqn. 5:

$$S^\circ(\text{Red}) - S^\circ(\text{Ox}) = \Delta S^\circ = nF(\epsilon^\circ - 0.195 \text{ mV K}^{-1})$$

Table II gives the calculated ΔS° for the systems investigated with comparison with the values published by Fuger & Oetting in their critical review of the thermodynamic properties of actinide ions [8], and those published by Latimer [7] used by de Bethune *et al.* [1] for their calculations.

ΔS° estimated values for M^{4+}/M^{3+} couples obtained in this study are in agreement with the literature.

For MO_2^{2+}/MO_2^+ systems the data published by Latimer and by Fuger & Oetting display a wide discrepancy. Thus, only the values published by Fuger & Oetting are taken into consideration because they are more recent. The experimental and published ΔS° for PuO_2^{2+}/PuO_2^+ couples are in excellent agreement, but a wide difference is observed for the NpO_2^{2+}/NpO_2^+ couple. No explanation is found for this result since these MO_2^{2+}/MO_2^+ couples are expected to display similar behavior. In terms of entropy, therefore, this deviation points to some unexpected difference in the structure of the MO_2^{2+} or MO_2^+ aquo ions between neptunium and plutonium.

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