Thermodynamic data for hydrous and anhydrous PuO$_{2+x}$(s)

V. Neck [a,*], M. Altmaier [a], Th. Fanghänel [a,b]

[a] *Forschungszentrum Karlsruhe, Institut für Nukleare Entsorgung, PO Box 3640, D-76021 Karlsruhe, Germany*
[b] *European Commission, Joint Research Centre, Institute for Transuranium Elements, PO Box 2340, D-76125 Karlsruhe, Germany*

Abstract

Mixed valent PuO$_{2+x}$(s, hyd) = (Pu^{V})$_{2x}$(Pu^{IV})$_{1-2x}$O$_{2+x}$(s, hyd) is formed by the reaction of hydrous Pu(IV) oxyhydroxide precipitates, PuO$_2$(s, hyd), with oxygen. The standard molar Gibbs energy of formation is calculated from the Pu(IV) and Pu(V) concentrations at 20–25 °C in equilibrium with PuO$_{2+x}$(s, hyd) which may be written formally as (PuO$_{2.5}$)$_{2x}$(PuO$_2$)$_{1-2x}$(s, hyd) where $x < 0.1$:

$$\Delta_f G_m^\circ(\text{PuO}_{2+x}(s, \text{hyd})) = \{2x(-971.2 \pm 5.4) + (1 - 2x)(-965.5 \pm 4.0)\} \text{ (kJ/mol)}.$$

This value is only slightly more negative than $\Delta_f G_m^\circ(\text{PuO}_2(s, \text{hyd})) = -965.5 \pm 4.0$ kJ/mol. The formation of PuO$_{2+x}$(s, hyd) with $x > 0.25$, e.g. pure Pu(V) oxide, PuO$_{2.5}$(s, hyd), is rather questionable.

Anhydrous crystalline Pu(IV) dioxide ($\Delta_f G_m^\circ(\text{PuO}_2(\text{cr})) = -998.1 \pm 1.0$ kJ/mol) is not oxidised by O$_2$(g) unless the presence of water creates a surface layer of hydrous oxide. (The standard molar Gibbs energy for surface hydration is negative while $\Delta_r G_m^\circ$ for the hydration of the bulk crystalline phase is positive.) Assuming analogous differences between the $\Delta_f G_m^\circ$ values of AnO$_3$(cr) and An(VI) oxyhydroxides or similar stabilization energies for analogous mixed valent compounds of U, Np and Pu, the known thermodynamic data for An(IV, V, VI) oxides and oxyhydroxides are used to estimate the following standard molar Gibbs energies of formation at 25 °C: $\Delta_f G_m^\circ(\text{PuO}_{2.25}(\text{cr})) = -995 \pm 3$ kJ/mol, $\Delta_f G_m^\circ(\text{PuO}_{2.5}(\text{cr})) = -987 \pm 10$ kJ/mol, and $\Delta_f G_m^\circ(\text{PuO}_3(\text{cr})) = -952 \pm 10$ kJ/mol. These compounds are less stable than PuO$_2$(cr).
© 2007 Elsevier B.V. All rights reserved.

Keywords: Plutonium; Solubility; Hydrous PuO$_{2+x}$(s, hyd); Anhydrous PuO$_{2+x}$(cr); Actinide oxides and oxyhydroxides; Standard molar Gibbs energies

1. Introduction

During the last years the formation and thermodynamics of PuO$_{2+x}$(s) have been discussed very controversially in the literature. The formation of PuO$_{2+x}$(s) has been reported first by Haschke et al. [1–4] who claimed that PuO$_2$(s) is oxidised by liquid water or water vapour according to the reaction:

$$\text{PuO}_2(s) + x\text{H}_2\text{O} \rightarrow \text{PuO}_{2+x}(s) + x\text{H}_2(g) \quad (1)$$
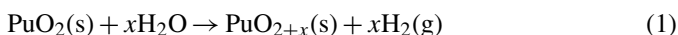
In the presence of both water and oxygen they proposed a water-catalyzed oxidation mechanism [2,3] with the net reaction:

$$\text{PuO}_2(s) + \tfrac{x}{2}O_2(g) \rightarrow \text{PuO}_{2+x}(s) \quad (2)$$
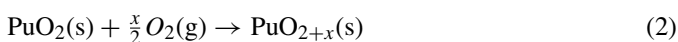
Theoretical studies cast doubts on the stability of PuO$_{2+x}$(s) [5,6] and a recent attempt to oxidise PuO$_2$(cr) with water vapour (under strict exclusion of oxygen) at 315 °C failed [7]. On the other hand, EXAFS and XPS studies [8,9] provide clear evidence for the formation of hydrous PuO$_{2+x}$(s, hyd) which has been characterized as partially oxidised mixed valent oxyhydroxide (Pu^{V})$_{2x}$(Pu^{IV})$_{1-2x}$O$_{2+x-n}$(OH)$_{2n}$(s, hyd). The maximum value of x observed by Haschke et al. [1–4] is $x = 0.27$ (approximately equal to PuO$_{2.25}$(s) = (1/4)Pu$_4$O$_9$(s)) but they supposed that PuO$_{2.5}$(s) = (1/2)Pu$_2$O$_5$(s) should be most stable [2–4]. Moreover, Haschke et al. [3] claimed that PuO$_{2+x}$(s) is more stable than PuO$_2$(s) and that the measured Pu concentrations and oxidation state distributions do not represent equilibrium thermodynamics but kinetically controlled steady-state concentrations resulting from the leaching of Pu(V) fractions and subsequent disproportionation reactions.

In a recent paper [10] we have analyzed solubility studies with PuO$_2$(s, hyd) in solutions without complexing ligands (carbonate, phosphate and silicate, etc.). Comparing total Pu

* Corresponding author.
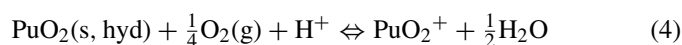*E-mail address:* neck@ine.fzk.de (V. Neck).

concentrations, oxidation state distributions and simultaneously measured redox potentials under air (at pH < 8) and under Ar (with only traces of O_2 present) strongly indicates that O_2 is scavenged by solid PuO_2(s, hyd) yielding mixed valent PuO_{2+x}(s, hyd) = $(Pu^V)_{2x}(Pu^{IV})_{1-2x}O_{2+x}$(s, hyd). Both the experimental Pu(IV) and Pu(V) concentrations and the measured redox potentials can be explained in terms of equilibrium thermodynamics [10]. In the present paper the thermodynamic data derived for PuO_{2+x}(s, hyd) from experimental solubility data are discussed in comparison with known standard molar Gibbs energies of pure and mixed valent anhydrous oxides and hydrous oxyhydroxides of uranium, neptunium and plutonium in the oxidation states An(IV), An(V), and An(VI).

2. Solubility control by PuO_{2+x}(s, hyd)

As discussed in recent reviews of the solubility of tetravalent actinides [11,12] the available solubility data for AnO_2(cr) with An = Th, U, Np and Pu strongly indicate that the solubility is not controlled by the thermodynamically stable crystalline dioxides AnO_2(cr) but by small fractions of small amorphous particles included in the bulk crystalline solids or by amorphous hydrated surface layers. The measured An(IV) concentrations are similar to those determined with (metastable) oxyhydroxides, AnO_2(s, hyd), prepared by precipitation from solution. The solubility of Pu(IV) oxide or oxyhydroxide is further complicated by redox reactions. The total Pu concentration (log $[Pu]_{tot}$) measured in solubility studies with Pu(IV) hydrous oxide precipitates at pH > 3 is dominated by Pu(V) for both studies under air (Rai et al. [13–15]) and studies under Ar atmosphere containing only traces of oxygen [10,16,17] (Fig. 1). The studies under air and Ar led to very similar Pu(V) concentrations and redox potentials in these suspensions. A profound analysis of the experimental data in these studies [10] has shown that the Pu(V) concentrations and pe values are not consistent with the equilibria

$$PuO_2(s, hyd) \Leftrightarrow PuO_2^+ + e^- \qquad (3)$$

or

$$PuO_2(s, hyd) + \tfrac{1}{4}O_2(g) + H^+ \Leftrightarrow PuO_2^+ + \tfrac{1}{2}H_2O \qquad (4)$$

The experimental data can only be explained if oxygen is scavenged by the abundantly present solid phase PuO_2(s, hyd) yielding PuO_{2+x}(s, hyd) [10]:

$$PuO_2(s, hyd) + \tfrac{x}{2}O_2 \rightarrow PuO_{2+x}(s, hyd) \qquad (5)$$
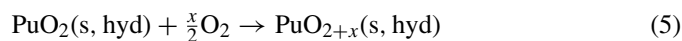
The fraction of Pu(V) in PuO_{2+x}(s, hyd)) can be calculated from the constant concentration at pH < 3 where the rather small fraction of oxidised Pu is completely dissolved and from the total Pu inventory in the samples initially present in the solid precipitates [10]. This is about 0.5% ($x = 0.003$) in our recent study under Ar (<10 ppm O_2) where the constant level of dissolved Pu(V) at pH < 4 corresponds to the amount of Pu(VI) in the initial Pu(IV) stock solution from which the solid phase was precipitated [10]. The solids in the studies of Rai et al. [14,15] contain 10–12%
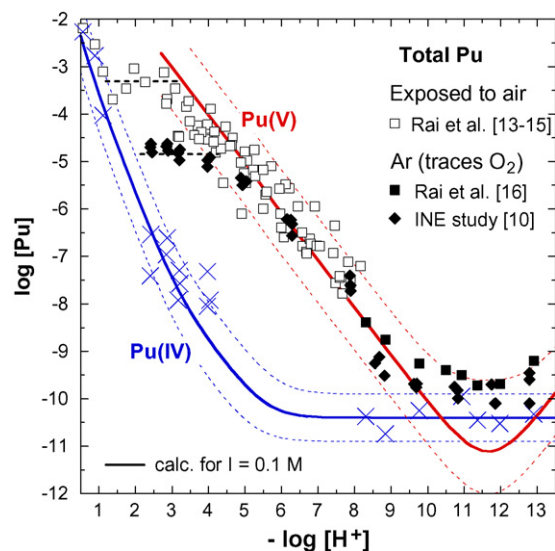

Fig. 1. Solubility of PuO_{2+x}(s, hyd) = at pH 1–13 and $I < 0.5$ M (20–25 °C); experimental solubility data after ultrafiltration: $[Pu]_{tot}$ (predominantly Pu(V)) under air [13–15] (open symbols) or under Ar containing less than 10 ppm O_2 [10] (filled symbols) and Pu(IV) concentrations (crosses) determined by spectroscopy or solvent extraction. The calculated Pu(IV) concentration is based on the solubility product of PuO_2(s, hyd) and the Pu(IV) hydrolysis constants selected in [11,19]. The calculated Pu(V) concentration is based on log $K_{sp}^\circ = -14.0 \pm 0.8$ and the hydrolysis constants selected in [18,19] for the analogous Np(V) species $NpO_2(OH)$(aq) and $NpO_2(OH)_2^-$.

Pu(V) ($x = 0.05$–0.06) which corresponds to the amount of oxygen in their samples exposed to air and then kept in closed vials, i.e., to the sum of $[O_2]_{aq} = 2.5 \times 10^{-4}$ M at pO_2(g) = 0.2 bar and O_2(g) in the gas phase above the solution [10].

Mixed valent PuO_{2+x}(s, hyd) = $(Pu^V)_{2x}(Pu^{IV})_{1-2x}O_{2+x}$(s, hyd) may be written formally as $(PuO_{2.5})_{2x}(PuO_2)_{1-2x}$(s, hyd) in equilibrium with both Pu(V) and Pu(IV) in solution (Fig. 1):

$$PuO_{2+x}(s, hyd) + (2 - 3x)H_2O(l)$$
$$\Leftrightarrow 2xPuO_2^+ + (1 - 2x)Pu^{4+} + (4 - 6x)OH^- \qquad (6)$$
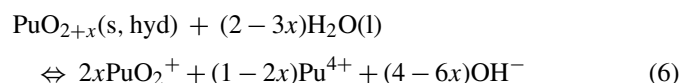
Since PuO_2^+ and Pu^{4+} ions and their hydroxide complexes do not undergo reversible redox reactions, their equilibrium concentrations can be described separately by the solubility products for the formal fractions of $PuO_{2.5}$(s, hyd) and PuO_2(s, hyd) in PuO_{2+x}(s, hyd):

$$K_{sp}(PuO_{2.5} \text{ in } PuO_{2+x}(s, hyd)) = [PuO_2^+][OH^-] \qquad (7)$$

$$K_{sp}(PuO_2 \text{ in } PuO_{2+x}(s, hyd)) = [Pu^{4+}][OH^-]^4 \qquad (8)$$

with

$$\log K_{sp}(PuO_{2+x}(s, hyd))$$
$$= 2x \log K_{sp}(PuO_{2.5} \text{ in } PuO_{2+x}(s, hyd))$$
$$+ (1 - 2x) \log K_{sp}(PuO_2 \text{ in } PuO_{2+x}(s, hyd)) \qquad (9)$$

The standard molar Gibbs energy can be calculated from the solubility constants at zero ionic strength. log $K_{sp}^\circ(PuO_{2.5}$ in PuO_{2+x}(s, hyd)) = -14.0 ± 0.8 [10] and log $K_{sp}^\circ(PuO_2$ in PuO_{2+x}(s, hyd)) $\approx$ log $K_{sp}^\circ(PuO_2$(s, hyd)) = -58.33 ± 0.52 [19]

according to

$$\Delta_f G_m^\circ(PuO_{2.5}(s, hyd))$$
$$= RT \ln K_{sp}^\circ(PuO_{2.5}(s, hyd)) + \Delta_f G_m^\circ(PuO_2^+)$$
$$+ \Delta_f G_m^\circ(OH^-) - 0.5\Delta_f G_m^\circ(H_2O(l)) \qquad (10)$$

and

$$\Delta_f G_m^\circ(PuO_2(s, hyd))$$
$$= RT \ln K_{sp}^\circ(PuO_2(s, hyd)) + \Delta_f G_m^\circ(Pu^{4+})$$
$$+ 4\Delta_f G_m^\circ(OH^-) - 2\Delta_f G_m^\circ(H_2O(l)) \qquad (11)$$

with $\Delta_f G_m^\circ(PuO_2^+) = -852.65 \pm 2.87$ kJ/mol, $\Delta_f G_m^\circ(Pu^{4+}) = -477.99 \pm 2.70$ kJ/mol, $\Delta_f G_m^\circ(OH^-) = -157.22 \pm 0.07$ kJ/mol, and $\Delta_f G_m^\circ(H_2O(l)) = -237.14 \pm 0.04$ kJ/mol [19]. Hence the standard molar Gibbs energy of formation of $PuO_{2+x}(s, hyd)$ is given by

$$\Delta_f G_m^\circ(PuO_{2+x}(s, hyd))$$
$$= 2x\Delta_f G_m^\circ(PuO_{2.5}(s, hyd)) + (1 - 2x)\Delta_f G_m^\circ(PuO_2(s, hyd))$$
$$= \{2x(-971.2 \pm 5.4) + (1 - 2x)(-965.5 \pm 4.0)\} \text{ (kJ/mol)} \qquad (12)$$

for $PuO_{2+x}(s, hyd)$) with $x < 0.1$ present in the solubility studies discussed above. It is only slightly lower than $\Delta_f G_m^\circ(PuO_2(s, hyd)) = -965.5 \pm 4.0$ kJ/mol.

It has to be emphasized that amorphous or slightly crystalline hydrous oxides or oxyhydroxides like $PuO_2(s, hyd)$ or $PuO_{2+x}(s, hyd)$ formed in aqueous solution are not well defined compounds. They are inhomogeneous with regard to the degree of hydration and crystallite size. Hence their thermodynamic properties can vary with time of ageing and with the solution conditions affecting the recrystallization kinetics [19]. The solubility constants and $\Delta_f G_m^\circ$ values must therefore be considered as average values. On the other hand, these are the compounds relevant for aqueous systems and the storage of nuclear waste. Particularly in the case of highly active Pu wastes α-radiation damage leads to the amorphization of crystalline compounds.

3. Discussion of thermodynamic data for $PuO_{2+x}(s, hyd)$ and $PuO_{2+x}(cr)$ in comparison with known data for oxides and oxyhydroxides of uranium and neptunium

In the following sections, the thermodynamic data derived for hydrous $PuO_{2+x}(s, hyd)$ from experimental solubility data and those for possible anhydrous crystalline compounds like $PuO_{2.25}(cr) = (1/4)Pu_4O_9(cr)$, $PuO_{2.5}(cr) = (1/2)Pu_2O_5(cr)$, and $PuO_3(cr)$ are discussed by comparing known standard molar Gibbs energies of formation $\Delta_f G_m^\circ$ (298.15 K) of pure and mixed valent anhydrous oxides and hydrous oxyhydroxides of uranium, neptunium and plutonium in the oxidation states An(IV), An(V) and An(VI). The $\Delta_f G_m^\circ$ values derived from solubility constants for hydrous An(IV) and An(V) oxyhydroxides correspond to the formula $AnO_{2+x}(s, hyd)$, i.e., the contribution of H_2O molecules is not included in the values for $\Delta_f G_m^\circ(AnO_{2+x}(s,$
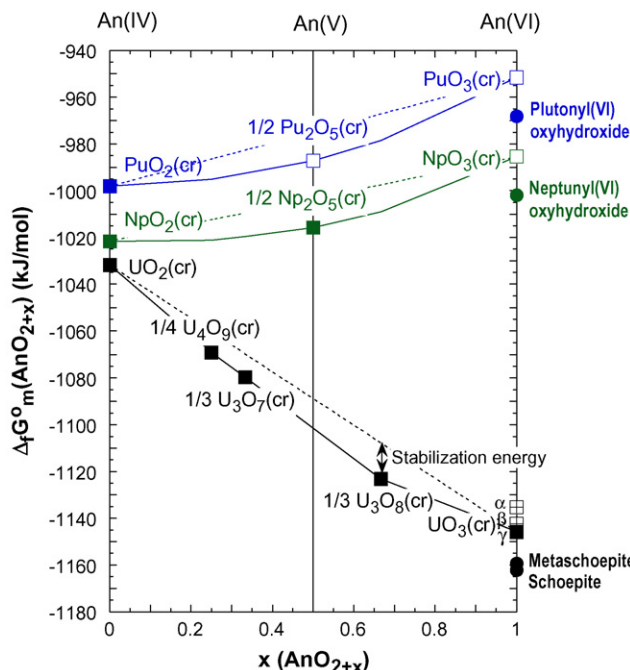

Fig. 2. Normalized standard molar Gibbs energies of formation of crystalline An(IV, V, VI) oxides $AnO_{2+x}(cr)$ and actinyl(VI) oxyhydroxides $AnO_3(cr, hyd)$ as a function of x; known data (filled symbols) selected in the NEA-TDB [19] and estimated values for unknown Np and Pu oxides (open symbols).

hyd)). For better comparison, the $\Delta_f G_m^\circ$ values derived from thermochemical or solubility data for the crystalline An(VI) oxyhydroxides with the formula $AnO_2O_{1-n/2}(OH)_n \cdot yH_2O(cr)$ are normalized to values referring to the formula $AnO_3(cr, hyd)$ by subtracting $(n/2 + y) \Delta_f G_m^\circ(H_2O(l))$, e.g., the value of $\Delta_f G_m^\circ(PuO_2(OH)_2 \cdot H_2O(cr)) = -1442.4$ kJ/mol [19] $((n/2 + y) = 2)$ is transformed into $\Delta_f G_m^\circ(PuO_3(cr, hyd)) = -968.1$ kJ/mol.

3.1. Standard molar Gibbs energies of formation of crystalline An(IV–V–VI) oxides and actinyl(VI) oxyhydroxides $\Delta_f G_m^\circ(AnO_{2+x}(cr), 298.15 K)$

The standard molar Gibbs energies of formation $\Delta_f G_m^\circ(AnO_{2+x}(cr), 298.15 K)$ selected in the NEA-TDB [19] from experimental (thermochemical) data for anhydrous crystalline U(IV–V–VI) oxides, $NpO_2(cr)$, $NpO_{2.5}(cr) = (1/2)Np_2O_5(cr)$ and $PuO_2(cr)$ are shown in Fig. 2 (filled squares). The normalized values for the actinyl(VI) oxyhydroxides $AnO_3(s, hyd)$ of U(VI) (schoepite, metaschoepite), Np(VI) and Pu(VI) (filled circles) were derived from the selected solubility constants [19]. Fig. 2 also includes estimated $\Delta_f G_m^\circ$ values for $NpO_3(cr)$, $PuO_3(cr)$, and $PuO_{2.5}(cr) = (1/2)Pu_2O_5(cr)$ (open squares). These estimates for the unknown Np and Pu oxides are based on the two following assumptions:

(1) The difference between the standard molar Gibbs energies of formation of the known neptunyl(VI) and plutonyl(VI) oxyhydroxides and the (unknown) anhydrous trioxides, $NpO_3(cr)$ and $PuO_3(cr)$, is assumed to be similar as for

the analogous U(VI) compounds: $\Delta_f G_m^\circ$(UO$_3$(cr, hyd), schoepite) $- \Delta_f G_m^\circ(\gamma$-UO$_3$(cr))$ = -16.5 \pm 2.1$ kJ/mol [19].

(2) Mixed valent An(IV–V) and An(IV–VI) oxides are more stable than corresponding mixtures of the pure An(IV) and An(V) or An(VI) oxides (e.g.: 1/3 $\Delta_f G_m^\circ$(U$_3$O$_8$(cr)) $- \{2/3 \Delta_f G_m^\circ$(UO$_3$(cr)) $+ 1/3 \Delta_f G_m^\circ$(UO$_2$(cr))$\} = -15.4$ kJ/mol). In Fig. 2, this stabilization effect is illustrated by the deviation of $\Delta_f G_m^\circ$ for a mixed valent oxide from the dotted straight line between the $\Delta_f G_m^\circ$ values of the pure An(IV) and An(VI) oxides. It should be noted that the stabilization of mixed valent An(IV–V) oxides compared to mixtures of AnO$_2$(cr) and AnO$_{2.5}$(cr) is less than 50% of that in An(IV–VI) oxides. We may assume that the stabilisation energy for mixed valent oxides is approximately the same for analogous compounds of U, Np and Pu as illustrated by analogous deviations between the solid and dotted lines in Fig. 2.

The data in Fig. 2 clearly show that the standard molar Gibbs energy $\Delta_r G_m^\circ$ for the oxidation of dry crystalline An(IV) dioxide AnO$_2$(cr) with oxygen ($\Delta_f G_m^\circ$(O$_2$(g)) $= 0$),

$$\text{AnO}_2(\text{cr}) + \tfrac{x}{2}\text{O}_2(\text{g}) \rightarrow \text{AnO}_{2+x}(\text{cr}) \tag{13}$$
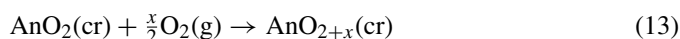
is negative for U and positive for Np and Pu. These simple thermodynamic considerations are consistent with the experimental observations that dry NpO$_2$(cr) and PuO$_2$(cr) are not oxidised by O$_2$(g) (c.f., [18], p. 121 and Haschke et al. [1–3]).

The close analogy between the known data for Np and Pu compounds (Fig. 2) and also the standard molar Gibbs energies calculated for PuO$_{2+x}$(s, hyd) and estimated for PuO$_{2.25}$(cr), PuO$_{2.5}$(cr) and PuO$_3$(cr) (Table 1) indicate that the standard molar Gibbs energies of formation reported by Haschke and Allen [4] for PuO$_{2+x}$(s) with $x = 0.05$–0.5 are considerably in error. For instance the values of $\Delta_f G_m^\circ$(PuO$_{2.25}$(s)) $= -1080$ kJ/mol and $\Delta_f G_m^\circ$(PuO$_{2.5}$(s)) $= -1146$ kJ/mol [4] are too negative by about 85 and 159 kJ/mol, respectively. They are calculated

assuming that PuO$_2$(s) is oxidised by water according to

$$\text{PuO}_2(\text{s}) + x\text{H}_2\text{O} \rightarrow \text{PuO}_{2+x}(\text{s}) + x\text{H}_2(\text{g}) \tag{14}$$
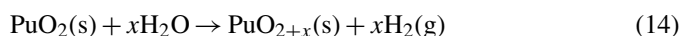
The observed formation of H$_2$(g) [1] cannot be explained by the thermodynamics of reaction (14) ($\Delta_r G_m^\circ > x200$ kJ/mol), it must be caused by other mechanisms (e.g., induced by radiolysis effects). However, Haschke et al. [1–3] recognized very well that water plays an important role for the formation of PuO$_{2+x}$(s) that will be discussed in the following section.

3.2. Standard molar Gibbs energies of formation of hydrous Np(IV–V) and Pu(IV–V) oxides $\Delta_f G_m^\circ$(AnO$_{2+x}$(s,hyd), 298.15 K)

The normalized values of $\Delta_f G_m^\circ$(AnO$_{2+x}$(s, hyd)) are shown in Fig. 3 for the hydrous oxides/oxyhydroxides of Np and Pu. The data for PuO$_{2+x}$(s, hyd) with $x = 0.003$, 0.05 and 0.06 are calculated with Eqs. (10)–(12) from the solubility studies under Ar with traces of oxygen [10] and under air [14,15], respectively. The values for Np are calculated in an analogous way from the experimental solubility constants for NpO$_2$(am, hyd) (log $K_{sp}^\circ = -56.7 \pm 0.5$ [11,19]), and NpO$_{2.5}$(s, hyd) (log $K_{sp}^\circ = -11.4 \pm 0.4$ [20] and -10.1 ± 0.2 [21]), i.e., from solids in contact with or formed in aqueous solution. Auxiliary data used for calculation ($\Delta_f G_m^\circ$(Np^{4+}) $= -491.8 \pm \pm 5.6$ kJ/mol, $\Delta_f G_m^\circ$(NpO$_2^+$) $= -907.8 \pm 5.6$ kJ/mol) were taken from the NEA-TDB [18,19].

The standard molar Gibbs energies of formation of An(IV) hydrous oxides are considerably less negative than those of the corresponding anhydrous crystalline An(IV) dioxides [11,12,19]. The difference of about 40 ± 10 kJ/mol, corresponding to 7 log-units in the solubility constants, is due to effects from hydration and crystallinity (particle or crystallite size) as shown for ThO$_2$(s) [12]. For the pentavalent actinides, e.g. Np(V), the difference between the standard molar Gibbs energies of hydrous oxides used in solubility studies and anhydrous crystalline oxides is much smaller. The hydrous actinyl(VI) oxyhydroxides formed in aqueous solution like schoepite or metaschoepite are usually crystalline and even more stable than

Table 1
Standard molar Gibbs energies of formation $\Delta_f G_m^\circ$ of Pu(IV, V, VI) oxides and oxyhydroxides at 25 °C

Solid	$\Delta_f G_m^\circ$ (kJ/mol)
Anhydrous crystalline oxides	
PuO$_2$(cr)	-998.1 ± 1.0 [19]
PuO$_{2.25}$(cr) = 1/4 Pu$_4$O$_9$(cr)	-995 ± 3[a]
PuO$_{2.5}$(cr) = 1/2 Pu$_2$O$_5$(cr)	-987 ± 10[a]
PuO$_3$(cr)	-952 ± 10[a]
Hydrous oxides/oxyhydroxides[b]	
PuO$_2$(s, hyd)	-965.5 ± 4.0 [19]
PuO$_{2+x}$(s, hyd) with $x < 0.1$ = (PuO$_{2.5}$)$_{2x}$(PuO$_2$)$_{1-2x}$(s, hyd)	$2x(-971.2 \pm 5.4) + (1-2x)(-965.5 \pm 4.0)$
PuO$_{2.25}$(s, hyd)	$\geq -968.4 \pm 4.7$
PuO$_{2.5}$(s, hyd)	$> -971.2 \pm 5.4$ (-965 ± 7)[c]
"PuO$_3$(s, hyd)" = PuO$_2$(OH)$_2 \cdot$H$_2$O(s)	-968.1 ± 6.4 [19]

[a] Estimated from known data for pure and mixed valent An(IV, V, VI) oxides and oxyhydroxides of An = U, Np and Pu (see text).

[b] Calculated from experimental solubility constants using $\Delta_f G_m^\circ$(Pu^{4+}), $\Delta_f G_m^\circ$(PuO$_2^+$) and auxiliary data from the NEA-TDB [19].

[c] Pure PuO$_{2.5}$(s, hyd) is assumed to be less stable than the formal value for the PuO$_{2.5}$(s, hyd) fraction in the mixed valent compound PuO$_{2+x}$(s, hyd), typically by 5–10 kJ/mol.
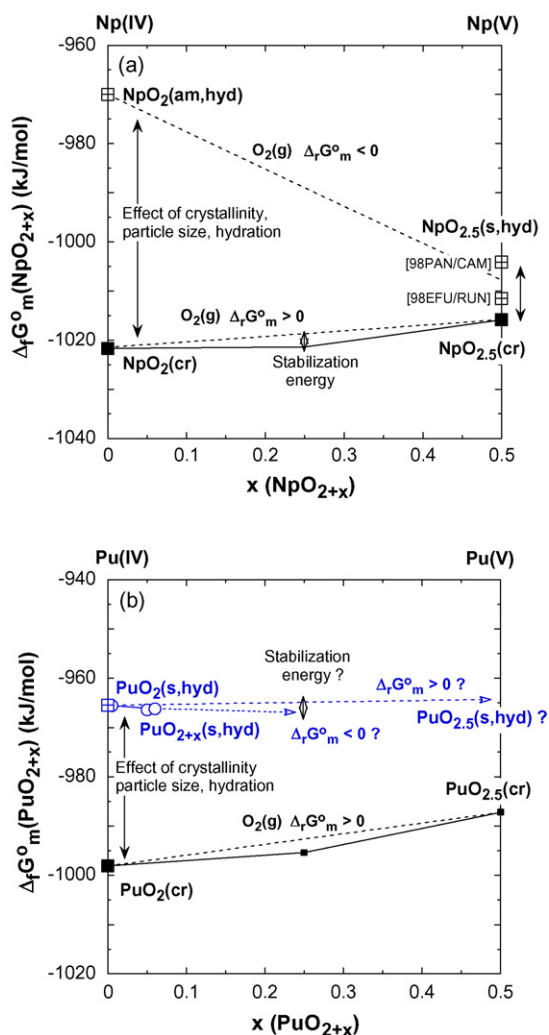
Fig. 3. Normalized standard molar Gibbs energies of formation of hydrous Np(IV–V) and Pu(IV–V) oxides AnO_{2+x}(s, hyd) as a function of x in comparison with the data for the anhydrous crystalline oxides AnO_{2+x}(cr) from Fig. 2.

anhydrous AnO_3(cr):

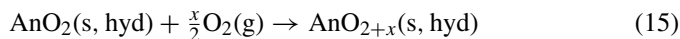$$\Delta_f G_m^\circ(AnO_2(am, hyd)) - \Delta_f G_m^\circ(AnO_2(cr)) = 40 \pm 10 \, kJ/mol$$

(for An = Th, U, Np, Pu),

$$\Delta_f G_m^\circ(NpO_{2.5}(s, hyd)) - \Delta_f G_m^\circ(NpO_{2.5}(cr)) = 8 \pm 5 \, kJ/mol,$$

$$\Delta_f G_m^\circ(UO_3(cr, hyd), schoepite) - \Delta_f G_m^\circ(\gamma\text{-}UO_3(cr))$$

$$= -16.5 \pm 2.1 \, kJ/mol$$

This trend leads to important consequences for the reaction

$$AnO_2(s, hyd) + \tfrac{x}{2}O_2(g) \rightarrow AnO_{2+x}(s, hyd) \qquad (15)$$

The standard molar Gibbs energy $\Delta_r G_m^\circ$ for the oxidation of hydrous UO_2(am, hyd)) with oxygen is strongly negative up to $x = 1$ ($\Delta_f G_m^\circ(UO_2(am, hyd)) = -995.5 \pm 6.0 \, kJ/mol$, $\Delta_f G_m^\circ(UO_3(s, hyd), schoepite) = -1162.2 \pm 1.7 \, kJ/mol$ [19]). In the case of uranium the same holds also for dry UO_2(cr) (c.f., Fig. 2). However, contrary to the slightly positive standard Gibbs energy for the oxidation of dry NpO_2(cr), $\Delta_r G_m^\circ$

for reaction (15) is negative for hydrous NpO_2(am, hyd), up to $x = 0.5$ (c.f., Fig. 3a). For hydrous Pu oxide (Fig. 3b), the value of $\Delta_r G_m^\circ$ is close to zero. As discussed in Section 2, $\Delta_r G_m^\circ$ is slightly negative for $x < 0.1$ (and possibly up to $x = = 0.25$) whereas $\Delta_r G_m^\circ$ for $x > 0.25$ is expected to be equal to zero or slightly positive, if we take into account that the value of $\Delta_f G_m^\circ = -971.2 \pm 5.4 \, kJ/mol$ calculated for $PuO_{2.5}$(s, hyd) as a small fraction of PuO_{2+x}(s, hyd) (c.f., Eq. (10)), includes a stabilization energy of about 5–10 kJ/mol compared to pure $PuO_{2.5}$(s, hyd). Therefore PuO_{2+x}(s, hyd) is probably not stable beyond values of $x > 0.25$.

4. Conclusions

Pu(IV) hydrous oxide, PuO_2(s, hyd), is oxidized by O_2 to mixed valent PuO_{2+x}(s, hyd) $= (Pu^V)_{2x}(Pu^{IV})_{1-2x}O_{2+x}$(s, hyd). The standard molar Gibbs energy of formation, calculated from the Pu(V) and Pu(IV) concentrations in equilibrium with PuO_{2+x}(s, hyd) for $x = 0.003$ [10] and $x = 0.05$–0.06 [14,15], is slightly more negative than that of PuO_2(s, hyd). Anhydrous crystalline dioxides AnO_2(cr) are considerably more stable than the corresponding An(IV) hydrous oxides/oxyhydroxides. PuO_2(cr) cannot be oxidised by O_2(g) in the absence of H_2O(l) or H_2O(g) that is required to obtain a surface layer of hydrous oxide. The standard molar Gibbs energy for the hydration of the bulk PuO_2(cr) is of course positive, but $\Delta_r G_m^\circ$ for surface hydration is negative [22]. Hence in the presence of both water and oxygen, PuO_2(s) is partially oxidized to PuO_{2+x}(s) by reaction (2) as reported by Haschke et al. [2,3]. However, contrary to the proposed water catalyzed mechanism [2,3], the calculations in the present paper show that the role of water can be explained in terms of thermodynamics. The oxidation of PuO_2(s) by reaction (1) with water and the extremely high stability of PuO_{2+x}(s) also claimed by Haschke et al. [1–4] can be ruled out. The standard molar Gibbs energy for the oxidation of tetravalent actinide oxides and oxyhydroxides increases in the order U(IV) $\ll$ Np(IV) < Pu(IV).

References

[1] J.M. Haschke, T.H. Allen, L.A. Morales, Science 287 (2000) 285–287.
[2] J.M. Haschke, T.H. Allen, L.A. Morales, J. Alloys Comp. 314 (2001) 78–91.
[3] J.M. Haschke, V.M. Oversby, J. Nucl. Mat. 305 (2002) 187–201.
[4] J.M. Haschke, T.H. Allen:, J. Alloys Comp. 336 (2002) 124–131.
[5] L. Petit, A. Svane, Z. Szotek, W.M. Temmerman, Science 301 (2003) 498–501.
[6] P.A. Korzhavyi, L. Vitos, D.A. Andersson, B. Johansson, Nat. Mater. 3 (2004) 225–228.
[7] P. Martin, S. Grandjean, M. Ripert, M. Freyss, P. Blanc, T. Petit, J. Nucl. Mat. 320 (2003) 138–141.
[8] S.D. Conradson, B.D. Begg, D.L. Clark, et al., J. Am. Chem. Soc. 126 (2004) 13443–13458.
[9] D.J. Farr, R.K. Schulze, M.P. Neu, J. Nucl. Mat. 328 (2004) 124–136.
[10] V. Neck, M. Altmaier, Th. Fanghänel, Solubility and redox reactions of plutonium(IV) hydrous oxide in the presence of oxygen. In: I. May, R. Alvarez, N. Bryan, (Eds.), Recent Advances in Actinide Science, The Royal Society of Chemistry, Spec. Publ. No. 305 Proc. of the conf. Actinides 2005, RCS Publishing, Cambridge, UK, 2006, pp. 479–484.

[11] V. Neck, J.I. Kim:, Radiochim. Acta 89 (2001) 1–16.

[12] Th. Fanghänel, V. Neck, Pure Appl. Chem. 74 (2002) 1895–1907.

[13] D. Rai, R.J. Serne, D.A. Moore, Soil Sci. Am. J. 44 (1980) 490–495.

[14] D. Rai, Radiochim. Acta 35 (1984) 97–106.

[15] D. Rai, D.A. Moore, A.R. Felmy, G.R. Choppin, R.C. Moore, Radiochim. Acta 89 (2001) 491–498.

[16] D. Rai, N.J. Hess, A.R. Felmy, D.A. Moore, M. Yui, P. Vitorge, Radiochim. Acta 86 (1999) 89–99.

[17] Ch. Lierse, J.I. Kim Chemisches Verhalten von Plutonium in natürlichen aquatischen Systemen: Hydrolyse, Carbonatkomplexierung und Redoxreaktionen, Report RCM 02286, Inst. für Radiochemie, Technische Universität München, 1986.

[18] R.J. Lemire, J. Fuger, H. Nitsche, P. Potter, M.H. Rand, J. Rydberg, K. Spahiu, J.C. Sullivan, W.J. Ullman, P. Vitorge, H. Wanner, OECD, NEA-TDB, Chemical Thermodynamics, vol. 4: Chemical Thermodynamics of Neptunium and Plutonium, Elsevier, North-Holland, Amsterdam, 2001.

[19] R. Guillaumont, Th. Fanghänel, J. Fuger, I. Grenthe, V. Neck, D.A. Palmer, M.H. Rand, OECD, NEA-TDB, Chemical Thermodynamics, vol. 5: Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium, Elsevier, North-Holland, Amsterdam, 2003.

[20] D.W. Efurd, W. Runde, J.C. Banar, D.R. Janecky, J.P. Kaszuba, P.D. Palmer, F.R. Roensch, C.D. Tait:, Environ. Sci. Technol. 32 (1998) 3893–3900.

[21] P. Pan, A.B. Campbell, Radiochim. Acta 81 (1998) 73–82.

[22] J.M. Haschke, J. Nucl. Mat. 344 (2005) 8–12.