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Solubility of plutonium hydroxides/hydrous oxides under reducing conditions and in the presence of oxygen

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Abstract

The present paper analyzes solubility data reported for plutonium hydroxides or hydrous oxides under different redox conditions (in the presence of reducing chemicals, in solutions without reducing or oxidising agents under Ar atmosphere and under air). Special attention is dedicated to the solubility controlling solid phases, total Pu concentrations, oxidation-state distributions and simultaneously measured redox potentials. Thermodynamic calculations and experimental data show that $Pu(OH)_3(s)$ is not stable. Under reducing conditions in the stability field of water it converts into PuO_2(s,hyd). The solubility is given by the equilibrium concentrations of aqueous Pu(III) and Pu(IV) species. In the absence of reducing and oxidising agents but in the presence of traces of O_2(g), the total Pu concentration at pH > 3 is dominated by Pu(V) and the solubility is controlled by PuO_{2+x}(s,hyd), mixed valent $(Pu^{V})_{2x}(Pu^{IV})_{1-2x}O_{2+x}$(s,hyd). Small Pu(IV) colloids/polymers present in neutral to alkaline solutions at a constant level of $\log[Pu(IV)]_{coll} = -8.3 \pm 1.0$ play an important role for the redox potentials in these systems. Including these species, the experimental results in the system $Pu/e^-/H^+/OH^-/NaClO_4$ or $NaCl/H_2O$ (25 °C) can be described in terms of equilibrium thermodynamics. ***To cite this article: V. Neck et al., C. R. Chimie 10 (2007).***

Résumé

Cet article présente une analyse des solubilités publiées pour des hydroxydes et oxydes de plutonium dans différentes conditions d'oxydo-réduction (présence de réducteurs ou absence d'oxydant et de réducteur, sous atmosphère d'argon ou à l'air). Une attention particulière est portée à la nature des phases solides contrôlant la solubilité, la concentration totale de plutonium, la distribution des états d'oxydation et la mesure simultanée des potentiels redox indiqués. Des calculs thermodynamiques et des données expérimentales montrent que le $Pu(OH)_3(s)$ n'est pas stable. En milieu réducteur, dans le domaine de stabilité de l'eau, il se transforme en PuO_2(s,hyd). La solubilité est déterminée par les concentrations à l'équilibre des espèces aqueuses de Pu(III) et Pu(IV). En l'absence d'oxydant ou de réducteur, mais en présence de traces d'O_2(g), la concentration totale en plutonium à pH > 3 est déterminée par le Pu(V). La solubilité est alors contrôlée par PuO_{2+x}(s,hyd), l'oxyde de valence mixte $(Pu^{V})_{2x}(Pu^{IV})_{1-2x}O_{2+x}$(s,hyd). Des colloïdes ou polymères de Pu(IV) se forment et donnent une concentration constante ($\log[Pu(IV)]_{coll} = -8{,}3 \pm 1{,}0$) en solutions neutres à alcalines, où ils jouent un rôle important pour les potentiels redox mesurés de ces systèmes. La prise en compte de

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ces espèces permet de décrire les résultats expérimentaux dans le système $Pu/e^-/H^+/OH^-/NaClO_4$ ou $NaCl/H_2O$ (25 °C) en termes d'équilibres thermodynamiques. ***Pour citer cet article : V. Neck et al., C. R. Chimie 10 (2007).***

Keywords: Plutonium; Oxides; Hydroxides; PuO_{2+x}; Solubility; Redox reactions; Pu(IV) colloids; Thermodynamics

Mots-clés : Plutonium ; Oxydes ; Hydroxydes ; PuO_{2+x} ; Solubilité ; Pu(IV) colloïdes ; Réactions d'oxydo-réduction ; Données thermodynamiques

1. Introduction

The chemical thermodynamics of plutonium have been critically discussed in recent OECD/NEA-TDB reviews [1,2] which provide a well ascertained set of thermodynamic data and ion interaction coefficients for the system $Pu/e^-/H^+/OH^-/NaClO_4$ or $NaCl/H_2O$. However, there is still a lack of knowledge and it is difficult to ascertain reliable predictions of the total concentration of dissolved plutonium under the geochemical conditions of nuclear waste repositories. The interpretation of experimental results is complicated by redox reactions of aqueous plutonium species, Pu(IV) colloids and solid plutonium phases. In particular the redox reactions of Pu(IV) colloids have not yet been understood. The present paper gives an overview on the solubility of plutonium at 20–25 °C in solutions without complexing ligands (carbonate, phosphate, silicate, etc.) where oxides, oxyhydroxides or hydroxides are the solubility controlling solids. The discussion covers solubility studies in the presence of reducing chemicals [3–7], in the absence of reducing or oxidising agents under Ar atmosphere [8–10] and in the presence of O_2(g)/air [11–15].

Under reducing conditions Pu(III) is the dominant oxidation state in solution. However, there is only one study (Felmy et al. [3]) that provides experimental solubility data for Pu(III) hydroxide, $Pu(OH)_3$(s), as equilibrium solid phase. Thermodynamic calculations show that $Pu(OH)_3$(s) is a metastable solid phase, even under reducing conditions. The border line for the conversion into PuO_2(am,hyd) is close to the line for the decomposition of water.

Crystalline PuO_2(cr) is the stable Pu(IV) solid phase. However, recent papers on the solubility of tetravalent actinides [16–20] pointed out that the available solubility data for AnO_2(cr) strongly indicate that the solubility is controlled by 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 oxyhydroxide precipitates $AnO_{2-n}(OH)_{2n}\cdot xH_2O$(am) which may be designated as amorphous hydroxide, $An(OH)_4$(am), or hydrous oxide, $AnO_2\cdot xH_2O$(am) or AnO_2(am,hyd). It has to be emphasized that amorphous or slightly crystalline hydrous oxides or oxyhydroxides like aged PuO_2(s,hyd) that may show a weak XRD pattern [10,21] are not well defined compounds. They are inhomogeneous with regard to the degree of hydration and crystallite size. These properties can vary with time of ageing and with the solution conditions affecting the recrystallization kinetics [2]. The selected values for the solubility constant and standard molar Gibbs energy of formation must therefore be considered as average values for this kind of solids formed in aqueous solutions. 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 PuO_2(cr) [21]. Despite these problems there is good agreement between the values derived for the solubility constant of Pu(IV) hydrous oxide by different authors and approaches [2]: (a) the solubility products calculated in Ref. [16,22] from the available Pu(IV) equilibrium concentrations with the hydrolysis constants for $Pu(OH)_n^{4-n}$ reported in Ref. [23], (b) those derived from the solubility of PuO_2(am,hyd) under reducing conditions in equilibrium with Pu^{3+} [4–6], and (c) the value obtained for colloidal PuO_2(am,hyd) particles in equilibrium with Pu^{3+}, PuO_2^+ and PuO_2^{2+} at $pH_c = 1.0$ [24]. The equilibrium concentration of aqueous Pu(IV) species is usually low compared to those of Pu(III), Pu(V) and Pu(VI) which result from the known redox equilibria and depend on the redox potential and pH.

The solubility of amorphous Pu(V) hydroxide, PuO_2OH(am), is relatively high and does not represent a retention barrier. Oxyhydroxides of Pu(VI) (thermodynamic data are only known for $PuO_2(OH)_2\cdot H_2O$(cr) [1,2]) might control the solubility under strongly oxidising conditions (e.g., in case of radiolysis in concentrated chloride brines where Pu(VI) is the dominant oxidation state in solution [8,15]), but these conditions are not further discussed here.

A few years ago Haschke et al. [25–28] reported the formation of $PuO_{2+x}(s)$ which has been discussed very controversially. Recent EXAFS and XPS studies [29,30] report that the formation of PuO_{2+x}(s,hyd) is a partially oxidised mixed valent hydrated oxyhydroxide $(Pu^{V})_{2x}(Pu^{IV})_{1-2x}O_{2+x-n}(OH)_{2n}$(s,hyd). Our recent analysis of total Pu concentrations, oxidation state distributions and simultaneously measured redox potentials in solubility studies under air and under Ar (with only traces of $O_2(g)$ present) also indicates that oxygen is scavenged by solid PuO_2(s,hyd) yielding mixed valent PuO_{2+x}(s,hyd) that controls the solubility, i.e., the equilibrium concentrations of both Pu(IV) and Pu(V) [10]. However, the extreme stability of $PuO_{2+x}(s)$ and the thermodynamic data reported by Haschke et al. [27,28] cannot be correct [31,32]. These important findings are summarized in the present paper; thermodynamic data for PuO_{2+x}(s,hyd) will be discussed as well.

1.1. Definition of redox conditions

The decisive solution parameters that govern the solubility and oxidation-state distributions of plutonium (in the absence of complexing ligands) are the H^+ activity ($pH = -\log a_{H^+}$) or concentration ($pH_c = -\log [H^+]$) and the redox potential. The redox potential can be expressed as E_h versus the standard hydrogen electrode (SHE) or, analogous to pH, in terms of the apparent electron activity ($pe = -\log a_{e^-}$). E_h and pe are related by:

$$E_h = -(RT/F)\ln a_{e^-} \tag{1}$$

where R is the universal gas constant, T is the temperature (K) and F is the Faraday constant ($(RT/F)\ln(10) = 59.16$ mV and $pe = 16.9\, E_h$ at 25 °C where E_h is given in volts). Geochemical modelling codes often calculate the redox speciation by using the oxygen or hydrogen partial pressures and the reactions:

$$0.5H_2O(l) \leftrightharpoons 0.25O_2(g) + H^+ + e^- \tag{2}$$

$$H^+ + e^- \leftrightharpoons 0.5H_2(g) \tag{3}$$

with the equilibrium constants $\log K°(2) = 0.25 \log P(O_2(g)) - pH - pe - 0.5 \log a_w = -20.77$ and $\log K°(3) = 0.5 \log P(H_2(g)) + pH + pe = 0$. The $\log K°$ values are calculated from the standard molar Gibbs energies of reaction ($\Delta_r G°_m = -RT \ln K°$ with $RT \ln(10) = 5.708$ kJ/mol at 25 °C). They are given by the standard molar Gibbs energies of formation of the reactants: $\Delta_f G°_m(H_2O(l)) = -237.14 \pm 0.04$ kJ/mol and $\Delta_f G°_m = 0$ for $H_2(g)$, $O_2(g)$, H^+, and e^- [2]. Since reactions (2) and (3) are kinetically hindered and not really reversible in the absence of a large catalytic surface, the values of $\log P(O_2(g))$ and $\log P(H_2(g))$ calculated from the measured redox potentials are often hypothetical values and must not be set equal to real oxygen or hydrogen partial pressures in the system. Therefore it is more convenient to express the redox conditions in terms of (pe + pH) with:

$$\begin{aligned}(pe + pH) &= -0.5 \log P(H_2(g)) \\ &= 0.25 \log P(O_2(g)) + 20.77 - 0.5 \log a_w\end{aligned} \tag{4}$$

where a_w is the activity of water. Eqs. (2)–(4) define the stability field of water at 25 °C, with the upper decomposition line ($P(O_2(g)) = 1$ bar) at $pe = 20.77 - pH$ and the lower decomposition line ($P(H_2(g)) = 1$ bar) at $pe = -pH$. For "redox-neutral" aqueous solutions without additions of reducing or oxidising agents, hypothetical partial pressures of $P(H_2(g)) = 2P(O_2(g)) = 2.5 \times 10^{-28}$ bar are calculated for the irreversible reaction $H_2O(l) \rightleftharpoons H_2(g) + 0.5O_2(g)$, i.e., $\log P(O_2(g)) = -27.9$ and $\log P(H_2(g)) = -27.6$, equivalent to $(pe + pH) = 13.8$. (This definition is analogous to $pH = 7$ in an aqueous solution without acidic or basic agents and $[H^+] = [OH^-] = 10^{-7}$ M for the reaction $H_2O(l) \rightleftharpoons H^+ + OH^-$). The redox potentials of inert (HCl, NaCl, NaOH, etc.) background solutions kept under Ar atmosphere are usually close to this "redox-neutral" line ($pe = 13.8 - pH$) in the pe–pH diagram.

For many other redox couples involving H^+ ions the value of (pe + pH) is also constant, i.e., pe decreases with a slope of −1 with increasing pH. Typical examples relevant for nuclear waste repositories are reducing redox systems buffered at $(pe + pH) = 2 \pm 2$ by mixtures of solid Fe(II) and/or Fe(III) and mixed valent Fe(II–III) oxides and oxyhydroxides which result from the corrosion of metallic iron (c.f., Ref. [3] and discussion in Section 2) or steal canisters. For example a redox buffer consisting of solid $Fe(OH)_2(s)$ or FeO(s,hyd) and $Fe(OH)_3(s)$ or $FeO_{1.5}$(s,hyd) = 1/2 Fe_2O_3(s,hyd):

$$FeO(s,hyd) + 0.5H_2O(l) \leftrightharpoons FeO_{1.5}(s,hyd) + e^- + H^+ \tag{5}$$

leads to $\log K°(5) = -(pe + pH) - 0.5 \log a_w = \log {}^*K°_{IIs,0} + \log K°_{II-III} - \log {}^*K°_{IIIs,0} = -2 \pm 2$, calculated from $\log {}^*K°_{IIs,0} = 13 \pm 1$ [33,34], $\log {}^*K°_{IIIs,0} = 2 \pm 2$ (mean value covering experimental data for Fe(III) hydroxide, ferrihydrites and hematite [33–36]) and $\log K°_{II-III} = -13.0 \pm 0.1$ [34,35,37] (for

$Fe^{2+} \rightleftharpoons Fe^{3+} + e^-$). Accordingly the solution is buffered in the range of (pe + pH) = 2 ± 2. The values of (pe + pH) calculated for analogous reactions of the couples FeO(cr)/Fe_2O_3(cr), FeO(cr)/Fe_3O_4(cr) or Fe_3O_4(cr)/Fe_2O_3(cr) with $\Delta_f G^\circ_m$ values from Refs. [34,35,37] fall also into this range. Redox conditions resulting from the corrosion of uranium dioxide might be controlled by UO_2(s,hyd) and $UO_3 \cdot 2H_2O$(cr) or mixed valent oxides, e.g., by the reaction:

$$UO_2(s,hyd) + 3H_2O(l) \leftrightharpoons UO_3 \cdot 2H_2O(cr) + 2(e^- + H^+) \qquad (6)$$

with $\log K^\circ(6) = -2\,(pe + pH) - 3 \log a_w = -12.3 \pm 1.1$ (calculated from data selected in the NEA-TDB [2]) and hence with (pe + pH) = 6.2 ± 0.6. Somewhat less reducing conditions are calculated from the $\Delta_f G^\circ_m$ values for UO_2(cr) and mixed valent crystalline oxides [2], e.g., redox control by the couple UO_2(cr)/U_3O_8(cr) would lead to (pe + pH) = 8.8.

1.2. Equilibrium constants at zero ionic strength and ionic strength corrections

The standard-state equilibrium constants ($I = 0$, 25 °C) used to calculate redox, solubility and hydrolysis equilibria of plutonium in the oxidation states III, IV, V, VI are given in Table 1 (Appendix). Most of these equilibrium constants for solid compounds and aqueous complexes of plutonium and some oxidation state analogs are taken from the NEA-TDB reviews [1,2]. Some additional equilibrium constants will be discussed in the present paper. The specific ion interaction theory (SIT) recommended in the NEA-TDB reviews [1,2] is used for ionic strength corrections. The activity coefficients γ_i of aqueous species i are given by:

$$\log \gamma_i = -z_i^2 D + \sum \varepsilon_{ij} m_j \qquad (7)$$

where z_i is the charge of ion i, ε_{ij} is the interaction parameter for a pair of oppositely charged ions, m_j (mol/kg H_2O) is the molal concentration of ion j, and D is the Debye−Hückel term: $D = A\sqrt{I_m}/(1 + Ba_j\sqrt{I_m})$ with $A = 0.509\ kg^{1/2}\ mol^{-1/2}$ and $Ba_j = 1.5\ kg^{1/2}\ mol^{-1/2}$ at 25 °C. I_m is the molal ionic strength. It is to note that for redox reactions written with e^- as reactant, the value of pe always refers to the activity scale (also for conditional equilibrium constants in a given electrolyte medium), i.e., it needs not to be considered in ionic strength corrections. The interaction coefficients are taken from the NEA-TDB [2], with ε_{ij} values used for i = aquo ions and hydroxide complexes of Pu(III), Pu(V) and Pu(VI) and $j = Cl^-$ adopted from analogous Am(III), Np(V) and U(VI) species; those of Pu(IV) species are taken from Ref. [16]. The water activity a_w is also taken from Ref. [2, p. 712], but the term $\log a_w$ has only at high-ionic strength a significant effect on the calculations. For most of the studies discussed in the present paper, the ionic strength is below 0.5 M where $\log a_w$ is close to zero.

2. Solubility of plutonium under reducing conditions

If the solubility of plutonium under reducing conditions is controlled by $Pu(OH)_3$(s) (analogous to other trivalent actinides or lanthanides in the absence of carbonate, phosphate, etc.), the concentration of Pu^{3+} and its hydroxide complexes $Pu(OH)_n^{3-n}$ is given by the solubility product ($K_{sp} = [Pu^{3+}][OH^-]^3$) and the formation constants ($\beta_n = [Pu(OH)_n^{3-n}]/[Pu^{3+}][OH^-]^n$) for the reactions:

$$Pu(OH)_3(s) \leftrightharpoons Pu^{3+} + 3OH^- \qquad (8)$$

$$Pu^{3+} + nOH^- \leftrightharpoons Pu(OH)_n^{3-n} \qquad (9)$$

The dissolution and hydrolysis reactions may also be written as:

$$Pu(OH)_3(s) + 3H^+ \leftrightharpoons Pu^{3+} + 3H_2O \qquad (10)$$

$$Pu^{3+} + nH_2O \leftrightharpoons Pu(OH)_n^{3-n} + nH^+ \qquad (11)$$

The corresponding equilibrium constants at zero ionic strength, $\log {}^*K^\circ_{s,0}$ and $\log {}^*\beta^\circ_n$, respectively, are related to the $\log K^\circ_{sp}$ and $\log \beta^\circ_n$ by the ion product of water ($\log K^\circ_w = -14.00$). The concentration of the Pu^{3+} ion is related to $pH = -\log[H^+] - \log \gamma H^+$ by:

$$\log\left[Pu^{3+}\right] = \log {}^*K^\circ_{IIIs,0} - \log \gamma_{Pu^{3+}} - 3 \log a_w - 3pH \qquad (12)$$

with $\log {}^*K^\circ_{IIIs,0} = 15.8 \pm 0.8$ [3]. This value is accepted in the NEA-TDB [1,2] with an increased uncertainty (±1.5), because there is no other reliable data for $Pu(OH)_3$(s).

Depending on the given redox conditions, the equilibrium between dissolved Pu(III) and Pu(IV) can lead to Pu(IV) concentrations exceeding the solubility of Pu(IV) hydrous oxide; consequently this will lead to the precipitation of PuO_2(am,hyd) and the complete dissolution of $Pu(OH)_3$(s). Combining reactions (13)−(15) with the equilibrium constants $\log {}^*K^\circ_{s,0} = 15.8 \pm 0.8$ for $Pu(OH)_3$(s) and -2.33 ± 0.52 for PuO_2(am,hyd) and $\log K^\circ_{III-IV} = -17.69 \pm 0.04$ for the redox couple Pu^{3+}/Pu^{4+} [2]:

$$Pu(OH)_3(s) + 3H^+ \leftrightharpoons Pu^{3+} + 3H_2O \qquad (13)$$

$$Pu^{3+} \leftrightharpoons Pu^{4+} + e^- \quad (14)$$

$$Pu^{4+} + 2H_2O \leftrightharpoons PuO_2(am,hyd) + 4H^+ \quad (15)$$

yields:

$$Pu(OH)_3(s) \leftrightharpoons PuO_2(am,hyd) + H_2O + H^+ + e^- \quad (16)$$

with $\log K°(16) = \log a_w - (pe + pH) = (15.8 \pm 0.8) + (-17.69 \pm 0.04) - (-2.33 \pm 0.52) = 0.4 \pm 1.0$. This means that $Pu(OH)_3(s)$ is only stable up to redox conditions of $(pe + pH) = -0.4 \pm 1.0$ which is close to the lower border line of the stability field of water $(0 < (pe + pH) < 20.77)$. Less reducing conditions will lead to the formation of PuO_2(am,hyd).

In the case of solubility control by PuO_2(am,hyd), the equilibrium Pu(IV) concentration is given by the solubility product of PuO_2(am,hyd) ($K_{sp} = [Pu^{4+}][OH^-]^4$) and the formation constants of the Pu(IV) hydroxide complexes ($\beta_n = [Pu(OH)_n^{4-n}]/[Pu^{4+}][OH^-]^4$). In addition PuO_2(am,hyd) is in equilibrium with aqueous Pu(III) species. The dissolution equilibrium of PuO_2 (am,hyd) and the redox equilibrium between Pu^{4+} and Pu^{3+}:

$$PuO_2(am,hyd) + 4H^+ \leftrightharpoons Pu^{4+} + 2H_2O \quad (17)$$

$$Pu^{4+} + e^- \leftrightharpoons Pu^{3+} \quad (18)$$

lead to the reductive dissolution reaction:

$$PuO_2(am,hyd) + e^- + 4H^+ \leftrightharpoons Pu^{3+} + 2H_2O \quad (19)$$

with $\log {}^*K°_{IVs/III} = \log {}^*K°_{IVs,0} - \log K°_{III-IV} = (-2.33 \pm 0.52) - (-17.69 \pm 0.04) = 15.36 \pm 0.52$. The Pu^{3+} concentration in equilibrium with PuO_2(am,hyd):

$$\log\left[Pu^{3+}\right] = \log {}^*K^{\circ}_{IVs/III} - \log \gamma_{Pu^{3+}} - 2\log a_w - 3pH - \left(pe + pH\right) \quad (20)$$

has the same dependence on pH as the Pu^{3+} concentration in equilibrium with $Pu(OH)_3(s)$, (c.f. Eqs. (12) and (20)), but in addition it depends on the redox conditions (pe + pH). At (pe + pH) = −0.4 the Pu(III) concentrations in equilibrium with PuO_2(am,hyd) or $Pu(OH)_3(s)$ are the same. An increase of (pe + pH) by n log-units leads to a decrease of the Pu(III) concentration by n log-units.

With this background the results of Felmy et al. [3], the only available study providing solubility data for $Pu(OH)_3(s)$, are discussed here. The experiments were performed at 23 °C under inert-gas atmosphere in the presence of iron powder. The solid was precipitated from a Pu(III) stock solution but not further characterised and suspended either in deoxygenated water or in concentrated chloride solutions (synthetic WIPP brines). The plutonium concentrations (after 1.8 nm filtration) were measured after relatively short equilibration times of 1–24 days. Fig. 1 shows the solubility data in the dilute solutions ($I < 0.01$ M) and the measured E_h values (those in the chloride brines are similar). The redox potentials are in the range $(pe + pH) = 2 \pm 1$, typical for values in suspensions of corroding iron and clearly above the stability line of $Pu(OH)_3(s)$ at $(pe + pH) = -0.4 \pm 1.0$ (fat dashed line in Fig. 1b). Under these conditions the initial $Pu(OH)_3(s)$ precipitate is metastable and should convert slowly into PuO_2(am,hyd). Fig. 1a shows the equilibrium Pu(III) concentration calculated for $Pu(OH)_3(s)$ as solid phase (dashed line) and also the equilibrium Pu(IV) and Pu(III) concentrations calculated for $(pe + pH) = 2$ with PuO_2(am,hyd) as solid phase (solid lines). The experimental Pu(III) concentrations of Felmy et al. [3] are between the dashed and solid line. The short equilibration times of 1–24 days are not sufficient for a complete solid phase transformation and the solubility constant derived from the data at pH 6–7, $\log {}^*K°_{s,0}$ $(Pu(OH)_3(s)) = 15.8 \pm 0.8$ [3], is most probably correct. However, as indicated by the arrow in Fig. 1a, a number of data points show a tendency to the lower curve expected after transformation into PuO_2(am,hyd).

Contrary to the solubility constant of $Pu(OH)_3(s)$, the equilibrium constant for the reductive dissolution of PuO_2(am,hyd) (Eqs. (19) and (20)) is well ascertained. A few years ago, Fujiwara et al. [4,5] and Rai et al. [6] investigated this reaction directly by measuring the Pu^{3+} concentration in solubility studies with PuO_2 (am,hyd) under various reducing conditions: (a) in 0.5, 1.0 and 2.0 M $NaClO_4$ + 0.001 M $Na_2S_2O_4$ (pH 3–9) with $(pe + pH) = 10 \pm 1$ [4,5], (b) in 0.005 M $CaCl_2$ or 0.01 M $NaClO_4$ + 5.2×10^{-4} M hydroquinone (pH 3–9) with $(pe + pH) = 4.0 \pm 0.5$ [6], and (c) in 0.01 M NaCl + 0.001 M $FeCl_2$ with pe = 11 at pH 2 decreasing to pe = −7 at pH 11 [6]. All results can be consistently described with $\log {}^*K°_{IVs/III} = 15.5 \pm 0.6$, close to the value of $\log {}^*K°_{IVs/III} = 15.4 \pm 0.5$ based on the NEA-TDB selections [2]. The experimental solubilities and redox potentials in the $Na_2S_2O_4$ and hydroquinone solutions and the corresponding calculations for (pe + pH) = 10 and 4, respectively, are compared in Fig. 2. As predicted according to Eq. (20), the increase of (pe + pH) from 4 and 10 leads to a decrease of the Pu(III) concentration by about six orders of magnitude.

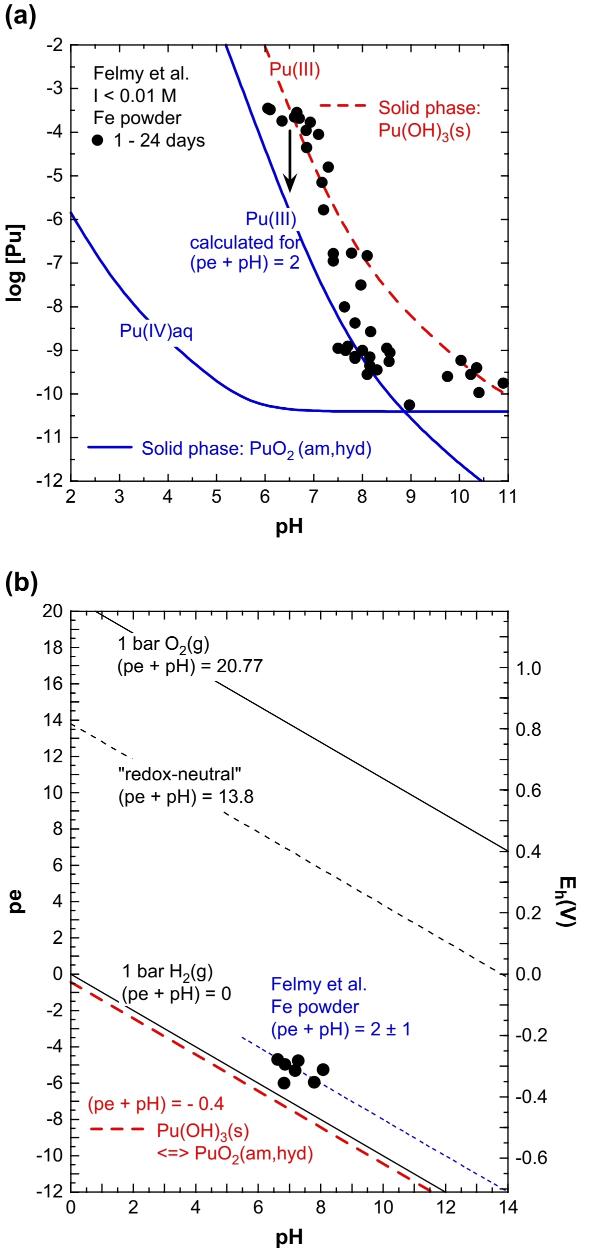

Fig. 1. Solubility study of Felmy et al. [3] with $Pu(OH)_3(s)$ at 23 °C and $I < 0.01$ M. a) Experimental Pu concentration measured after 1.8-nm filtration and calculated solubility; the dashed line is calculated for solubility control by $Pu(OH)_3(s)$, the solid lines for solubility control by PuO_2(am,hyd) at $(pe + pH) = 2 \pm 1$. b) Redox potentials in the suspensions containing Fe powder [3]. The fat dashed line at $(pe + pH) = -0.4$ represents the stability line of $Pu(OH)_3(s)$ with regard to its transformation into PuO_2(am,hyd). The solid lines at $(pe + pH) = 0$ and 20.77 define the stability field of water, the dashed line at $(pe + pH) = 13.8$ is calculated for redox-neutral aqueous solutions.

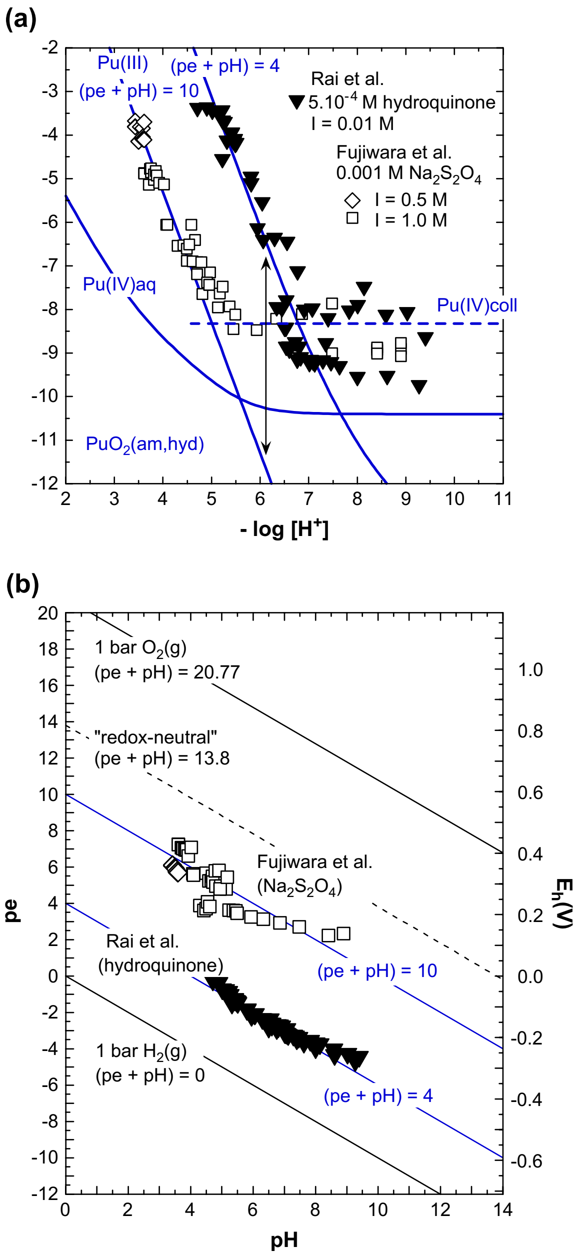

Fig. 2. The effect of (pe + pH) on the solubility of Pu(IV) hydrous oxide under reducing conditions. (a) Solubility data of Fujiwara et al. [4,5] at $(pe + pH) = 10 \pm 1$ (in 0.5 and 1.0 M $NaClO_4$ + 0.001 M $Na_2S_2O_4$) and Rai et al. [6] at $(pe + pH) = 4.0 \pm 0.5$ (in 5.2×10^{-4} M hydroquinone solutions at $I = 0.01$ M) and corresponding calculations for these redox conditions, and (b) experimental redox potentials.

In a recent study, Nilsson [7] tried to determine the solubility of $Pu(OH)_3(s)$ at ambient temperature in 0.1 M NaCl under a pressure of 50 bar $H_2(g)$ in an autoclave containing a piece of Pt wire. Under these extremely reducing conditions, corresponding to

$(pe + pH) = -0.85$, the X-ray amorphous $Pu(OH)_3$ (am) precipitated from a Pu(III) stock solution was expected to remain stable. However, the Pu concentrations measured after centrifugation (analyzed for $[Pu]_{tot} = [Pu(III)] + [Pu(IV)]$ after 150, 320 and 480 days and for [Pu(IV)] after 480 days) were much lower than expected for $Pu(OH)_3(s)$ (Fig. 3a) and the redox potentials measured after 480 days were much higher than expected for $P(H_2(g)) = 50$ bar (Fig. 3b). Obviously, pe was not controlled by the reaction $0.5H_2(g) \rightleftharpoons H^+ + e^-$. From pH changes in their samples in the near neutral pH range and the changed colour of the solid Nilsson [7] concluded that the initially blue $Pu(OH)_3$(am) transformed into green $PuO_{2\pm x}$(am,hyd), but gave no quantitative data interpretation. Fig. 3 shows that the results can be well explained by Eq. (20) for the reductive dissolution of PuO_2(am,hyd). The measured solubility data are reasonably consistent with the Pu(III) concentrations calculated for the experimental values of $(pe + pH) = 8.5 \pm 2$ and an additional contribution from Pu(IV) colloids. It is difficult to find an explanation for the measured redox potentials, but accepting the measured pe values it is possible to calculate the solubility and aqueous speciation of plutonium.

The concentration line for polymeric Pu(IV) oxyhydroxide species (1.5–2 nm colloids) included in Figs. 2a and 3a ($\log[Pu(IV)]_{coll} = -8.3 \pm 1.0$) was determined in our recent solubility study with Pu(IV) hydrous oxide [10] from the difference of the Pu concentrations measured after 10 kDa ultrafiltration and in unfiltered aliquots taken carefully from the clear supernatant. Similar as in a previous study where we determined the pH-independent concentration of colloidal or polymeric Th(IV) at pH 6.5–13.5 ($\log[Th(IV)]_{coll} = -6.3 \pm 0.5$) [38] the concentration $[Pu(IV)]_{coll}$ at pH 8–13 was reasonably reproducible and at a constant level. For both Th(IV) and Pu(IV) the level of $[An(IV)]_{coll}$ is about two orders of magnitude higher than the An(IV) concentration after 1.5 nm ultrafiltration or ultracentrifugation. This is consistent with a model on Pu(IV) polymer formation proposed by Fujiwara et al. [4] who supposed that the concentration of $\log[Pu(IV)] = -9$ measured in 1 M $NaClO_4$ (pH 7–9) after 2 nm filtration is primarily caused by small Pu(IV) polymers; $[Pu(IV)]_{tot}$ is expected to include further contributions from eigencolloids larger than 2 nm. The equilibrium concentration of mononuclear Pu(IV) species was calculated to be $\log[Pu(OH)_4(aq)] = -10.3 \pm 0.2$ [4] which is close to the value of -10.4 ± 0.5 determined by Rai et al. [9] and used in the present calculations.

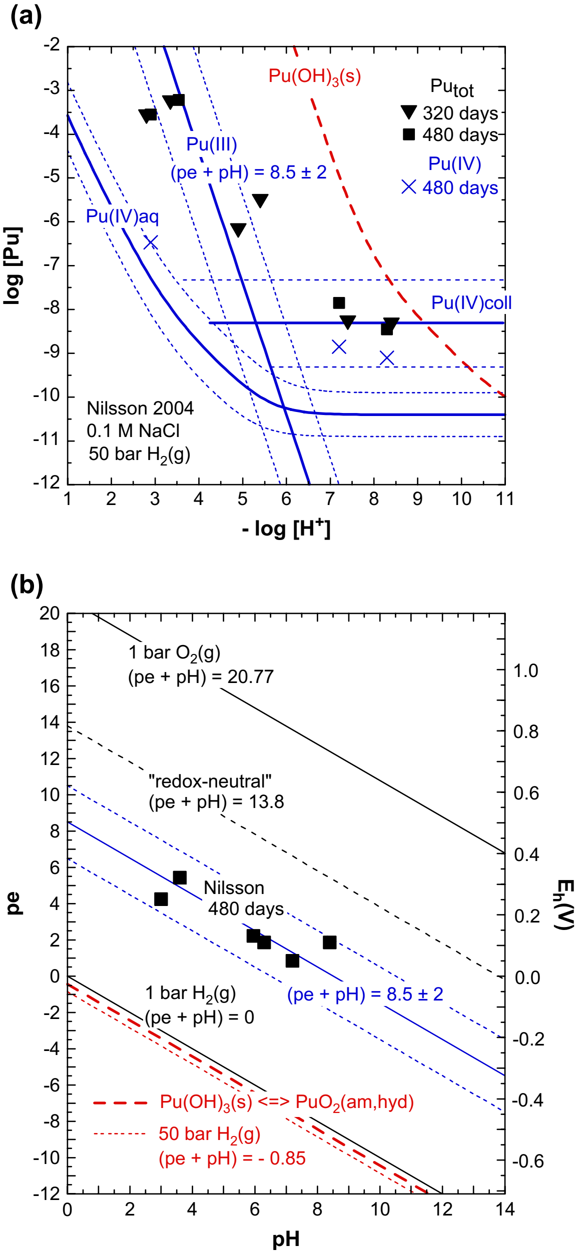

Fig. 3. Solubility of Pu(IV) hydrous oxide (a) and redox potentials (b) determined by Nilsson [7] after 320 and 480 days in 0.1 M NaCl solutions under a pressure of 50 bar $H_2(g)$ after the transformation of the initial Pu(III) hydroxide precipitate. The calculated Pu(III) concentration refers to the experimental redox conditions of $(pe + pH) = 8.5 \pm 2$. The dotted line at $(pe + pH) = -0.85$, calculated for $P(H_2(g)) = 50$ bar is in the stability field of $Pu(OH)_3(s)$, slightly below the fat dashed stability line at $(pe + pH) = -0.4$. The expected solubility curve for the initial $Pu(OH)_3(s)$ precipitate is shown for comparison also as fat dashed line.

3. Solubility of plutonium in redox-inert solutions under argon atmosphere

In a recent study at our laboratory [10], Pu(IV) hydrous oxide was precipitated from an electrochemically prepared Pu(IV) stock solution containing a contamination of 0.5% Pu(VI) and the solubility was determined at $I = 0.1$ M (NaCl) and 22 ± 2 °C. The work was carried out in an Ar glove box (<10 ppm O_2) using long-lived Pu-242 ($t_{1/2} = 3.8 \times 10^5$ a) to minimize radiolysis effects. The batch samples at pH 2.5–13 (ca. 20 mg Pu-242 in 50 mL solution) were analyzed after equilibration periods between 6 and 104 days: E_h and pH were measured directly in the samples, the Pu concentrations (total Pu and the different Pu oxidation states) were measured after 10 kDa ultrafiltration (pore size ca. 1.5 nm). The constant values obtained after 34 days indicated that equilibrium was attained. The results are shown in Fig. 4.

The samples at pH 2.5 and 3.0 contained about equimolar concentrations of Pu(III) and Pu(V), whereas the samples at pH > 3 showed only the absorption bands of the PuO_2^+ ion. Aqueous Pu(IV) species could not be detected by absorption spectroscopy and redox speciation by solvent extraction showed that the Pu(IV) concentrations are very low compared to the total dissolved Pu, almost exclusively non-extractable Pu(V). The Pu(IV) concentrations at pH < 4 are in the expected range (c.f., Fig. 4a). The total Pu concentrations at pH 8–13 were in the range of 10^{-9} to 10^{-10} M, close to values determined by Rai et al. [9] in dilute KOH solutions. The redox potentials measured in samples containing solid and colloidal Pu(IV) have a relatively large experimental uncertainty of ±50 mV [10], but the pe values at pH 4–13 clearly show a linear decrease with pH (slope −1, Fig. 4b). The values of (pe + pH) decreased from 14.9 ± 0.8 after 6 days to 13.5 ± 0.8 after 34 days and to constant values of 11.7 ± 0.8 after 54–104 days.

The Pu(III) concentrations at pH 2.5–3.3 and pe = 10–12 can be described by the reductive dissolution of PuO_2(am,hyd). The experimental Pu^{3+} concentrations and the steep decrease of $\log[Pu^{3+}]$ at pH > 3 are consistent with Eq. (20) and the calculations for (pe + pH) = 14 ± 1 (c.f., Fig. 4a). However, the experimental Pu(V) concentrations, up to pH 5 at a constant level of $\log[Pu(V)] = -5$ and at pH 5–10 decreasing with a slope of −1, are not consistent with the oxidative dissolution of Pu(IV) hydrous oxide:

$$PuO_2(am,hyd) \leftrightharpoons PuO_2^+ + e^- \tag{21}$$

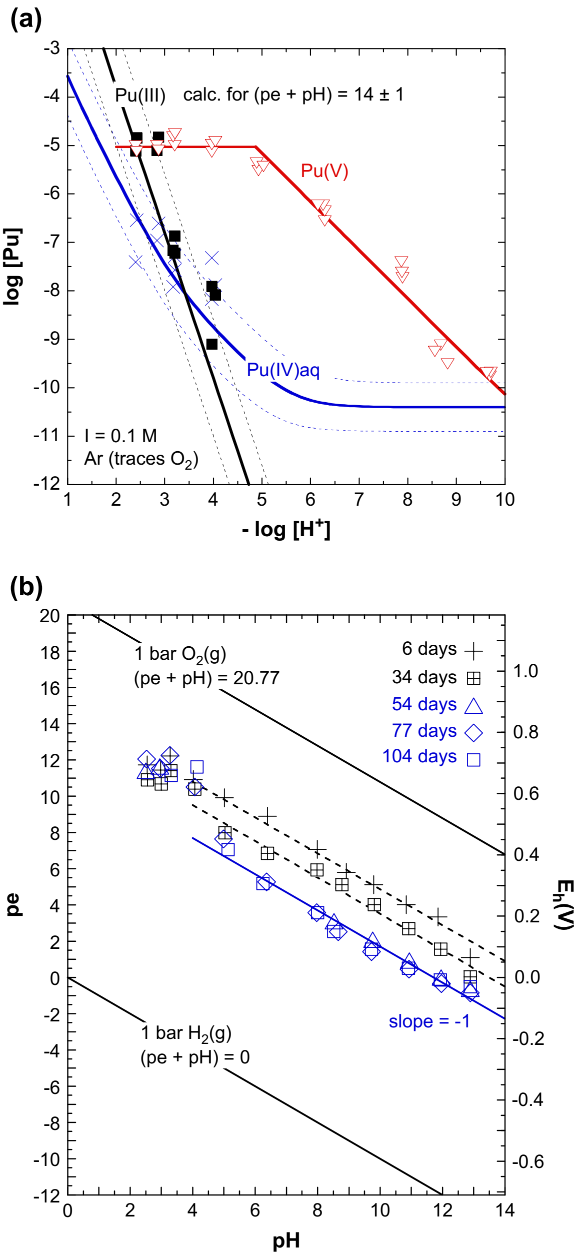

Fig. 4. Experimental results from our solubility study with Pu(IV) hydrous oxide under Ar (<10 ppm O_2) at 22 °C in 0.1 M NaCl [10]. (a) Equilibrium concentrations after 1.5 nm filtration: Pu(IV) (crosses), Pu(III) (filled squares) and Pu(V) (triangles), and (b) redox potentials measured after 6–104 days.

with:

$$\log[PuO_2^+] = \log K^\circ_{IVs/V} - \log \gamma_{PuO_2^+} + pe \tag{22}$$

The values calculated for the equilibrium constant $\log K^\circ_{IVs/V}$ from the experimental PuO_2^+ concentrations and pe values deviate up to seven log-units from the value of $\log K^{\circ}_{\mathrm{IVs/V}} = -19.8 \pm 0.9$ based on the data selected in the NEA-TDB [2] for PuO_2(am,hyd) and PuO_2^+. Similar discrepancies observed in solubility studies under air [13–15] will be discussed below.

Another solubility study under Ar atmosphere was reported by Lierse and Kim [8] who titrated PuO_2(s,hyd) suspensions in 1 M $NaClO_4$ from pH 12 to pH 1. They obtained a similar solubility curve with $\log[\mathrm{Pu}]_{\mathrm{tot}}$ decreasing with a slope of -1 from pH 3 to 10, but they did not report oxidation state analysis and redox potential measurements.

4. Solubility of plutonium in the presence of oxygen

4.1. The effect of oxygen on the total Pu concentration in solution

Fig. 5 shows the total Pu and Pu(IV) concentrations measured by Rai et al. [13–15] at pH 1–8 after up to 106 days and a few data from other authors at pH < 2 [11,12] in solubility studies with PuO_2(s,hyd) at $I = 0.01$–1 M and 20–25 °C. In these studies the solutions were exposed to air and then kept in closed vials. The total Pu concentration at pH < 1.5 ($\log[\mathrm{Pu}]_{\mathrm{tot}}$, open points in Fig. 5) is slightly increased compared to log $[\mathrm{Pu(IV)}]_{\mathrm{aq}}$ (crosses). It passes through a plateau at pH 1–3 and decreases with a slope of -1 at pH > 3. Aqueous speciation by spectroscopy and solvent extraction showed that the dissolved Pu at pH 1–3 consists mainly of PuO_2^{2+} and PuO_2^+ while PuO_2^+ predominates at pH 3–9 [13–15]. The concentration of oxidised Pu ($[PuO_2^{2+}] + [PuO_2^+]$) at pH < 3 corresponds to the available oxygen in these closed systems, given by the sum of $[O_2]_{aq} = 2.5 \times 10^{-4}$ M at $P(O_2(g)) = 0.2$ bar and O_2(g) in the gas phase above the solution [31].

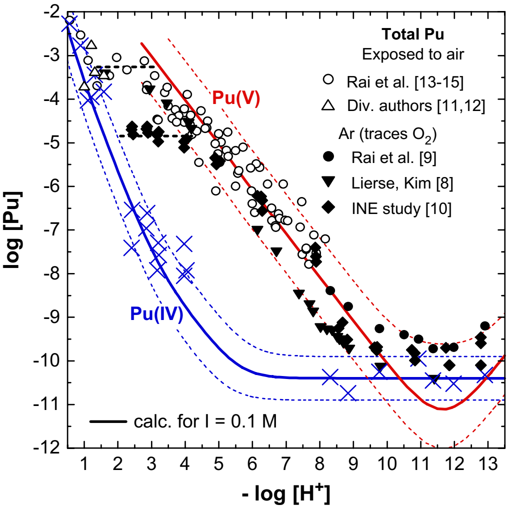

Fig. 5. Solubility of Pu(IV) hydrous oxide at 20–25 °C and $I = 0.01$–1.0 M. Experimental data measured after ultrafiltration; open symbols: total Pu concentration in studies under air [11–15], filled symbols: total Pu concentration in studies under Ar atmosphere [8–10], and crosses: Pu(IV) concentrations [8–14].

The Pu concentrations measured by Lierse and Kim [8], Rai et al. [9] and in our previous study [10] under Ar atmosphere containing only traces of O_2(g) are shown for comparison as filled points in Fig. 5. The Pu(V) concentrations at pH > 4 are, within the uncertainties, the same as those determined by Rai et al. [13–15] in samples kept under air. However, the constant level of $[\mathrm{Pu(V)}] = 10^{-5}$ M at pH < 5 in our study under Ar is considerably lower than the corresponding values under air. It corresponds to the 0.5% Pu(VI) in the initial Pu(IV) stock solution, if this fraction of oxidised Pu is co-precipitated with the Pu(IV) hydrous oxide and re-dissolved in the solubility experiments. The data of Lierse and Kim [8] who titrated PuO_2(am,hyd) suspensions in 1 M $NaClO_4$ under a continuous Ar stream from pH 12 to pH 1 may be explained if we assume that the Ar stream included a contamination of a few ppm O_2 and that the total amount of oxidised Pu species accumulated during the titration experiment (2–3 months) [31].

4.2. Equilibrium Pu(V) concentrations and redox potentials: evidence for the formation of PuO_{2+x}(s,hyd)

The Pu concentrations measured in the solubility studies under air or under Ar atmosphere cannot be explained without the knowledge of the redox potentials. It is helpful to divide the experimental data into different pH regions (Figs. 6a and b). Rai [14] has shown that the solubility of PuO_2(am,hyd) under air at pH 1–3 (region A) is dominated by the oxidative dissolution reaction (23) and the redox equilibrium (24) between PuO_2^+ and PuO_2^{2+}:

$$PuO_2(s,hyd) \leftrightharpoons PuO_2^+ + e^- \tag{23}$$

$$PuO_2^+ \leftrightharpoons PuO_2^{2+} + e^- \tag{24}$$

The redox potentials in region A, pe = 16.0 ± 0.3 [14], are consistent with the spectroscopically determined PuO_2^+ and PuO_2^{2+} concentrations and $\log K^{\circ}_{\mathrm{V/VI}} = -15.82 \pm 0.09$ [1,2]. The equilibrium constant derived by Rai [14] for the oxidative dissolution of PuO_2(am,hyd) from the experimental pe values and Pu(V) concentrations, $\log K^{\circ}_{\mathrm{IVs/V}} = -19.45 \pm 0.23$ [14], is also in

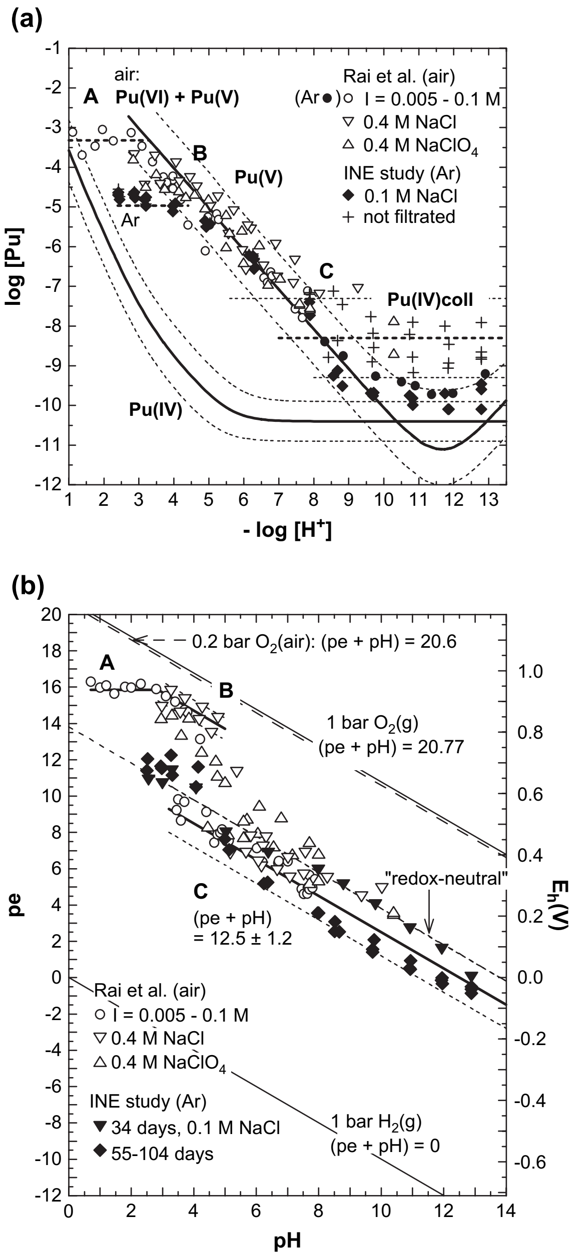

Fig. 6. (a) Solubility of PuO_{2+x}(s,hyd) at 20–25 °C; Pu concentration measured after ultrafiltration and without removal of Pu(IV) colloids/polymers (crosses); comparison of data measured under air (open symbols) [13–15] and under Ar (filled symbols) [9,10]. (b) Simultaneously measured redox potentials (analogous symbols).

agreement with the value of $\log K^\circ_{IVs/V} = -19.8 \pm 0.9$ calculated with the standard molar Gibbs energies selected in the NEA-TDB [2] for PuO_2(am,hyd), Pu^{4+} and PuO_2^+ from different, independent data. In our study under Ar [10] the redox potentials at pH 2.5–3.3 are much lower. Hence Pu(VI) is not observed, but only Pu(V) (and Pu(III) as expected according to Eq. (20)). However, the values of pe = 10–12 and $\log[PuO_2^+] = -5$ are strongly inconsistent with $\log K^\circ_{IVs/V} = -19.8 \pm 0.9$.

At pH 3–4 the pe values in the studies under air [13–15] drop drastically to about 7 log-units lower values (Fig. 6b) while the solubility ($\log[Pu]_{tot} \approx \log[PuO_2^+]$) decreases continuously with a slope of −1 (Fig. 6a). Accordingly, the solubility constant $\log K^\circ_{IVs/V}$ derived from the experimental values of pe and $[PuO_2^+]$ in region C would differ by seven orders of magnitude from the value derived in regions A and B [13,14]. As there was no evident explanation for this discrepancy, it was ascribed to possible experimental problems in the E_h measurements [14,15]. However, our results under Ar ($P(O_2(g)) < 10^{-5}$ bar) show that the redox potentials in region C are reproducible within a certain range. Moreover they coincide with those measured by Rai et al. [13–15] under air ($P(O_2(g)) = 0.2$ bar). The redox potentials in region C and also the slopes of −1 in regions B and C (pe + pH = constant) can neither be explained by equilibria between aqueous Pu species nor by the oxygen partial pressures [10,15]. The experimental results in regions B and C are not consistent with the equilibria:

$$PuO_2(s,hyd) \leftrightharpoons PuO_2^+ + e^- \tag{25}$$

or

$$PuO_2(s,hyd) + 1/4\,O_2(g) + H^+ \leftrightharpoons PuO_2^+ + 1/2\,H_2O \tag{26}$$

The Pu(V) concentrations and pe values at pH > 3, which are more or less the same in the studies under air [13–15] and under Ar [10] can be explained with PuO_{2+x}(s,hyd), mixed valent hydrous oxide $(Pu^V)_{2x}(Pu^{IV})_{1-2x}O_{2+x}$(s,hyd) or $(PuO_{2.5})_{2x}(PuO_2)_{1-2x}$ (s,hyd), as solubility controlling solid phase in equilibrium with both Pu(V) and Pu(IV) in solution. It can be formed by the oxidation of PuO_2(s,hyd) with the oxygen present in the system:

$$PuO_2(s,hyd) + x/2\,O_2 \rightarrow PuO_{2+x}(s,hyd) \tag{27}$$

or by co-precipitation of Pu(V) during the preparation of Pu(IV) hydrous oxide [10]. At pH < 3 (region A), the Pu(V) fractions in the PuO_{2+x}(s,hyd) solids are below the Pu(V) saturation line (slope −1) and hence completely soluble. This allows to estimate the Pu(V) fraction in the solids used in the solubility studies from the amount of oxidised Pu dissolved at the plateau at low pH ($[Pu(V+VI)]_{max}$) and the total Pu inventory

$[Pu]_{inv}$ in the samples (initially present as solid precipitates). This is 10–12% in the samples of Rai et al. [14,15] under air ($x = 0.5$ $[Pu(V+VI)]_{max}/[Pu]_{inv} = 0.05–0.06$) and about 0.5% ($x = 0.003$) in our study under Ar [10]. Haschke et al. [25–28] observed a maximum value of $x = 0.27$ but they supposed that $PuO_{2+x}(s)$ should be stable up to $x = 0.5$ ($PuO_{2.5}(s) = 1/2\,Pu_2O_5(s)$) [27,28].

The mixed valent hydrous oxide $PuO_{2+x}(s,hyd) = (Pu^{V})_{2x}(Pu^{IV})_{1-2x}O_{2+x}(s,hyd)$ 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:

$$PuO_{2+x}(s,hyd) + (2-3x)H_2O(l) \leftrightharpoons 2xPuO_2^+ + (1-2x)Pu^{4+} + (4-6x)OH^- \quad (28)$$

with:

$$\log K_{sp}\left(PuO_{2+x}(s,hyd)\right) = 2x\log\left[PuO_2^+\right] + (1-2x)\log\left[Pu^{4+}\right] + (4-6x)\log\left[OH^-\right] = 2x\log K_{sp}\left(PuO_{2.5}\text{ in }PuO_{2+x}(s,hyd)\right) + (1-2x)\log K_{sp}\left(PuO_2\text{ in }PuO_{2+x}(s,hyd)\right) \quad (29)$$

The solubility products for the formal fractions of $PuO_{2.5}(s,hyd)$ and $PuO_2(s,hyd)$ in $PuO_{2+x}(s,hyd)$ can be calculated separately, because the dissolved PuO_2^+ and Pu^{4+} ions and their hydroxide complexes do not undergo reversible redox reactions:

$$K_{sp}(PuO_{2.5}\text{in}PuO_{2+x}(s,hyd)) = [PuO_2^+][OH^-] \quad (30)$$

$$K_{sp}(PuO_2\text{in}PuO_{2+x}(s,hyd)) = [Pu^{4+}][OH^-]^4 \quad (31)$$

The experimental Pu(IV) concentrations were previously used to calculate the solubility product of $PuO_2(am,hyd)$ [2,16,22] and the evaluation of the PuO_2^+ concentrations at pH 3–9 is given in detail in our recent paper [10]. The solubility product of $PuO_{2.5}(s,hyd)$ as a fraction of $PuO_{2+x}(s,hyd)$ was calculated from the different sets of data determined by Rai et al. [13–15] under air in dilute solutions of low ionic strength and in 0.4 and 4.0 M $NaClO_4$ and NaCl and from the data determined under Ar atmosphere by Lierse and Kim [8] in 1.0 M $NaClO_4$ and in our recent work in 0.1 M NaCl. All data sets yield consistent equilibrium constants at $I = 0$ with a mean value ($\pm 2\sigma$) of $\log K^\circ_{sp}(PuO_{2.5}\text{ in }PuO_{2+x}(s,hyd)) = -14.0 \pm 0.8$ or $\log{}^*K^\circ_{s,0}(PuO_{2.5}\text{ in }PuO_{2+x}(s,hyd)) = 0.0 \pm 0.8$ [10] for the reactions:

$$PuO_{2.5}(s,hyd) + 1/2\,H_2O \leftrightharpoons PuO_2^+ + OH^- \quad (32)$$

or

$$PuO_{2.5}(s,hyd) + H^+ \leftrightharpoons PuO_2^+ + 1/2\,H_2O \quad (33)$$

The solubility product of $PuO_{2.5}(s,hyd)$ as a formal fraction of $PuO_{2+x}(s,hyd)$ is five orders of magnitude lower than that of Pu(V) hydroxide ($\log K^\circ_{sp}(PuO_2OH(am,hyd)) = -9.0 \pm 0.5$ [1,2]). It compares well with the values for Np(V) pentoxide: $\log K^\circ_{sp}(NpO_{2.5}(cr)) = -12.2 \pm 0.8$ (calculated from thermochemical data in Refs. [1,2]) and $\log K^\circ_{sp}(NpO_{2.5}(s,hyd)) = -11.4 \pm 0.4$ (solubility study of Efurd et al. [40]) and appears to be in a reasonable order of magnitude, in particular as the solubility product of $PuO_2(am,hyd)$ is also about 2 log-units lower than that of $NpO_2(am,hyd)$ ($\log K_{sp} = \log([An^{4+}][OH^-]^4)$; $\log K^\circ_{sp} = -58.3 \pm 0.5$ for Pu(IV) and -56.7 ± 0.5 for Np(IV) [2]).

Solubility control by $PuO_{2+x}(s,hyd)$ explains the redox potentials at pH > 3 under air, in particular the slope of −1 at pH 3–5 (region B in Fig. 6b) that could not be explained by Rai [14]. At low pH (region A) the Pu(V) fractions in the $PuO_{2+x}(s,hyd)$ solids are below the Pu(V) saturation concentration and completely soluble, but at pH > 3 they exceed the solubility of $PuO_{2+x}(s,hyd)$. Combining Eqs. (34) and (35) and the corresponding equilibrium constants ($\log K^\circ_{IVs/V} = -19.8 \pm 0.9$ [2], $\log{}^*K^\circ_{s,0}(PuO_{2.5}\text{ in }PuO_{2+x}(s,hyd)) = 0.0 \pm 0.8$ [10]):

$$PuO_2(s,hyd) \leftrightharpoons PuO_2^+ + e^- \quad (34)$$

$$PuO_2^+ + 1/2\,H_2O \leftrightharpoons PuO_{2.5}(s,hyd) + H^+ \quad (35)$$

yields

$$PuO_2(s,hyd) + 1/2\,H_2O \leftrightharpoons PuO_{2.5}(s,hyd) + e^- + H^+ \quad (36)$$

with $\log K^\circ(36) = -(pe + pH) - 0.5\ \log a_w = (-19.8 \pm 0.9) - (0.0 \pm 0.8) = -19.8 \pm 1.2$. This means that the Pu(V) concentration is controlled by $PuO_{2+x}(s)$ and the value of (pe + pH) is buffered by the $PuO_2(s,hyd)$ and $PuO_{2.5}(s,hyd)$ fractions in $PuO_{2+x}(s,hyd)$, similar as in the case of Fe(II–III) and U(IV–VI) oxide/oxyhydroxide redox buffers (c.f., Section 1.1). This explains the slope of −1 in region B (Fig. 6b) and is, within the range of uncertainty, consistent with the experimental values of $(pe + pH) = 18.7 \pm 0.6$ [14,15], in particular if one takes into account that other redox couples (e.g., PuO_2^+/PuO_2^{2+}) may also contribute to pe.

At pH > 4, the pe values drop to drastically lower values and decrease up to pH 13 with a slope of −1 (c.f., region C in Fig. 6b where the line of (pe + pH) = 12.5 ± 1.2 covers the experimental data). These redox potentials can only be explained if the small colloidal or polymeric Pu(IV) oxyhydroxide species prevailing in neutral to alkaline solution (c.f., Fig. 6a and discussion in Section 2), are taken into consideration. On the one hand they have properties of small solid particles designated here as PuO_2(coll,hyd), on the other hand they must be considered as large polynuclear aqueous species, in equilibrium with both small aqueous species and solid PuO_2(s,hyd):

$$PuO_2(s,hyd) \leftrightharpoons PuO_2(coll,hyd,aq) \quad (37)$$

with $\log K^\circ_{IVcoll} = \log[Pu(IV)]_{coll} = -8.3 \pm 1.0$ [10]. Using $\Delta_f G^\circ_m(PuO_2(am,hyd)) = -965.5 \pm 4.0$ kJ/mol [2] an average value of $\Delta_f G^\circ_m(PuO_2(coll,hyd)) = -918.1 \pm 7.0$ kJ/mol is calculated for these Pu(IV) colloids or polymers. Their size (1.5–2 nm) is estimated in Ref. [10] by applying Schindler's relation between the standard molar Gibbs energy of formation and particle size [39]. Similar as solid PuO_2(s,hyd), the Pu(IV) colloids or polymers can also be oxidised by oxygen. However, because of their significantly greater standard molar Gibbs energy of formation the Pu(V) fraction is highly soluble:

$$PuO_2(coll,hyd) + x/2\,O_2 + 2xH^+ \rightarrow (PuO_{2.5})_{2x}(PuO_2)_{1-2x}(coll,hyd) + 2xH^+$$
$$\rightarrow 2xPuO_2^+ + xH_2O + (1-2x)PuO_2(coll,hyd) \quad (38)$$

so that the remaining colloids consist exclusively of Pu(IV). The equilibrium PuO_2^+ concentration is limited to the solubility of $PuO_{2.5}$(s,hyd) in PuO_{2+x}(s,hyd):

$$PuO_2(coll,hyd) \leftrightharpoons PuO_2^+ + e^- \quad (39)$$

$$PuO_2^+ + 1/2\,H_2O \leftrightharpoons PuO_{2.5}(s,hyd) + H^+ \quad (40)$$

The equilibrium constant for reaction (39), $\log K^\circ_{IVcoll/V} = -11.5 \pm 1.3$, can be calculated from $\Delta_f G^\circ_m(PuO_2(coll,hyd)) = -918.1 \pm 7.0$ kJ/mol and $\Delta_f G^\circ_m(PuO_2^+) = -852.65 \pm 2.87$ kJ/mol [1]. Combining Eqs. (39) and (40) yields:

$$PuO_2(coll,hyd) + 1/2\,H_2O \leftrightharpoons PuO_{2.5}(s,hyd) + e^- + H^+ \quad (41)$$

with $\log K^\circ(41) = -(pe + pH) - 0.5 \log a_w = (-11.5 \pm 1.3) - (0.0 \pm 0.8) = -11.5 \pm 1.5$. This is consistent with the slope of −1 (Fig. 6b) in region C. The calculated value of (pe + pH) = 11.5 ± 1.5 agrees, within the uncertainties, with the experimental values measured under Ar after 54–104 days: (pe + pH) = 11.7 ± 0.8 [10] and under air after 90 and 106 days: (pe + pH) = 12.8 ± 1.1 [13,15]. The redox potentials in region C can be described by equilibria between PuO_{2+x}(s,hyd), PuO_2^+ and Pu(IV) colloids which are in Eqs. (39)–(41) considered as small solid particles. This means that the large difference between the pe values in regions B and C (Fig. 6b) can be explained as a particle size effect, i.e., by the formation of small Pu(IV) colloids (1.5–2 nm) with an increased molar surface and standard Gibbs energy compared to PuO_2(am,hyd) precipitates which consist of agglomerates of 3–5 nm crystallites [10,17]. Colloidal Pu(IV) oxyhydroxide particles formed at low pH are larger than 5 nm. They can be detected by laser-induced breakdown detection LIBD [22,42] and have thermodynamic properties of PuO_2(am,hyd), as indicated by the solubility products determined for these particles [22,24,42].

5. The role of Pu(IV) colloids/polymers in the Pu(IV)–Pu(V) redox chemistry

Since tetravalent actinides have a high tendency towards polynucleation and colloid formation the solubility is usually measured after ultrafiltration or ultracentrifugation to remove these species, whereas redox potentials are usually measured directly in the samples [3–7,10,13–15]. As discussed above, the colloidal or polymeric Pu(IV) oxyhydroxide species present in neutral and alkaline solutions have a significant impact on the redox potentials in systems without oxidising or reducing chemicals. They are not "notorious troublemakers" in plutonium chemistry as recently stated by Nilsson [7] but part of the thermodynamic system as illustrated in Fig. 7.

Further experiments reported in Ref. [10] support the conclusion that the redox potentials in near neutral Pu(IV)–Pu(V) solutions correspond to a reversible equilibrium between PuO_2(coll,hyd) particles and PuO_2^+ ions:

$$PuO_2(coll,hyd) \leftrightharpoons PuO_2^+ + e^- \quad (42)$$

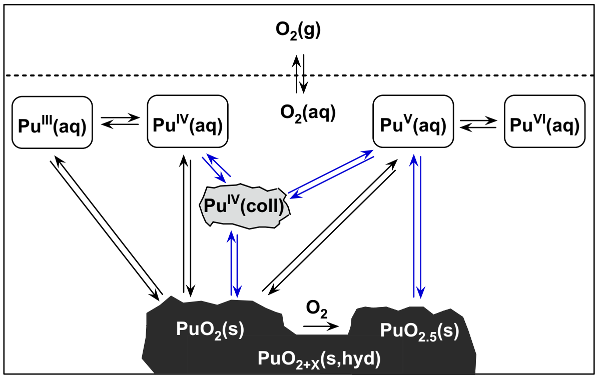

Fig. 7. Solid–liquid and redox equilibria of plutonium under reducing conditions, in redox-neutral solutions and in the presence of oxygen.

with $\log K^\circ_{\mathrm{IVcoll/V}} = \log[\mathrm{PuO_2^+}] + \log \gamma_{\mathrm{PuO_2^+}} - \mathrm{pe} = -11.5 \pm 1.3$ (c.f., Section 4.2). In these experiments [10] an electrochemically prepared Pu(VI) stock solution was diluted to 2.1×10^{-4} M in 0.1 M NaCl with pH values adjusted to 3.3, 5.5 and 6.7 by redox-inert organic buffer solutions. The solutions were kept in closed cuvettes under Ar atmosphere and studied as a function of time. In the solution at pH 3.3 Pu(VI) was partly reduced to Pu(V), accompanied by a corresponding decrease of pe from 16.8 to 15.8. The measured redox potentials and spectroscopically determined concentrations of $\mathrm{PuO_2^{2+}}$ and $\mathrm{PuO_2^+}$ were in accord with the equilibrium constant $\log K_{\mathrm{V/VI}} = -15.5 \pm 0.1$ in 0.1 M NaCl [2]. At pH 5.5 and 6.7 the initial Pu(VI) was "completely" reduced to Pu(V) and (at pH 6.7) further to colloidal Pu(IV) and a visible greenish precipitate. In particular the reduction of the solution at pH 6.7 and $[\mathrm{Pu}]_{\mathrm{tot}} = 2.1 \times 10^{-4}$ M would yield Pu(V) and colloidal Pu(IV) concentrations considerably exceeding the equilibrium values in the solubility studies with $\mathrm{PuO_{2+\mathit{x}}}$(s,hyd); consequently this led to the observed precipitation and the decrease of the Pu concentration to about 10^{-5} M. Within a few days the redox potentials decreased drastically to values in the range of those in the solubility studies shown in Fig. 6b. The Pu(V) concentrations and pe values measured after 101 days (pH 5.5: $\log[\mathrm{PuO_2^+}] = -3.70$, $\mathrm{pe} = 8.4$; pH 6.7: $\log[\mathrm{PuO_2^+}] = -5.5$, $\mathrm{pe} = 6.5$) are consistent with $\log K_{\mathrm{IVcoll/V}} = \log[\mathrm{PuO_2^+}] - \mathrm{pe} = -11.4 \pm 1.3$ in 0.1 M NaCl. Obviously they refer to an equilibrium state between $\mathrm{PuO_2^+}$ and colloidal Pu(IV) particles that is reached as well from undersaturation in solubility studies with $\mathrm{PuO_{2+\mathit{x}}}$(s,hyd) and from oversaturation with initially Pu(VI) solutions.

Another recent study indicates that colloidal or polymeric Pu(IV) species play also an important role for the redox behaviour of Pu(IV) in acidic solutions [43]. Electrochemically prepared Pu(IV) solutions at $\mathrm{pH_c} = 0.3$–2.5 were investigated spectroscopically to study the formation of Pu(III), Pu(V) and/or Pu(VI), which is usually ascribed to the disproportionation of Pu(IV) into Pu(III) and Pu(V), followed by the reaction of Pu(V) with Pu(IV) into Pu(VI) and Pu(III) or by the disproportionation of Pu(V) into Pu(III) and Pu(VI). The steady state oxidation state distributions and pe values observed after 10–20 days were consistent with the known redox equilibria [1,2,24,44]. However, particularly the oxidation state distributions observed after short reaction times provide evidence that the underlying mechanism is not consistent with disproportionation reactions but with the formation of $\mathrm{PuO_2^+}$ from colloidal or smaller polynuclear Pu(IV) species followed by the simultaneous equilibration of the reversible redox couples Pu(V)/Pu(VI) and Pu(III)/Pu(IV) which are related by pe (and pH because of Pu(IV) hydrolysis equilibria) [43]. Contrary to the reversible redox couples $\mathrm{Pu^{3+}/Pu^{4+}}$ and $\mathrm{PuO_2^+/PuO_2^{2+}}$ the $\mathrm{PuO_2^+}$ and $\mathrm{Pu^{4+}}$ ions and their mononuclear hydroxide complexes are not directly in equilibrium with each other but only indirectly via their reactions with solid, colloidal or polymeric Pu(IV).

6. Thermodynamic data for $\mathrm{PuO_{2+\mathit{x}}}$(cr) and $\mathrm{PuO_{2+\mathit{x}}}$(s,hyd)

In the following sections, thermodynamic data for hydrous $\mathrm{PuO_{2+\mathit{x}}}$(s,hyd) and for possible anhydrous crystalline compounds like $\mathrm{PuO_{2.25}(cr)} = 1/4\ \mathrm{Pu_4O_9(cr)}$, $\mathrm{PuO_{2.5}(cr)} = 1/2\ \mathrm{Pu_2O_5(cr)}$, and $\mathrm{PuO_3}$(cr) are discussed by comparing known standard molar Gibbs energies of formation $\Delta_f G^\circ_m(298.15\ \mathrm{K})$ 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 values for hydrous An(IV) and An(V) oxyhydroxides correspond to the formula $\mathrm{AnO_{2+\mathit{x}}}$(s,hyd), i.e., the contribution of H_2O molecules is not included in the values for $\Delta_f G^\circ_m$ ($\mathrm{AnO_{2+\mathit{x}}}$(s,hyd)). For better comparison, the $\Delta_f G^\circ_m$ values for crystalline An(VI) oxyhydroxides with the formula $\mathrm{AnO_2O_{1-\mathit{n}/2}(OH)_{\mathit{n}} \cdot \mathit{y}H_2O(cr)}$ are also normalized to values referring to the formula $\mathrm{AnO_3}$(cr,hyd) by subtracting $(n/2 + y)\Delta_f G^\circ_m(\mathrm{H_2O(l)})$, e.g., the value of $\Delta_f G^\circ_m(\mathrm{PuO_2(OH)_2 \cdot H_2O(cr)}) = -1442.4$ kJ/mol [1,2] $((n/2 + y) = 2)$ is transformed into $\Delta_f G^\circ_m(\mathrm{PuO_3(cr,hyd)}) = -968.1$ kJ/mol.

6.1. Standard molar Gibbs energies of formation of crystalline An(IV−V−VI) oxides and actinyl(VI) oxyhydroxides $\Delta_f G°_m(AnO_{2+x}(cr), 298.15\ K)$

The standard molar Gibbs energies of formation $\Delta_f G°_m(AnO_{2+x}(cr), 298.15\ K)$ selected in the NEA-TDB [1,2] 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. 8 (filled squares). The normalized values for the actinyl(VI) oxyhydroxides $AnO_3(s,hyd)$ of U(VI), Np(VI) and Pu(VI) (filled circles) were derived from the selected solubility constants [1,2]. Fig. 8 also includes estimated $\Delta_f G°_m$ values for $NpO_3(cr)$, $PuO_3(cr)$, and $PuO_{2.5}(cr)$ (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: $\Delta_f G°_m(UO_3(cr,hyd)$, schoepite) $- \Delta_f G°_m(\gamma\text{-}UO_3(cr)) = -16.5 \pm 2.1$ kJ/mol [2].

(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., $(1/3)\Delta_f G°_m(U_3O_8(cr)) - \{(2/3)\Delta_f G°_m(UO_3(cr)) + (1/3)\Delta_f G°_m(UO_2(cr))\} = -15.4$ kJ/mol). In Fig. 8, this stabilization effect is illustrated by the deviation of $\Delta_f G°_m$ for a mixed valent oxide from the dotted straight line between the $\Delta_f G°_m$ values of the pure An(IV) and An(VI) oxides. We may assume that the stabilization energy for mixed valent An(IV−VI) and An(IV−V) 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. 8.

The data in Fig. 8 clearly show that the standard molar Gibbs energy $\Delta_r G°_m$ for the oxidation of dry crystalline An(IV) dioxide $AnO_2(cr)$ with oxygen $(\Delta_f G°_m(O_2(g)) = 0)$:

$$AnO_2(cr) + (x/2)\,O_2(g) \rightarrow AnO_{2+x}(cr) \qquad (43)$$

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., [1], p. 121),

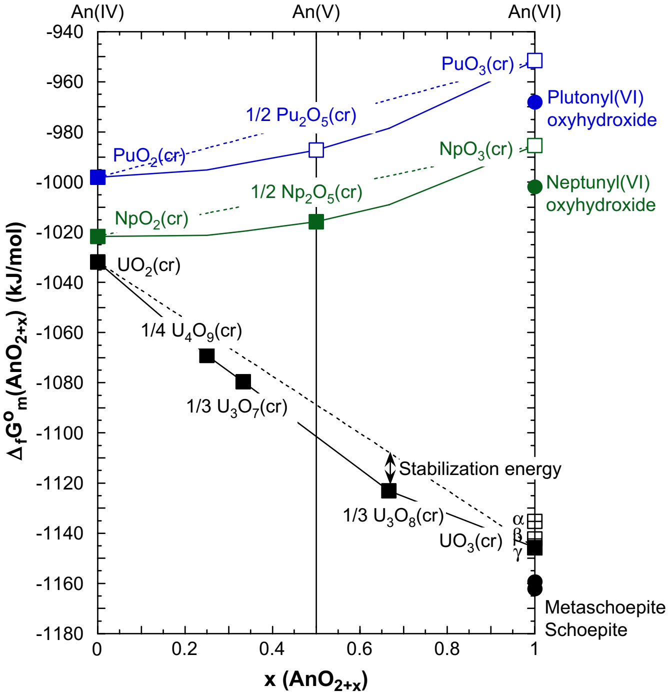

Fig. 8. Normalized standard molar Gibbs energies of formation of crystalline An(IV, V, VI) oxides $AnO_{2+x}(cr)$ and actinyl(VI) oxyhydroxides $AnO_3(cr,hyd)$ as a function of x; known data (filled symbols) selected in the NEA-TDB [1,2] and estimated values for unknown Np and Pu oxides (open symbols).

and Haschke et al. [25−27]). The close analogy between the known data for Np and Pu compounds (Fig. 8) and the standard molar Gibbs energies of formation that can be estimated for $PuO_{2.25}$(cr), $PuO_{2.5}$(cr) and PuO_3(cr) ($\Delta_f G^\circ_m = -995 \pm 3$, -987 ± 10 and -952 ± 10 kJ/mol, respectively) show that the values reported by Haschke and Allen [28] for PuO_{2+x}(s) with $x = 0.05$ to 0.5, e.g., $\Delta_f G^\circ_m(PuO_{2.25}(s)) = -1080$ kJ/mol and $\Delta_f G^\circ_m(PuO_{2.5}(s)) = -1146$ kJ/mol [28] are considerably too negative. They are calculated assuming that PuO_2(s) is oxidised by water according to

$$PuO_2(s) + xH_2O \rightarrow PuO_{2+x}(s) + xH_2(g) \qquad (44)$$

The observed formation of H_2(g) [25−28] cannot be explained by the thermodynamics of reaction (44) ($\Delta_r G^\circ_m(44) > x200$ kJ/mol), it must be caused by other mechanisms (e.g., induced by radiolysis effects). Another recent attempt to oxidise PuO_2(cr) with water vapour (under strict exclusion of oxygen) at 315 °C failed [45]. However, it will be shown below that the formation of PuO_{2+x}(s,hyd) in the presence of both water and oxygen is consistent with thermodynamic balances.

6.2. *Standard molar Gibbs energies of formation of hydrous Np(IV−V) and Pu(IV−V) oxides $\Delta_f G^\circ_m(AnO_{2+x}(s,hyd), 298.15\ K)$*

Mixed valent hydrous oxide $PuO_{2+x}(s,hyd) = (Pu^{V})_{2x}(Pu^{IV})_{1-2x}O_{2+x}(s,hyd)$ is formally written as $(PuO_{2.5})_{2x}(PuO_2)_{1-2x}(s,hyd)$ which might suggest that it is considered as a solid solution. The chemical nature and structure of PuO_{2+x}(s,hyd) is not yet clear. However, solubility studies with solids containing considerably different amounts of Pu(V) ($x = 0.003$ in a study under Ar [10] and $x = 0.05{-}0.06$ in studies under air [13−15]) led to very similar Pu(V) concentrations [10] (c.f., Section 4.2). This indicates that the Pu(V) concentration depends much less on the value of x than expected for a solid solution of $PuO_{2.5}$(s,hyd) and PuO_2(s,hyd). Accordingly PuO_{2+x}(s,hyd) is treated as mixed valent compound and the following calculations refer to the definitions given by Eqs. (28)−(31). The standard molar Gibbs energy of formation of mixed valent PuO_{2+x}(s,hyd) can be calculated from the formal solubility products of the Pu(V) and Pu(IV) fractions ($\log K^\circ_{sp}(PuO_{2.5}$ in $PuO_{2+x}(s,hyd)) = -14.0 \pm 0.8$, $\log K^\circ_{sp}(PuO_2$ in $PuO_{2+x}(s,hyd)) \approx \log K^\circ_{sp}(PuO_2(s,hyd)) = -58.33 \pm 0.52$ [2]) and $\Delta_f G^\circ_m(PuO_2^+) = -852.65 \pm 2.87$ kJ/mol, $\Delta_f G^\circ_m(Pu^{4+}) = -477.99 \pm 2.70$ kJ/mol, $\Delta_f G^\circ_m(OH^-) = -157.22 \pm 0.07$ kJ/mol, and $\Delta_f G^\circ_m(H_2O(l)) = -237.14 \pm 0.04$ kJ/mol [1,2]. With the $\Delta_f G^\circ_m$ values for the two formal fractions:

$$\Delta_f G^\circ_m(PuO_{2.5} \text{ in } PuO_{2+x}(s,hyd)) = -971.2 \pm 5.4 \text{ kJ/mol}$$

$$\Delta_f G^\circ_m(PuO_2 \text{ in } PuO_{2+x}(s,hyd)) = -965.5 \pm 4.0 \text{ kJ/mol}$$

the standard molar Gibbs energy of formation of mixed valent PuO_{2+x}(s,hyd) is given by Eq. (45):

$$\begin{aligned}\Delta_f G^\circ_m\left(PuO_{2+x}(s,hyd)\right) &= 2x\Delta_f G^\circ_m\left(PuO_{2.5}(s,hyd)\right) + (1-2x)\Delta_f G^\circ_m\left(PuO_2(s,hyd)\right)\\ &= \{2x(-971.2 \pm 5.4) + (1-2x)(-965.5 \pm 4.0)\}\ \text{kJ/mol}\end{aligned} \qquad (45)$$

for the small values of $x = 0.003$ and $x = 0.05{-}0.06$ in the solubility studies under Ar [10] and air [14,15]. Accordingly $\Delta_f G^\circ_m(PuO_{2+x}(s,hyd))$ is slightly lower than $\Delta_f G^\circ_m(PuO_2(s,hyd)) = -965.5 \pm 4.0$ kJ/mol. The values of $\Delta_f G^\circ_m(NpO_2(s,hyd))$ and $\Delta_f G^\circ_m(NpO_{2.5}(s,hyd))$ can be calculated from the experimental solubility constants for NpO_2(am,hyd) ($\log K^\circ_{sp} = -56.7 \pm 0.5$ [11,19]), and $NpO_{2.5}$(s,hyd) ($\log K^\circ_{sp} = -11.4 \pm 0.4$ [40] and -10.1 ± 0.2 [41]) with $\Delta_f G^\circ_m(Np^{4+}) = -491.8 \pm 5.6$ and $\Delta_f G^\circ_m(NpO_2^+) = -907.8 \pm 5.6$ kJ/mol [1,2].

As illustrated in Fig. 9 for Np and Pu 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 [2,16,17]. The difference of about 40 ± 10 kJ/mol, corresponding to seven log-units in the solubility constants, is due to effects from hydration and crystallinity (particle or crystallite size) as shown for ThO_2(s) [17]. 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. As a consequence and contrary to the slightly positive standard molar Gibbs energy for the oxidation of dry NpO_2(cr), $\Delta_r G^\circ_m$ for the oxidation hydrous NpO_2(am,hyd) is negative, up to $x = 0.5$ (c.f., Fig. 9a). For hydrous plutonium oxide (Fig. 9b), $\Delta_r G^\circ_m$ is slightly negative for $x < 0.1$ (and possibly up to $x = 0.25$), whereas $\Delta_r G^\circ_m$ is expected to be equal to zero or slightly positive for $x > 0.25$, if we take into account that the value of $\Delta_f G^\circ_m = -971.2 \pm 5.4$ kJ/mol

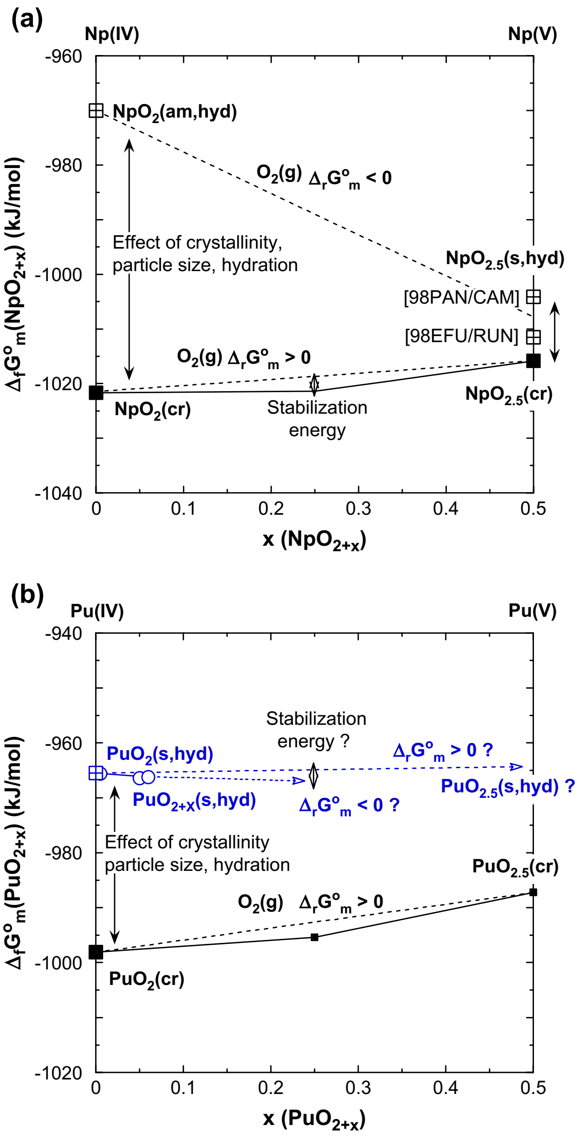

Fig. 9. Normalized standard molar Gibbs energies of formation of hydrous Np(IV–V) and Pu(IV–V) oxides AnO_{2+x}(s,hyd) as a function of x in comparison with the data for the anhydrous crystalline oxides AnO_{2+x}(cr) from Fig. 8.

calculated for $PuO_{2.5}$(s,hyd) as a small fraction of PuO_{2+x}(s,hyd), 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 $x > 0.25$.

Anhydrous PuO_2(cr) is considerably more stable than Pu(IV) hydrous oxide and cannot be oxidised by O_2(g) unless the H_2O(l) or H_2O(g) creates 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 $\Delta_rG°_m$ for surface hydration is negative [46]. Hence in the presence of both water and oxygen, PuO_2(s) is partially oxidised to PuO_{2+x}(s) as reported by Haschke et al. [26,27]. However, contrary to the proposed water catalyzed mechanism [26,27], the role of water can be explained in terms of thermodynamics. The oxidation of PuO_2(s) by water and the extremely high stability of PuO_{2+x}(s) also claimed by Haschke et al. [25–28] can be ruled out.

7. Conclusions

(1) The solubility and speciation of plutonium in the system $Pu/e^-/H^+/OH^-/H_2O$ (25 °C) can be described in terms of equilibrium thermodynamics, provided pH and redox potentials (pe) are known. A summary of equilibrium constants for solids and aqueous species of plutonium is given in Table 1 (Appendix). They include the values selected in the OECD/NEA-TDB [1,2], oxidation state analogs for unknown data and additional data for mixed valent PuO_{2+x}(s,hyd) and small Pu(IV) colloids/polymers in neutral to alkaline solutions. It has to be emphasized that irreversible redox reactions can lead to erroneous model predictions and must be excluded from the calculations (e.g., pe is usually not controlled by Eq. (2) and $P(O_2(g))$. For the reasons discussed previously [16,17] data for anhydrous PuO_2(cr) must be excluded as well.

(2) Thermodynamic calculations show that the border line for the conversion of $Pu(OH)_3$(s) into PuO_2(am,hyd) is close to the lower stability line of water. Under most reducing conditions PuO_2(am,hyd) is the solubility controlling solid phase, in equilibrium with aqueous Pu(IV) and Pu(III) species. In the absence of reducing agents, traces of O_2(g) are sufficient to produce mixed valent PuO_{2+x}(s,hyd). The equilibrium Pu(V) concentrations considerably exceed those of aqueous Pu(IV) species, but they are about 5 log-units lower than Pu(V) concentrations in equilibrium with PuO_2OH(am). The latter is not the solubility limiting solid phase. The solubility of PuO_{2+x}(s,hyd) can further be raised by Pu(VI) species, particularly at higher redox potentials caused by radiolysis in chloride brines [8,15] or in the presence of carbonate. Plutonyl(VI) oxyhydroxide is only stable under strongly oxidising conditions. The stability line of PuO_{2+x}(s,hyd) with regard to the transformation into $PuO_2(OH)_2 \cdot H_2O$(cr) is at $(pe + pH) = 21.0 \pm 1.3$, in the range of the upper stability line of water at $(pe + pH) = 20.77$).

(3) Aqueous Pu(IV) hydroxide complexes $Pu(OH)_n^{4-n}$ are generally of minor importance. Their concentration is low compared to Pu(III) species at (pe + pH) < 14 (under reducing conditions), compared to Pu(V) species at (pe + pH) = 11−16 (in redox-inert solutions and in the presence of oxygen) or compared to Pu(VI) species at (pe + pH) > 16 (in the presence of oxidising agents). The low Pu concentrations in neutral and alkaline solutions are dominated by small Pu(IV) colloids/polymers. They are part of the thermodynamic system and play an important role for the redox reactions between Pu(IV) and Pu(V). As these neutral oxyhydroxide polymers/colloids have a high tendency towards sorption on oxidic and hydroxidic mineral surfaces they are also important species in sorption studies. Accepting that their formation from PuO_2^+ is a (slow) reversible equilibrium reaction, the sorption of PuO_2(coll,hyd) from Pu(V) solutions has to be expected in any case, regardless whether the sorbing material is reducing or redox-inert, in particular if the Pu(V) concentration exceeds the solubility of PuO_{2+x}(s,hyd) at given pH. The same holds for Pu(III) solutions exceeding the Pu(III) concentration in equilibrium with PuO_2(am,hyd) at given pH and redox conditions (pe + pH). In this case the sorption of PuO_2(coll,hyd) should dominate as well, regardless whether the sorbing material is oxidising or not. Corresponding observations were made in plutonium sorption studies supported by EXAFS measurements and reported by different authors at international conferences during the last years. The present paper may help to explain these observations.

Appendix

Table 1
Equilibrium constants log K° for the system $Pu/e^-/H^+/OH^-/H_2O$ at $I = 0$ and 25 °C

Redox equilibria		
$Pu^{3+} \rightleftharpoons Pu^{4+} + e^-$	$\log K^\circ_{III/IV} = -17.69 \pm 0.04$	[1,2]
$PuO_2^+ \rightleftharpoons PuO_2^{2+} + e^-$	$\log K^\circ_{V/VI} = -15.82 \pm 0.09$	[1,2]
PuO_2(am,hyd) + $e^- + 4H^+ \rightleftharpoons Pu^{3+} + 2H_2O$	$\log {}^*K^\circ_{IVs/III} = 15.36 \pm 0.52$	[2]
PuO_2(am,hyd) $\rightleftharpoons PuO_2^+ + e^-$	$\log K^\circ_{IVs/V} = -19.78 \pm 0.86$	[2]
PuO_2(coll,hyd) $\rightleftharpoons PuO_2^+ + e^-$	$\log K^\circ_{IVcoll/V} = -11.5 \pm 1.3$[a]	[10]
Solubility and hydrolysis equilibria of Pu(III)		
$Pu(OH)_3$(s) $\rightleftharpoons Pu^{3+} + 3OH^-$	$\log K^\circ_{sp} = -26.2 \pm 0.8$[b]	[3]
$Pu^{3+} + OH^- \rightleftharpoons Pu(OH)^{2+}$	$\log \beta^\circ_{1,1} = 7.1 \pm 0.3$	[1,2]
$Pu^{3+} + 2OH^- \rightleftharpoons Pu(OH)_2^+$	$\log \beta^\circ_{1,2} = 12.9 \pm 0.7$	Am analog [2]
$Pu^{3+} + 3OH^- \rightleftharpoons Pu(OH)_3$(aq)	$\log \beta^\circ_{1,3} = 15.8 \pm 0.5$	Am analog [2]
Solubility and hydrolysis equilibria of Pu(IV)		
PuO_2(am,hyd) $\rightleftharpoons Pu^{4+} + 4OH^-$	$\log K^\circ_{sp} = -58.33 \pm 0.52$	[2]
	($\log K^\circ_{sp} = -58.5 \pm 0.7$)[c]	[16]
$Pu^{4+} + OH^- \rightleftharpoons Pu(OH)^{3+}$	$\log \beta^\circ_{1,1} = 14.6 \pm 0.2$	[2,16]
$Pu^{4+} + 2OH^- \rightleftharpoons Pu(OH)_2^{2+}$	$\log \beta^\circ_{1,2} = 28.6 \pm 0.3$	[2,16]
$Pu^{4+} + 3OH^- \rightleftharpoons Pu(OH)_3^+$	$\log \beta^\circ_{1,3} = 39.7 \pm 0.4$	[2,16]
$Pu^{4+} + 4OH^- \rightleftharpoons Pu(OH)_4$(aq)	$\log \beta^\circ_{1,4} = 47.5 \pm 0.5$	[2]
PuO_2(am,hyd) + $2H_2O \rightleftharpoons Pu(OH)_4$(aq)	($\log K^\circ_{s,4} = -10.4 \pm 0.5$)[c]	[16]
PuO_2(am,hyd) $\rightleftharpoons PuO_2$(coll,hyd,aq)	$\log K^\circ_{IVcoll} = -8.3 \pm 1.0$[a]	[10]
Solubility and hydrolysis equilibria of Pu(V)		
PuO_2OH(am) $\rightleftharpoons PuO_2^+ + OH^-$	$\log K^\circ_{sp} = -9.0 \pm 0.5$	[1,2]
$PuO_{2.5}$(s,hyd) $\rightleftharpoons PuO_2^+ + OH^-$	$\log K^\circ_{sp} = -14.0 \pm 0.8$[d]	[10]
$PuO_2^+ + OH^- \rightleftharpoons PuO_2OH$(aq)	$\log \beta^\circ_{1,1} = 2.7 \pm 0.7$	Np + Am analog [2]
$PuO_2^+ + 2OH^- \rightleftharpoons PuO_2(OH)_2^-$	$\log \beta^\circ_{1,2} = 4.4 \pm 0.5$	Np + Am analog [2]
Solubility and hydrolysis equilibria of Pu(VI)		
$PuO_2(OH)_2 \cdot H_2O$(s) $\rightleftharpoons PuO_2^{2+} + 2OH^- + H_2O$	$\log K^\circ_{sp} = -22.5 \pm 1.0$	[1,2]

(*continued on next page*)

Table 1 (*continued*)

$PuO_2^{2+} + OH^- \rightleftharpoons PuO_2(OH)^+$	$\log \beta^\circ_{1,1} = 8.5 \pm 0.5$	[1,2]
$PuO_2^{2+} + 2OH^- \rightleftharpoons PuO_2(OH)_2(aq)$	$\log \beta^\circ_{1,2} = 14.8 \pm 1.5$	[1,2]
$PuO_2^{2+} + 3OH^- \rightleftharpoons PuO_2(OH)_3^-$	$\log \beta^\circ_{1,3} = 21.7 \pm 0.4$	U analog [2]
$PuO_2^{2+} + 4OH- \rightleftharpoons PuO_2(OH)_4^{2-}$	$\log \beta^\circ_{1,4} = 23.6 \pm 0.7$	U analog [2]
$2PuO_2^{2+} + 2OH^- \rightleftharpoons (PuO_2)_2(OH)_2^{2+}$	$\log \beta^\circ_{2,2} = 20.5 \pm 1.0$	[1,2]

[a] Equilibrium constant for Pu(IV) polymers/colloids (1.5–2 nm) formed in neutral and alkaline solution.

[b] Also selected in the NEA-TDB [1,2], but with increased uncertainty (±1.5).

[c] Used for the calculation of Pu(IV) concentrations; not selected in the NEA-TDB [2].

[d] For the fraction of $PuO_{2.5}$(s,hyd) in PuO_{2+x}(s,hyd) with $x < 0.1$.

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