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Modeling Speciation and Solubility in Aqueous Systems Containing U(IV, VI), Np(IV, V, VI), Pu(III, IV, V, VI), Am(III), and Cm(III)

Peiming Wang¹ · Andrzej Anderko¹ · Jerzy J. Kosinski¹ · Ronald D. Springer¹ · Malgorzata M. Lencka¹

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Abstract A comprehensive thermodynamic model, referred to as the Mixed-Solvent Electrolyte model, has been applied to calculate phase equilibria and chemical speciation in selected aqueous actinide systems. The solution chemistry of U(IV, VI), Np(IV, V, VI), Pu(III, IV, V, VI), Am(III), and Cm(III) has been analyzed to develop the parameters of the model. These parameters include the standard-state thermochemical properties of aqueous and solid actinide species as well as the ion interaction parameters that reflect the solution's nonideality. The model reproduces the solubility behavior and accurately predicts the formation of competing solid phases as a function of pH (from 0 to 14 and higher), temperature (up to 573 K), partial pressure of CO₂ (up to $p_{CO_2} = 1$ bar), and concentrations of acids (to 127 mol·kg⁻¹), bases (to 18 mol·kg⁻¹), carbonates (to 6 mol·kg⁻¹) and other ionic components (i.e., Na⁺, Ca²⁺, Mg²⁺, OH⁻, Cl⁻, ClO₄⁻, and NO₃⁻). Redox effects on solubility and speciation have been incorporated into the model, as exemplified by the reductive and oxidative dissolution of Np(VI) and Pu(IV) solids, respectively. Thus, the model can be used to elucidate the phase and chemical equilibria for radionuclides in natural aquatic systems or in nuclear waste repository environments as a function of environmental conditions. Additionally, the model has been applied to systems relevant to nuclear fuel processing, in which nitric acid and nitrate salts of plutonium and uranium are present at high concentrations. The model reproduces speciation and solubility in the $U(VI) + HNO_3 + H_2O$ and $Pu(IV, VI) + HNO_3 + H_2O$ systems up to very high nitric acid concentrations ($x_{\text{HNO}_3} \approx 0.70$). Furthermore, the similarities and differences in the solubility behavior of the actinides have been analyzed in terms of aqueous speciation.

Keywords Actinides · Aqueous solutions · Phase equilibria · Solubility · Speciation · Transuranium elements

Peiming Wang pwang@olisystems.com

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¹ OLI Systems, Inc., 240 Cedar Knolls Road, Suite 301, Cedar Knolls, NJ 07927, USA

1 Introduction

Aqueous speciation and solid solubility in actinide systems are of particular interest in nuclear fuel recycling processes. They are also among the most fundamental issues for geochemical modeling associated with the safety assessment of nuclear waste management. The behavior of the radionuclides in these applications strongly depends on the conditions at which their chemical forms may change due to hydrolysis, complexation, and formation of solid phases. In addition, alteration of redox conditions can induce changes in the oxidation state of actinides that are redox-sensitive, resulting in the change of chemical and phase behavior that can potentially impact the outcomes of the processes. Detailed knowledge of the chemical speciation of actinides in solution and the solubility behavior of actinide solid phases are indispensable for developing efficient technologies in practical applications. Due to their industrial and environmental importance, actinide chemistry and phase behavior have been extensively studied for several decades. Although a tremendous amount of data and valuable insights have been accumulated in such studies, monitoring the chemical and phase behavior in actual settings involving radioactive actinides inevitably poses serious safety concerns and inherent difficulties. Therefore, a thermodynamic model that can realistically predict the solubility behavior and speciation can be of great value. However, the development of such a model is very challenging because the actinidecontaining systems are multicomponent and complex in nature and their chemical and phase behavior can be affected by a multitude of variables. Extensive reviews of various chemical features of actinides and compilations of thermochemical properties of various U, Np, Pu, Am, and Cm species have been published in the literature [1-7].

Critically evaluated thermochemical property data for actinides and fission products have been published by Phillips et al. [7], Lemire and Tremaine [6] and, more recently, by the Nuclear Energy Agency (NEA) [1–5]. These data provide a foundation for chemical equilibrium calculations in thermodynamic modeling. At the same time, experimental solubility data for actinide systems that were reported in the literature prior to 2005 have been compiled and evaluated by Hála et al. [8, 9] as part of the IUPAC-NIST Solubility Data Project. Additional thermodynamic data on solubility and speciation that are not included in the IUPAC-NIST collection are also available from more recent publications (see Tables 1, 2, 3, 4 and 5).

In this study, we extend a previously developed speciation-based thermodynamic model [10, 11] to selected actinide systems that are of importance in nuclear fuel recycling processes and in nuclear waste management. This model, referred to as the Mixed-Solvent Electrolyte (MSE) model, was previously shown to reproduce simultaneously vapor–liquid, solid–liquid and liquid–liquid equilibria, speciation, thermal and volumetric properties of electrolytes in water, organic, or mixed solvents [12–14]. The MSE model has been designed to be equally applicable to classical aqueous systems, those with more than one distinct solvent and those in which a given component may continuously vary from being a solute to being a solvent (e.g., in acid–water mixtures). The MSE model is capable of representing phase equilibria in multicomponent inorganic systems containing multiple salts, acids, and bases [12, 15–21] and in ionic liquid systems [22].

The systems analyzed in this work involve Am, Cm, Np, Pu and U. The objective of this study is to provide a comprehensive thermodynamic treatment on the basis of the available experimental data. The model is constructed to represent the properties of these systems with particular emphasis on chemical speciation and solubilities under conditions that are relevant to both nuclear waste disposal and nuclear fuel recycling processes. For this

System	Reference	T/K	PH range and ionic medium
Am(III)–H–OH– salt–H ₂ O	Silva [134]	298	pH 7–9.4; 0.1 mol·kg ⁻¹ NaClO ₄
	Peretrukhin et al. [95]	298	NaOH = 1.0 and 5.0 mol·kg ⁻¹
	Kim et al. [59, 135]	298	pH 6.5–13.3; 0.1 mol·kg ⁻¹ NaClO ₄
	Stadler and Kim [49, 53]	298	pH 6.3–13; 0.1 mol·kg ⁻¹ NaClO ₄ and 0.6 mol·kg ⁻¹ NaCl
	Rai et al. [46]	298	pH 7.1–13, 0.0015 mol·kg ⁻¹ CaCl ₂
	Runde and Kim [52]	298	pH 6.6–13.7; 5.6 mol·kg ⁻¹ NaCl
	Nitsche and Edelstein [136]	298	pH 7; 0.1 mol·kg ⁻¹ NaClO ₄
	Edelstein et al. [137]	298	pH 7.8–9.5; 0.1 mol·kg ⁻¹ NaClO ₄
Am(III)–H–OH– salt–CO ₂ /CO ₃ – H ₂ O	Bernkopf and Kim [59]	298	pH 6.2–10.9; 0.1 mol·kg ⁻¹ mol·kg ⁻¹ NaClO ₄ ; $pCO_2 = 0-3.2 \times 10^{-4}$ bar
	Felmy et al. [57]	298	pH 5.5–13; $pCO_2 = 1 \times 10^{-3}$ bar and Na ₂ CO ₃ = 0.003–0.1 mol·kg ⁻¹
	Ewart et al. [61]	298	pH 7–13; $CO_3(total) = 10^{-4} - 10^{-5} \text{ mol·kg}^{-1}$
	Meinrath and Kim [58]	298	pH 6.1–9.2; 0.1 and 0.3 mol·kg ⁻¹ NaClO ₄ ; $pCO_2 = 0.01$ bar, pH adjusted by HClO ₄ and Na ₂ CO ₃
	Nitsche [138]	296	pH 5.9–9.6; 0.1 mol·kg ⁻¹ NaClO ₄ ; $pCO_2 = 3.2 \times 10^{-4}$ bar
	Nitsche [139]	298	pH 6 and 8.5, 0.01 mol·kg ⁻¹ NaClO ₄ ; CO ₃ (total) = 2×10^{-3} mol·kg ⁻¹
	Hala [9]; Silva [140]	298	pH 6.1; 0.1 mol·kg ⁻¹ NaClO ₄ ; HCO ₃ = 2 × 10 ⁻⁴ mol·kg ⁻¹
	Giffaut [50]	293 ~ 343	pH 6.1–11.5; 0.1 and 4 mol·kg ⁻¹ NaCl; HCO ₃ or CO ₃ (total) = 10^{-3} –1 mol·kg ⁻¹
	Robouch [141]	293	pH 8.2–10.4; 3 mol·kg ⁻¹ NaClO ₄ ; CO ₃ (total) = 3 × 10 ⁻⁴ –0.8 mol·kg ⁻¹

Table 1 Literature solubility data sources for aqueous Am(III) systems

purpose, the effects of acids, bases, carbonates and other salts, as well as CO_2 , are investigated as these variables govern the chemical and phase behavior of the radionuclides in waste repositories and affect the immobilization of radioactive waste effluents under geological conditions. At the same time, the effects of acids, especially nitric acid, and temperature are investigated for Pu and U solutes in concentrated acid mixtures as such systems are of technological importance in nuclear fuel recycling processes. The results provide a thermodynamic foundation to explain variations in solid formation under changing conditions, and to evaluate how the properties of natural and industrial fluids may affect radionuclide behavior in these processes.

System	Reference	<i>T</i> /K	Type of data	PH range and ionic medium
Cm(III)–OH– Cl–Na–Ca– H ₂ O	Neck et al. [65]	298	Solubility	pH 10–15; 5.6 mol·kg ⁻¹ NaCl and 1.0–3.9 mol·kg ⁻¹ CaCl ₂
Cm(III)–OH– Cl–Ca–H ₂ O	Rabung et al. [66]	295	Solubility	pH 10.2–11.9; 1.0–3.9 mol·kg ⁻¹ CaCl ₂
Cm(III)–Cl– Ca–H ₂ O	Fanghänel et al. [69]	298	Speciation: Cm–Cl complexes	pH 2; 2.3–6.0 mol·kg ⁻¹ CaCl ₂
Cm(III)-Cl- Na-H ₂ O	Fanghänel et al. [70]	298	Speciation: hydrolysis constants of Cm(III)	0.01–6.15 mol·kg ⁻¹ NaCl
Cm(III)–Cl– SO ₄ –Na– H ₂ O	Paviet et al. [73]	298	Speciation: Cm–SO ₄ complexes	pH 2; $I = 3 \text{ mol} \cdot \text{kg}^{-1}$ NaCl + Na ₂ SO ₄ (0.031–0.367 mol \cdot \text{kg}^{-1} Na ₂ SO ₄)
Cm(III)-ClO ₄ - SO ₄ -Na- H ₂ O	Skerencak et al. [67]	298–473	Speciation: Cm–SO ₄ complexes	pH 1; $I = 2.0 \text{ mol·kg}^{-1} \text{ NaClO}_4$; 0–0.365 mol·kg ⁻¹ Na ₂ SO ₄
Cm(III)–Cl– CO ₃ –Na– H ₂ O	Fanghänel et al. [72]	298	Speciation: Cm–CO ₃ complexes	pH 5.1–9.4; 1 mol·kg ⁻¹ NaCl; Na ₂ CO ₃ and NaHCO ₃ – 0.6 mol·kg ⁻¹
Cm(III)–Cl– CO ₃ –Na– H ₂ O	Fanghänel et al. [71]	298	Speciation: Cm–CO ₃ complexation constants	$0-6 \text{ mol} \cdot \text{kg}^{-1} \text{ NaCl};$ $p\text{CO}_2 = 0.1-1 \text{ bar or CO}_3-0.01 \text{ mol} \cdot \text{kg}^{-1}$

Table 2 Literature data sources for aqueous Cm(III) systems

2 Thermodynamic Modeling

2.1 Chemical Speciation and Phase Equilibria

The hydrolysis reaction, as a particular case of complex formation, is the primary common property of all actinide ions in aqueous solutions. The actinide solubility is largely affected by the hydrolysis, which is highly dependent on the solution pH. Depending on the redox state, actinide ions may exist in aqueous acidic solutions as hydrated ions without ligands (e.g., Pu^{3+} and Pu^{4+}) at lower oxidation states, or as dioxo species (e.g., PuO_2^+ and PuO_2^{2+}) at higher oxidation states. In water solutions, these ions undergo hydrolysis to form multiple hydroxide complexes whose distribution is dependent on the concentration of the acid or base. For example, the hydrolysis in aqueous Pu(VI) solutions can be expressed as

$$\operatorname{PuO}_{2}^{2+} + 2n\operatorname{H}_{2}\operatorname{O} \rightleftharpoons \operatorname{PuO}_{2}(\operatorname{OH})_{n}^{2-n} + n\operatorname{H}_{3}\operatorname{O}^{+}$$
(1)

The actinide ions may also form complexes in the presence of complexing ligands, such as Cl^{-} and CO_{3}^{2-} , e.g.,

$$\mathrm{Cm}^{3+} + n\mathrm{Cl}^{-} \rightleftharpoons \mathrm{Cm}\mathrm{Cl}_{n}^{3-n} \tag{2}$$

$$\operatorname{Cm}^{3+} + n\operatorname{CO}_{3}^{2-} \rightleftharpoons \operatorname{Cm}(\operatorname{CO}_{3})_{n}^{3-2n}$$
(3)

$$\operatorname{PuO}_{2}^{2+} + n\operatorname{CO}_{3}^{2-} \rightleftharpoons \operatorname{PuO}_{2}(\operatorname{CO}_{3})_{n}^{2-2n}$$

$$\tag{4}$$

	•		•
System	Reference	<i>T</i> /K	PH range and ionic medium ($x =$ mole fraction)
U(IV)-OH-H- Na-Mg-Cl- ClO ₄ -H ₂ O	Ryan and Rai [88]	294	0.045–11.4 mol·kg ⁻¹ NaOH
	Gayer and Leider [93]	298	0.039–0.39 $\text{mol}{\cdot}\text{kg}^{-1}$ HClO ₄ and 0–0.63 $\text{mol}{\cdot}\text{kg}^{-1}$ NaOH
	Rai et al. [89]	294	pH 2-12 adjusted by HCl and NaOH
	Casas et al. [142]	298	pH 1.0–9.4; 1.0 mol·kg ⁻¹ NaCl or 0.008 mol·kg ⁻¹ NaClO ₄
	Rai et al. [90]	298	pH 1.9–5; 0.2–6 mol·kg ^{-1} NaCl or 1–3 mol·kg ^{-1} MgCl ₂
	Galkin and Stepanov [92]	298	$0.02-7.7 \text{ mol}\cdot\text{kg}^{-1} \text{ NaOH}$
	Bruno et al. [143]	298	pH 1.7–9.8; 0.5 mol·kg ⁻¹ NaClO ₄
	Aguilar et al. [144]	298	pH 7.5; 0.05–4.4 mol·kg ⁻¹ NaCl
	Fujiwara et al. [91]	298	pH 12–14; 0.5–2 mol·kg ⁻¹ NaClO ₄
	Parks and Pohl [85]	373–573	pH 1–10 adjusted by HCl, NaOH or LiOH; $pH_2 = 50 \text{ MPa}$
	Rai et al. [83]	295	pH 0.22–5.33 adjusted by HCl in 0.01 mol·kg $^{-1}$ EuCl ₂
	Tremaine et al. [96]	293-573	0.0035 mol·kg ^{-1} and 0.037 mol·kg ^{-1} LiOH
	Torrero et al. [145]	298	pH 2–12 adjusted by HClO ₄ and NaOH; $0.008 \text{ mol} \cdot \text{kg}^{-1} \text{ NaClO}_4$; 1 and 5 mol $\cdot \text{kg}^{-1} \text{ NaCl}$
	Yajima et al. [86]	298	pH 2–12 adjusted by HClO ₄ and NaOH; 0.1 mol·kg ⁻¹ NaClO ₄ and 0.01 mol·kg ⁻¹ Na $_2S_2O_4$
U(IV)-OH-CO ₃ - Na-K-H ₂ O	Rai et al. [98]	298	0.0003-2 mol·kg ⁻¹ Na ₂ CO ₃ ; 0.3-6.5 mol·kg ⁻¹ K ₂ CO ₃ ; 0.02-1 mol·kg ⁻¹ NaHCO ₃ ; 0.01-0.5 mol·kg ⁻¹ NaOH
	Rai et al. [97]	298	$\begin{array}{l} 0.0005-2 \ \text{mol} \cdot \text{kg}^{-1} \ \text{Na}_2 \text{CO}_3; \ 0.001-6.3 \ \text{mol} \cdot \text{kg}^{-1} \\ \text{K}_2 \text{CO}_3 \\ 0.02-1 \ \text{mol} \cdot \text{kg}^{-1} \ \text{Na}\text{HCO}_3; \ 0.02-1 \ \text{mol} \cdot \text{kg}^{-1} \\ \text{KHCO}_3; \ 0.01-0.1 \ \text{mol} \cdot \text{kg}^{-1} \ \text{Na}\text{OH}; \\ 0.01-0.8 \ \text{mol} \cdot \text{kg}^{-1} \ \text{KOH} \end{array}$
U(VI)-OH-H- Na-Cl-ClO ₄ - H ₂ O	Fujiwara et al. [117]	298	pH 4–6 adjusted by HClO ₄ and NaOH; 0.1, 0.5, $1.0 \text{ mol} \cdot \text{kg}^{-1} \text{ NaClO}_4$
	Diaz Arocas and Grambow [116]	298	pH 4–9; 0.5 mol·kg ^{-1} NaClO ₄ , 3 and 5 mol·kg ^{-1} NaCl
	Kramer-Schnabel et al. [121]	298	pH 4.3–5.7; 0.1 mol·kg ⁻¹ NaClO ₄
	Bruno and Sadino [115]	298	pH 6.7–8.8; 0.5 mol·kg ⁻¹ NaClO ₄
	Torrero et al. [125]	298	pH 4.3–5.5; 1.0 mol·kg ⁻¹ NaCl
	Kim et al. [120]	298	pH 5.2–9.8; 0.1 mol·kg ⁻¹ NaClO ₄
	Krupka et al. [122]	298	pH 3-12 adjusted by HClO ₄ and (CH ₃) ₄ NOH
	Gayer and Leider [118]	298	pH 4–5.2; 0–0.77 mol·kg ⁻¹ NaOH; 0–1.0 mol·kg ⁻¹ HClO ₄

Table 3 Literature solubility data sources for aqueous U systems

System	Reference	<i>T</i> /K	PH range and ionic medium ($x =$ mole fraction)
U(VI)–OH–H– Na–Cl–ClO ₄ – H ₂ O	Redkin and Wood [124]	298	pH 2.7–11; 0.1 mol·kg ⁻¹ NaCl
	Nikitin et al. [123]	298-473	Solubility of UO ₂ (OH) ₂ ·H ₂ O in water
	Valsami-Jones and Ragnarsdottir [126]	573	Solubility of UO ₂ (OH) ₂ in water
	Fanghänel and Neck [113]	298	pH 4–10; 0.5 mol·kg ⁻¹ NaCl
	Gorman-Lewis et al. [119]	298	pH 4–6.4; 0.1 mol·kg $^{-1}$ NaNO ₃
	Gaona et al., Altmaier et al. [114, 129]	298	pH 5.7–14.5; 0.5–5.6 mol·kg ⁻¹ NaCl
U(VI)–OH–H– Na–Cl–ClO ₄ – CO ₃ –H ₂ O	Jang et al. [146]	298	pH 5.9–7.8; $pCO_2 = 3 \times 10^{-4}$ bar
	Kato et al. [131]	298	pH 3–5; 0.1 mol·kg ⁻¹ NaClO ₄ ; $pCO_2 = 3 \times 10^{-4}$ and 1 bar
	Meinrath et al. [147–149]	297	pH 3–7; 0.1 mol·kg ⁻¹ NaClO ₄ ; $pCO_2 = 3 \times 10^{-4}$, 0.01, 1 bar
	Yamamura et al. [150]	298	0.0018–0.72 mol·kg ⁻¹ NaOH; 0.0018–0.19 mol·kg ⁻¹ NaHCO ₃ ; 0.5–2.0 mol·kg ⁻¹ NaClO ₄
	Grenthe et al. [151]	298	pH 3.5–6.2; 0.5–3 mol·kg ⁻¹ NaClO ₄ ; $pCO_2 = 0.1-1$ bar
	Giammar and Hering [152]	298	pH 5–9.5; 0.01 mol·kg ⁻¹ NaCl; $pCO_2 = 3 \times 10^{-4}$ bar
	Pashalidis et al. [153, 154]	295	pH 3–6; 0.1 mol·kg ^{-1} NaClO ₄ ; <i>p</i> CO ₂ = 1 bar
	Krammer-Schnabel et al. [121]	295	pH 3.6–5.5; 0.1 mol·kg ^{-1} NaClO ₄ ; <i>p</i> CO ₂ = 1 bar
	Sergeyeva et al. [155]	298–473	pH 3.2–6.2; $pCO_2 = 1$ bar
	Pirozhkov and Nikolaeva [156]	298–423	pH 4; 0.003–0.03 mol·kg ⁻¹ CO ₂
	Blake et al. [157]	299–303	$\begin{array}{l} 0-3 \ mol \cdot kg^{-1} \ Na_2 CO_3; \ 1-4 \ mol \cdot kg^{-1} \ NaCl; \\ 0.3-3 \ mol \cdot kg^{-1} \ Na_2 SO_4; \ 0.5-3.5 \ mol \cdot kg^{-1} \\ NaClO_4; \ 0.3-1 \ mol \cdot kg^{-1} \ NaHCO_3 \end{array}$
	Brown and Schmitt [158]	299	$\begin{array}{c} 0.28,\ 0.57\ \text{mol}\cdot\text{kg}^{-1}\ \text{Na}_2\text{CO}_3;\ 0\text{4}\ \text{mol}\cdot\text{kg}^{-1}\ \text{NaCl};\\ 0\text{3}\ \text{mol}\cdot\text{kg}^{-1}\ \text{Na}_2\text{SO}_4;\ 0.5\text{3.4}\ \text{mol}\cdot\text{kg}^{-1}\ \text{NaClO}_4 \end{array}$
	Korolev et al. [159]	373–673	0–0.38 mol·kg ⁻¹ NaHCO ₃ ; 0.5 mol·kg ⁻¹ Na ₂ CO ₃ ; 0.5 mol·kg ⁻¹ NaOH, $p = 507$ bar
U(VI)–H–NO ₃ – H ₂ O	Marshall and Slusher [160]	298–623	$m_{\rm HNO_3} = 0.001 - 6.34 \text{ mol} \cdot \text{kg}^{-1} (\text{UO}_3 - \text{HNO}_3 - \text{H}_2\text{O})$
	Lacher et al. [161]	298-332	$x_{\text{HNO}_3} = 0.003 - 0.66 \text{ (UO}_3 - \text{HNO}_3 - \text{H}_2\text{O})$
	Efimova and Gromov [162]	293, 368	$m_{\rm UO_2(NO_3)_2} = 0.1-3.5 \text{ mol} \cdot \text{kg}^{-1} (\text{UO}_3-\text{UO}_2(\text{NO}_3)_2-\text{H}_2\text{O})$
	Cordfunke [163]	298	$m_{\rm UO_2(NO_3)_2} = 0.03-3.5 \text{ mol}\cdot\text{kg}^{-1} (\text{UO}_3-\text{UO}_2(\text{NO}_3)_2-\text{H}_2\text{O})$

Table 3 continued

System	Reference	<i>T</i> /K	PH range and ionic medium ($x =$ mole fraction)
	Linke and Seidell [164] and refs. therein	293, 298	$x_{\text{HNO}_3} = 0-0.67 \text{ (UO}_2(\text{NO}_3)_2-\text{HNO}_3-\text{H}_2\text{O})$
	Linke and Seidell [164] and refs. therein	255–457	Solubility of $UO_2(NO_3)_2$ in water

Table 3 continued

 Table 4
 Literature solubility data sources for aqueous Pu systems

System	Reference	T/K	PH range and ionic medium
Pu(III)–OH–H– Na–Cl–H ₂ O	Felmy et al. [48]	296	pH 6–13 adjusted by HCl and NaOH
Pu(IV)-OH-H- Ca-Na-Cl- ClO ₄ -H ₂ O	Rai et al. [165]	298	pH 3.8–7.9 adjusted by HCl and NaOH; 0.0015 mol·kg $^{-1}$ CaCl ₂
	Lierse and Kim [103] (data taken from [84])	298	pH 1.5–11.5 in 1 mol·kg ^{-1} NaClO ₄
	Perez-Bustamante [166]	297	pH 0.5–3.5 in HClO ₄
	Fujiwara et al. [167]	298	pH 4–9 adjusted by HClO ₄ and NaOH in 1 mol·kg ⁻¹ NaClO ₄
	Efurd et al. [168]	298-363	рН 6-8.5
	Pazukhin and Kudryavtsev [104]	293	pH 1.5–10.3 in 3 mol·kg ⁻¹ (Na + H)ClO ₄
	Rothe et al. [169]	298	pH 0.45–0.73 adjusted by HCl in 0.5 mol·kg ⁻¹ NaCl
	Ewart et al. [61]	298	рН 7.4–13
	Peretrukhin et al. [95]	299	$0.5-16.7 \text{ mol}\cdot\text{kg}^{-1}$ NaOH
	Krot et al. [170] in Delegard [171]	298	$0.11-8 \text{ mol}\cdot\text{kg}^{-1}$ NaOH
	Shilov and Fedoseev [172] in Delegard [171]	298	0.09–0.9 mol·kg $^{-1}$ NaOH
	Delegard [78]	297	1–17.8 mol·kg ^{-1} NaOH and 1–5 mol·kg ^{-1} NaNO ₃
Pu(IV)-OH-Na- K-CO ₃ -H ₂ O	Delegard [78]	297	3.0–5.2 mol·kg ⁻¹ NaOH and $0.3-1.1$ mol·kg ⁻¹ Na ₂ CO ₃
	Yamaguchi et al. [173]	298	0.1 mol·kg ⁻¹ KCl; 0.0005–0.05 mol·kg ⁻¹ K ₂ CO ₃ ; 0.0001–0.1 mol·kg ⁻¹ KHCO ₃
	Rai et al. [38]	296	$\begin{array}{c} 0.1{-}6.2 \ \text{mol}{\cdot}\text{kg}^{-1} \ \text{K}_2\text{CO}_3 \ (0.01 \ \text{mol}{\cdot}\text{kg}^{-1} \\ \text{KOH}); \ 0.01{-}1.04 \ \text{mol}{\cdot}\text{kg}^{-1} \ \text{KHCO}_3 \end{array}$
	Moskvin and Gelman [174]	293	0.4–4.0 mol·kg ⁻¹ K ₂ CO ₃ ; $I = 7$ and 10 mol·kg ⁻¹ by KCl and KClO ₄
Pu(IV)-H-NO ₃ - H ₂ O	Brunstad [175]	298-373	0.1–0.7 mol·kg ⁻¹ HNO ₃ (Pu(OH) ₄ –HNO ₃ – H ₂ O)
	Rai [176]	295	pH 0.5–4.9 in 1.23×10^{-5} –0.316 mol·kg ⁻¹ HNO ₃ (Pu(OH) ₄ –HNO ₃ –H ₂ O)

System	Reference	<i>T</i> /K	PH range and ionic medium
	Gray and Swanson [79] in Clark and Delegard [80]	298, 323	2–7 mol·kg ⁻¹ HNO ₃ (Pu(NO ₃) ₄ –HNO ₃ –H ₂ O)
	Bohm [177] in Clark and Delegard [80]	298	2–7.5 mol·kg ⁻¹ HNO ₃ (Pu(NO ₃) ₄ –HNO ₃ – H ₂ O)
	Pugh [81] ^a in Clark and Delegard [80]	374–398	2–19 mol·kg ⁻¹ HNO ₃ (Pu(NO ₃) ₄ –HNO ₃ – H ₂ O)
	Glazyrin et al. [82] ^a in Clark and Delegard [80]	379–394	1–5 mol·kg ⁻¹ HNO ₃ (Pu(NO ₃) ₄ –HNO ₃ –H ₂ O)
Pu(V)–OH–Na– H ₂ O	Peretrukhin [95]	298	$0.6-16 \text{ mol}\cdot\text{kg}^{-1}$ NaOH
	Budantseva et al. [178]	298	8.4 mol·kg ^{-1} NaOH
	Barney and Delegard [108]	298	pH 8.3
Pu(VI)–OH–H– Na–H ₂ O	Pashalidis et al. [179]	295	pH 4.8–6; 0.1 mol·kg ⁻¹ NaClO ₄
	Fujiwara et al. [180]	298	pH 4.14–5; 0.1, 0.5, 1.0 mol·kg ⁻¹ NaClO ₄
	Kim et al. [135]	298	pH 5.6–12.4 adjusted by HClO ₄ and NaOH; 0.1 mol·kg ⁻¹ NaClO ₄
Pu(VI)-OH-CO ₃ - Na-H ₂ O	Reilly et al. [181] ^b	298	0.1–5.6 mol·kg ⁻¹ NaCl and 5.6 mol·kg ⁻¹ NaClO ₄ ; $pCO_2 = 1$ bar
	Wittenberg and Steinmeyer [182]	297	0–1 mol·kg ⁻¹ LiHCO ₃
	Robouch and Vitorge [183]	293	pH 3.3 and 7.6; 3 mol·kg ⁻¹ NaClO ₄ ; $pCO_2 = 0.3$ and 1 bar (solubility product and solubility)
	Pashalidis et al. [153, 154]	295	pH 3.5–7.9; 0.1 mol·kg ⁻¹ NaClO ₄ ; $pCO_2 = 0.01$ and 1 bar
	Neu et al. [184]	295	$0.1-5.0 \text{ mol} \cdot \text{kg}^{-1}$ NaCl; $pCO_2 = 1$ bar
	Drabkina [185]	293	0.5-3.5 mol·kg ⁻¹ (NH ₄) ₂ CO ₃
	Gelman et al. [186]	298	0.5–2.6 mol·kg ⁻¹ (NH ₄) ₂ CO ₃
Pu(VI)-H-NO ₃ - H ₂ O	Krevinskaia et al. [187]	298	2–20 mol·kg ⁻¹ HNO ₃ (PuO ₂ (NO ₃) ₂ –HNO ₃ – H ₂ O)
	Siekierski and Phillips [128] and references therein	298	0–20 mol·kg ⁻¹ HNO ₃ (PuO ₂ (NO ₃) ₂ –HNO ₃ – H ₂ O)
	Clark and Delegard [80]	298	$3 \ mol \cdot kg^{-1} \ HNO_3 \ (PuO_2(NO_3)_2 - HNO_3 - H_2O)$

Table 4 continue	d
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^a Boiling point data

^b Solubility product of PuO₂CO₃(s)

Formation of complexes in actinide solutions can be experimentally detected, as will be discussed in the sections that follow. These complexation reactions need to be taken into consideration simultaneously with the equilibria due to the dissociation of water and CO₂:

$$2H_2O \rightleftharpoons OH^- + H_3O^+ \tag{5}$$

$$CO_{2(aq)} + 2H_2O \rightleftharpoons HCO_3^- + H_3O^+$$
(6)

System	Reference	<i>T/</i> K	PH range and ionic medium
Np(IV)-OH-H-Na- Ca-Cl-ClO ₄ -H ₂ O	Moskvin[130]	298	pH 0.5–3; 0.1 mol·kg ^{-1} N ₂ H ₄
	Fellhauer et al. [188]	295	pH 11–12; 1.02–5.26 mol·kg ⁻¹ CaCl ₂
	Neck et al. [189]	296	pH 1.7–3.25; 0.1 mol·kg ⁻¹ NaClO ₄
	Ewart et al. [100]	298	pH 10–13; 10^{-4} – 10^{-3} mol·kg ⁻¹ Na ₂ S ₂ O ₄
	Rai and Ryan [102]	298	pH 6.9–14.2; 0.05 mol·kg ⁻¹ Na ₂ S ₂ O ₄
	Rai et al. [190]	298	pH 0.182.42; 0.01 mol·kg ⁻¹ NaCl; 0.01 mol·kg ⁻¹ CuCl/CuCl ₂ redox buffer
	Eriksen et al. [99]	298	pH 6–12; pH adjusted by HClO ₄ and NaOH, under Ar
	Nakayama et al. [101]	298	pH 5–14; 0.1 and 1.0 mol·kg ⁻¹ NaClO ₄ ; 0.05 mol·kg ⁻¹ Na ₂ S ₂ O ₄ or Fe or Cu
Np(IV)-OH-Na-K- ClO ₄ -CO ₃ -H ₂ O	Rai et al. [191]	295	$\begin{array}{l} 0.01-1.38 \ \text{mol}\cdot\text{kg}^{-1} \ \text{KOH}; \ 10^{-3}-2.13 \ \text{mol}\cdot\text{kg}^{-1} \\ \text{K}_2\text{CO}_3; \ 0.01-1 \ \text{mol}\cdot\text{kg}^{-1} \ \text{KHCO}_3; \ 0.05 \ \text{mol}\cdot\text{kg}^{-1} \\ \text{Na}_2\text{S}_2\text{O}_4 \end{array}$
	Kitamura and Kohara [192]	295	pH 8.5–13; 2 mol·kg ⁻¹ NaClO ₄ ; 0.005–0.1 mol·kg ⁻¹ NaHCO ₃
	Kim et al. [193]	298	pH 9.5–13; $1.3 \times 10^{-3} \text{ mol·kg}^{-1} \text{ Na}_2\text{CO}_3$
Np(V)-OH-H-Na- Cl-ClO ₄ -H ₂ O	Ewart et al. [60]	298	pH 9-13 adjusted by HCl and NaOH
	Lierse et al. [111]	298	pH 7–13 adjusted by HClO ₄ and NaOH; 1 mol·kg ⁻¹ NaClO ₄
	Nitsche and Edelstein [136]	298	pH 7; 0.1 mol·kg ⁻¹ NaClO ₄
	Yamaguchi et al. [194]	298	pH 6.5–13; 0.1 mol·kg ⁻¹ NaClO ₄
	Neck et al. [110]	298	pH 7.3–13.8; 0.1–3 mol·kg ⁻¹ NaClO ₄
	Moskvin [130]	298	pH 6.5–6.7; 0.1–0.2 mol·kg ⁻¹ NaNO ₂
	Sevostyanova and Khalturin [195]	296	pH 6.6–7.7; 0.02 mol·kg ⁻¹ NaNO ₃
	Nakayama et al. [196]	298	pH 7.2–12.5; 0.01 mol·kg ⁻¹ NaNO ₃
	Efurd et al. [168]	298-368	рН 6-8.5
Np(V)-OH-Na-Cl- ClO ₄ -CO ₂ /CO ₃ - H ₂ O	Neck et al. [112]	298	pH 6.6–10.8; $pCO_2 = 3 \times 10^{-4}$ –0.01 bar; 0.1–5 mol·kg ⁻¹ NaClO ₄ ; 5 mol·kg ⁻¹ NaCl
	Ueno and Saito [197]	293	$0.05-1.6 \text{ mol}\cdot\text{kg}^{-1} \text{ Na}_2\text{CO}_3$
	Maya [198]	298	pH 7–11; 1.0 mol·kg ⁻¹ NaClO ₄ ; $pCO_2 = 0-9 \times 10^{-3}$ bar; 1.5 × 10 ⁻⁶ – 0.093 mol·kg ⁻¹ Na ₂ CO ₃
	Meinrath [199]	298	pH 6.5–8.7; 0.1 mol·kg ⁻¹ NaClO ₄ ; $pCO_2 = 0.01$ bar
	Al Mahamid et al. [200]	295	$0.01-1.0 \text{ mol·kg}^{-1} \text{ Na}_2\text{CO}_3$; 5 mol·kg ⁻¹ NaCl; $0.1 \text{ mol·kg}^{-1} \text{ KCl}$

stem	Reference	<i>T</i> /K	PH range and ionic medium	
	Simakin [201]	298	$0.24-0.95 \text{ mol}\cdot\text{kg}^{-1} \text{ Na}_2\text{CO}_3; I = 3 \text{ mol}\cdot\text{kg}^{-1}$ (NaNO ₃)	
(VI)–OH–H–Na– Cl–H ₂ O	Gaona et al. [129]	295	pH 7.4–14.6; 0.1–5.6 mol·kg ⁻¹ NaCl	
	Moskvin [130]	298	рН 3.5–8.5	
(VI)–OH–Na– 2lO ₄ –CO ₂ /CO ₃ – I ₂ O	Kato et al. [131, 132]	298	pH 2.8–6.8; 0.1 mol·kg ⁻¹ NaClO ₄ ; $pCO_2 = 3 \times 10^{-4}$, 1.0 × 10 ⁻² , 0.8 bar	
(VI)–OH–H–Na– Cl–H ₂ O (VI)–OH–Na– ClO ₄ –CO ₂ /CO ₃ – H ₂ O	Gaona et al. [129] Moskvin [130] Kato et al. [131, 132]	295 298 298	pH 7.4–14.6; 0.1–5.6 mol·kg ⁻¹ NaCl pH 3.5–8.5 pH 2.8–6.8; 0.1 mol·kg ⁻¹ NaClO ₄ ; $pCO_2 = 3 \times 10^{-4}$, 1.0 × 10 ⁻² , 0.8 bar	

Table 5 continued

$$\mathrm{HCO}_{3}^{-} + \mathrm{H}_{2}\mathrm{O} \rightleftharpoons \mathrm{CO}_{3}^{2-} + \mathrm{H}_{3}\mathrm{O}^{+} \tag{7}$$

At solid–liquid equilibrium, the precipitation of solid actinide phases is accompanied by ionic equilibrium reactions, e.g.,

$$\operatorname{Am}(\operatorname{OH})\operatorname{CO}_{3(s)} \rightleftharpoons \operatorname{Am}^{3+} + \operatorname{CO}_3^{2-} + \operatorname{OH}^{-}$$
(8)

$$PuO_2(OH)_2 \cdot H_2O \rightleftharpoons PuO_2^{2+} + 2OH^- + H_2O$$
(9)

When the vapor phase above the solution contains CO₂, vapor–liquid equilibrium also needs to be considered:

$$CO_{2(aq)} \rightleftharpoons CO_{2(vap)}$$
 (10)

as the dissolved CO_2 can affect both the solution pH and the carbonate concentration (through Eqs. 6 and 7), which will in turn influence the hydrolysis (e.g., Eq. 1) and carbonate complexation of actinide ions (Eqs. 3 and 4). Thus, the thermodynamics of the system can be described simultaneously by the chemical equilibria (e.g., Eqs. 1–7), solid– liquid equilibria (e.g., Eqs. 8 and 9), and vapor–liquid equilibria (Eq. 10). A complete list of aqueous actinide species at various oxidation states that are considered in this study is given in Tables 6, 7, 8, 9 and 10, including the relevant hydroxide, chloride, and carbonate complexes. Table 11 contains a list of all solid phases. The methodology that is used for simultaneously solving chemical and phase equilibria in multicomponent systems has been described in detail in a previous work [23]. This methodology requires calculating the chemical potentials of all individual aqueous, solid, and vapor species. The chemical potentials of these species are determined using the MSE model.

2.2 The Mixed Solvent Electrolyte (MSE) Model

Details of the MSE model have been described previously [11, 13] and, therefore, only a brief summary is given here. The thermodynamic framework combines an excess Gibbs energy model for mixed-solvent electrolyte systems with a detailed treatment of chemical equilibria. The excess Gibbs energy is expressed as

$$\frac{G^{\text{ex}}}{RT} = \frac{G^{\text{ex}}_{\text{LR}}}{RT} + \frac{G^{\text{ex}}_{\text{II}}}{RT} + \frac{G^{\text{ex}}_{\text{SR}}}{RT}$$
(11)

where G_{LR}^{ex} represents the contribution of long-range electrostatic interactions, G_{II}^{ex} accounts for specific ionic (ion–ion and ion–molecule) interactions and G_{SR}^{ex} is a short-

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Species	$\Delta \overline{G}_{ m f}^{\circ}$	\overline{S}°	$c_{\mathrm{HKF},1}$
Am ³⁺	-599.417	-199.00^{a}	-88.00^{a}
AmOH ²⁺	-790.878	$-87.90^{\rm a}$	-13.00^{a}
$Am(OH)_2^+$	-977.203	-122.00^{a}	160.00 ^a
Am(OH) _{3(aq)}	-1161.130	-183.00^{a}	-509.00^{a}
AmCl ²⁺	-735.582	-173.00^{a}	44.00 ^a
$AmCl_2^+$	-868.821	-165.00^{a}	190.00 ^a
Am(OH) ₃ Cl ⁻	-1299.506	-126.26	-632.18
AmCO ₃ ^{+b}	-1177.012	-76.00^{a}	130.00 ^a
$\operatorname{Am}(\operatorname{CO}_3)_2^-$	-1731.820	$0.900^{\rm a}$	-140.00^{a}
$\operatorname{Am}(\operatorname{CO}_3)_3^{3-c}$	-2276.355	137.56	-430.79

Table 6 Standard partial molar Gibbs energies of formation, entropies, and parameters of the HKF equation of state for individual ionic and neutral Am(III) species

Parameters were determined in this study unless otherwise noted. Units: $\Delta \overline{G}_{f}^{\circ}$ in kJ·mol⁻¹, \overline{S}° and $c_{HKF,1}$ in J·mol⁻¹·K⁻¹. Other HKF parameters ($a_{HKF,1}$,..., $a_{HKF,4}$, $c_{HKF,2}$, ω) were set to zero due to insufficient experimental data for evaluating temperature and pressure dependence

^a Values were taken from Phillips et al. [7]

^b $\Delta \overline{G}_{\rm f}^{\circ}$ adjusted in this study, \overline{S}° and $c_{\rm HKF,1}$ estimated using values for Am(OH)_{3(aq)} and Cl⁻

^c $\Delta \overline{G}_{\rm f}^{\circ}$ and \overline{S}° adjusted in this study, $c_{\rm HKF,1}$ estimated using values for Am(CO₃)₂⁻ and CO₃²

Table 7 Standard partial molarGibbs energies of formation,	Species	$\Delta \overline{G}_{ m f}^{ m o}$	\overline{S}^{o}	c _{HKF,1}
entropies, and parameters of the HKF equation of state for indi-	Cm ³⁺	-596.002	-199.00^{a}	-88.00^{a}
vidual ionic and neutral Cm(III)	CmOH ²⁺	-790.069	-87.90^{a}	-13.00^{a}
species	$Cm(OH)_2^+$	-980.859	-122.00^{a}	160.00 ^a
	Cm(OH) _{3(aq)}	-1161.512	-183.00^{a}	-509.00^{a}
	CmCl ²⁺	-728.355	-173.00^{a}	44.00 ^a
	$CmCl_2^+$	-851.013	-165.00^{a}	190.00 ^a
	Cm(OH) ₃ Cl ⁻	-1297.166	-126.26^{a}	-632.18^{a}
	$CmSO_4^+$	-1362.151	11.72	71.71 ^b
	$\operatorname{Cm}(\operatorname{SO}_4)_2^-$	-2109.297	176.89	78.58 ^b
	$Cm(SO_4)_3^{3-}$	-2851.195	210.37	403.63
Parameters were determined in this study unless otherwise noted	$CmCO_3^+$	-1173.244	-76.00^{a}	130.00 ^a
Units: $\Delta \overline{G}_{f}^{\circ}$ in kJ·mol ⁻¹ , \overline{S}° and	$Cm(CO_3)_2^-$	-1730.795	$0.900^{\rm a}$	-140.00^{a}
$c_{\rm HKF,1}$ in J·mol ⁻¹ ·K ⁻¹ . Other	$Cm(CO_2)_3^{3-}$	-2273.414	71.34	-430.79^{a}
HKF parameters ($a_{HKF,1},,$ $a_{HKF,4}, c_{HKF,2}, \omega$) were set to zero due to insufficient experimental	$Cm(CO_3)_4^{5-}$	-2796.197	147.13	-721.58 ^b
	$CmHCO_3^{2+}$	-1203.034	-82.49	-123.40^{b}
data for evaluating temperature	Cm ₂ (HCO ₃) ₂ Cl ³⁺	-2572.553	203.81	-369.97^{b}
^a Values were set to be the same	$CaCm(OH)_{3}^{2+}$	-1717.808	-239.07 ^b	-88.34^{b}
as those for Am(III) species	$Ca_2Cm(OH)_4^{3+}$	-2443.021	-257.73 ^b	32.92 ^b
^b Values estimated using those of the constituent ions	$Ca_3Cm(OH)_6^{3+}$	-3339.531	-287.09 ^b	16.96 ^b

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thermodynamic proj	perties ($a_{HKF,1,4}$, c_{F}	HKF,1, $c_{HKF,2}$, ω) for in	dividual ionic and	l neutral Pu spec	ies			•	
Species	$\Delta \overline{G}_{\rm f}^{\rm o}$ /kJ·mol ⁻¹	\overline{S}^{0} /J·mol ⁻¹ ·K ⁻¹	$a_{HKF,1}$	$a_{ m HKF,2}$	<i>a</i> HKF,3	$a_{ m HKF,4}$	CHKF,1	CHKF,2	8
Pu ³⁺	-578.601^{a}	-185.00^{a}	0	0	0	0	-98.00^{a}	0	0
PuOH ²⁺	-777.923	-88.00^{a}	0	0	0	0	-12.00^{a}	0	0
$Pu(OH)_2^+$	-944.777	-122.00^{a}	0	0	0	0	160.00 ^b	0	0
$Pu(OH)_{3(aq)}$	-1152.098	-183.00^{b}	0	0	0	0	-508.98 ^b	0	0
Pu^{4+}	-481.599^{a}	-389.00^{a}	-1.46346^{c}	-6829.1°	50.8996°	88042°	98.396°	-355589 ^c	1499395 ^c
PuOH ³⁺	-715.899	-167.00^{a}	10.26080°	-42799.4°	-800.111^{c}	3969683°	112.41 ^c	-252298^{c}	1978158 ^c
$Pu(OH)_2^{2+}$	-951.701	-44.00^{a}	26.64844°	-99893.0°	-2221.70°	9841396°	117.52°	-150948^{c}	2303305°
$Pu(OH)_3^+$	-1187.691	44.00^{a}	36.40172°	-171076.2°	-1986.50^{c}	13722056°	47.729°	-1023239^{c}	2327869°
$Pu(OH)_{4(aq)}$	-1376.000	75.00^{a}	-26.89655°	122219.7°	2483.50°	-11032957^{c}	10.080°	2216533°	4428722 ^c
$Pu(OH)_5^-$	-1548.942	96.00^{a}	0	0	0	0	-66.00^{a}	0	0
$Pu(OH)_6^{2-}$	-1704.670	85.29 ^d	0	0	0	0	-203.19^{d}	0	0
$Pu(CO_3)_5^{6-}$	-3328.799	160.00°	0	0	0	0	-735.00^{e}	0	0
$Pu(OH)_2(CO_3)_2^{2-}$	-2107.355	-144.01 ^d	0	0	0	0	-623.58 ^d	0	0
$Pu(OH)_3(CO_3)_2^{3-}$	-2296.108	-154.72^{d}	0	0	0	0	-760.78^{a}	0	0
PuO_2^+	-852.645^{a}	-21.00^{a}	-0.71831°	-5009.7°	43.748°	-95563°	104.30°	61996°	259390°
$PuO_2OH_{(aq)}$	-1034.247	96.00^{a}	-5.65472°	20568.6°	650.252°	-2290359°	90.449°	479658°	989788°
$PuO_2(OH)_2^-$	-1181.315	-42.42 ^d	-0.16228°	-3652.0°	38.412°	-101176°	152.82°	76732°	742610 ^c
$PuO_2(OH)_3^{2-}$	-1366.913	-53.13^{d}	-0.16697^{c}	-3663.4°	38.457 ^c	-101129°	218.57 ^c	82843°	1437208^{c}
PuO_2^{2+}	-756.898^{a}	-88.00^{a}	-0.17061°	-3672.3°	38.492 ^c	-101092°	86.556°	-105038^{c}	588434°
PuO_2OH^+	-964.525	26.00^{a}	13.25864°	-41368.4°	-1198.61°	4569807°	86.164°	572693°	985236°
$PuO_2(OH)_{2(aq)}$	-1147.424	-109.42^{d}	0	0	0	0	-263.39^{d}	0	0
$PuO_2(OH)_3^-$	-1315.734	-120.13^{d}	0	0	0	0	-400.58^{d}	0	0
PuO ₂ CO _{3(aq)}	-1339.461	-36.00^{a}	0	0	0	0	-289.00^{a}	0	0
$PuO_2(CO_3)_2^{2-}$	-1899.310	175.00^{a}	0	0	0	0	-155.00^{a}	0	0

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Table 8 continued									
Species	$\Delta \overline{G}_{\mathrm{f}}^{\mathrm{o}}$ /kJ·mol ⁻¹	\overline{S}^0 /J·mol ⁻¹ ·K ⁻¹	<i>a</i> HKF,1	<i>a</i> HKF,2	<i>d</i> HKF,3	$a_{ m HKF,4}$	CHKF,1	CHKF,2	3
$PuO_2(CO_3)_3^{4-}$	-2441.285	-17.90 ^a	0	0	0	0	-527.00^{a}	0	0
Parameters were dete J \cdot mol ⁻¹ \cdot K ⁻¹ , c _{HKF,2}	ermined in this study in J-K-mol ⁻¹ , ω in .	/ unless otherwise no J·mol ⁻¹	ted. Units: a _{HKF,1}	in J·mol ⁻¹ ·bar ⁻¹	atter,2 in J-mol	-1, a _{HKF,3} in J·K·m	$\mathrm{nol}^{-1} \cdot \mathrm{bar}^{-1}, a_\mathrm{H}$	KF,4 in J·K·mol ⁻	¹ , c _{HKF,1} in
^a Values were taken	from literature [2, t	6, 7]							
^b Values are assume	ed to be the same as	those for the corresl	ponding Am(III)	species, and were	taken from Phi	llips et al. [7]			
^c Parameters were b	ased on Shock et al.	. [31, 42]							
^d Estimated using va	alues for constituent	ions							
e Values were taken	from literature [7]	for Np(CO ₃) $_{5}^{6-}$							

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Table 9Standarmolar thermodyn	d partial molar Gibt amic properties (a _{HK}	s energies of formatio E.1,4, $c_{HKF,1}$, $c_{HKF,2}$, ω)	n, entropies, and) for individual ic	parameters of th	e Helgeson-Kir U species	kham–Flowers e	quation of state	: [28-31] for star	ıdard partial
Species	$\Delta \overline{G}_{\rm f}^{\rm o}$ /kJ·mol ⁻¹	\overline{S}^0 /J·mol ⁻¹ ·K ⁻¹	<i>a</i> HKF,1	<i>a</i> HKF,2	aHKF,3	$a_{ m HKF,4}$	CHKF,1	CHKF,2	0
U^{4+}	-537.180	-416.73^{a}	-1.79226^{a}	-7628.23 ^a	53.9548^{a}	-84734^{a}	168.28^{a}	-125261 ^a	1541176 ^a
UOH ³⁺	-791.023	-376.69	0.90420^{a}	-1048.68^{a}	28.1960^{a}	-111935 ^a	157.10^{a}	20476^{a}	964747^{a}
UO^{2+}	-781.605	-316.44	$0.93734^{\rm a}$	-965.793^{a}	27.8290^{a}	-112278^{a}	30.596^{a}	-320432^{a}	656219 ^a
HUO_2^+	-975.709^{a}	-47.70^{a}	1.35106^{a}	44.1412^{a}	$23.8651^{\rm a}$	$-116453^{\rm a}$	58.792^{a}	-109918^{a}	304888^{a}
$\mathrm{UO}_{2(\mathrm{aq})}$	-978.219^{a}	-108.78^{a}	$1.03194^{\rm a}$	-735.840^{a}	26.9466^{a}	-113227^{a}	71.479^{a}	35819^{a}	-12552^{a}
HUO_3^-	-1146.834^{a}	-172.80^{a}	1.33152^{a}	-3.8493^{a}	24.0542^{a}	-116252^{a}	284.68^{a}	-471332^{a}	941526^{a}
UCl ³⁺	-669.863	-213.05	0	0	0	0	285.00^{b}	0	0
$UO(CO)_{3}^{4-}$	-2469.125	-289.74^{c}	0	0	0	0	-967.34°	0	0
UO_2^{2+}	-956.408	317.27	$1.26591^{\rm a}$	-1718.95^{a}	64.1516^{a}	-109165^{a}	88.157 ^a	17991 ^a	589902^{a}
UO_2OH^+	-327.289	406.48	1.99326^{a}	1612.05 ^a	17.7059^{a}	-122934^{a}	55.329 ^a	$-90316.^{a}$	206062 ^a
$UO_{3(aq)}$	-1130.935^{a}	-53.97^{a}	1.58159 ^a	607.18^{a}	21.6463^{a}	-118780^{a}	22.683^{a}	-133783^{a}	-12552^{a}
HUO_4^-	-1317.123^{a}	-84.10^{a}	2.06539^{a}	1788.58^{a}	17.0025^{a}	$-123662^{\rm a}$	154.54^{a}	61388^{a}	809144^{a}
UO_4^{2-}	-1238.464^{a}	-113.39^{a}	2.13233 ^a	1950.00^{a}	16.4109^{a}	-124332^{a}	56.538^{a}	-505377^{a}	1515403^{a}
$\rm UO_4OH^{3-}$	-1411.372	-124.10^{d}	2.65646 ^d	1980.87^{d}	24.1191 ^d	-240735 ^d	73.902 ^d	-938254^{d}	2236976 ^d
UO ₂ CO _{3(aq)}	-1542.126	418.53	2.45936°	3386.03°	90.9886°	-218547 ^e	74.363 ^e	-701310^{e}	2008864 ^e
$\mathrm{UO}_2(\mathrm{CO}_3)_2^{2-}$	-2110.196	459.74	3.65280°	-5053.10°	117.8256 ^e	-327929 ^e	60.370°	-1420610^{e}	3427826 ^e
${\rm UO}_2({\rm CO}_3)_3^{4-}$	-2637.853	167.28	4.84624 ^e	-6720.17 ^e	144.6626^{e}	-437312 ^e	46.477 ^e	-2139911 ^e	4846787 ^e

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Table 9 continue	þ								
Species	$\Delta \overline{G}_{\rm f}^{\rm o}$ /kJ·mol ⁻¹	\overline{S}^0 /J·mol ⁻¹ ·K ⁻¹	$a_{ m HKF,1}$	$a_{ m HKF,2}$	<i>a</i> HKF,3	$a_{ m HKF,4}$	CHKF,1	CHKF,2	з
UONO ⁺	-1057.586	149.91	4.32697^{f}	1118.80^{f}	44.5546 ^f	-237170 ^f	120.37 ^f	-263383°	1049180^{e}
Parameters were c J-mol ⁻¹ ·K ⁻¹ , c _{HK1}	determined in this stu 7,2 in J·K·mol ⁻¹ , ω	idy unless otherwise no in J.mol ⁻¹	ted. Units: a _{HKF,1}	in J·mol ⁻¹ ·bar ⁻¹	, a _{HKF,2} in J·mol	⁻¹ , $a_{HKF,3}$ in J·K	c.mol ⁻¹ ·bar ⁻¹ ,	² HKF,4 in J·K·mol ⁻	-1, c _{HKF,1} in
^a Parameters were	e taken from Shock	et al. [33]							
^b Values taken fr	om Lemire and Trei	maine [6]							
^c Estimated using	values for UO ²⁺ at	nd CO_3^{2-}							
^d Estimated using	; values for UO_4^{2-} at	-HO pu							
^e Estimated using	; values for UO_2^{2+} at	nd CO_3^{2-}							
f Estimated using	values for UO_2^{2+} ar	$1d NO_3^-$							

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molar thermodynamic pr	roperties $(a_{HKF,1,4}, c$	HKF,1, $c_{HKF,2}$, ω) for in	ldividual ionic a	nd neutral Np sp	ecies			,	
Species	$\Delta \overline{G}_{\mathrm{f}}^{\mathrm{o}}/\mathrm{kJ}\cdot\mathrm{mol}^{-1}$	$\overline{S}^0/J\cdot mol^{-1}\cdot K^{-1}$	<i>a</i> HKF,1	<i>d</i> HKF,2	<i>a</i> HKF,3	aHKF,4	CHKF,1	CHKF,2	З
Np^{4+}	-489.076	-389.10^{a}	0	0	0	0	-112.00^{a}	0	0
NpOH ³⁺	-738.217	-167.00^{a}	0	0	0	0	-110.00^{a}	0	0
$Np(OH)_2^{2+}$	-978.433	-44.00^{a}	0	0	0	0	-42.00^{a}	0	0
$Np(OH)_3^+$	-1222.908	44.00^{a}	0	0	0	0	50.00^{a}	0	0
Np(OH) _{4(aq)}	-1423.154	75.00^{a}	0	0	0	0	-695.00^{a}	0	0
$Np(OH)_{5}^{-}$	-1578.071	96.00^{a}	0	0	0	0	-76.00^{a}	0	0
$Np(OH)_2(CO_3)_3^{4-}$	-2686.839	-26.63^{a}	0	0	0	0	-83.68 ^b	0	0
$Np(CO_3)_5^{6-}$	-3370.890	160.00^{a}	0	0	0	0	-735.00^{a}	0	0
NpO_2^+	-921.279	-21.00^{a}	0	0	0	0	92.00^{a}	0	0
$NpO_2OH_{(aq)}$	-1095.610	25.00^{a}	0	0	0	0	-48.00^{a}	0	0
$NpO(OH)_2^-$	-1262.497	40.00°	0	0	0	0	-185.19 ^b	0	0
NpO ₂ Cl _(aq)	-1028.678	80.00^{a}	0	0	0	0	-33.00^{a}	0	0
$NpO_2CO_3^-$	-1474.032	200.00^{a}	0	0	0	0	-7.00^{a}	0	0
$NpO_2(CO_3)_2^{3-}$	-2014.341	110.00^{a}	0	0	0	0	-348.00^{a}	0	0
$NpO_2(CO_3)_3^{5-}$	-2536.362	80.00^{a}	0	0	0	0	-648.02^{a}	0	0
$ m NpO_2^{2+}$	-819.658	-94.00^{a}	0	0	0	0	-8.00^{a}	0	0
NpO_2OH^+	-1027.858	24.00^{a}	0	0	0	0	63.00^{a}	0	0
$(\mathrm{NpO}_2)_2(\mathrm{OH})_2^{2+}$	-2053.235	-14.00^{a}	0	0	0	0	-62.00^{a}	0	0
$(\mathrm{NpO}_2)_3(\mathrm{OH})_5^+$	-3497.858	116.00^{a}	0	0	0	0	2.00^{a}	0	0
$NpO_2(OH)_3^-$	-1409.410	-126.13 ^b	0	0	0	0	$-419.58^{\rm b}$	0	0
$NpO_2(OH)_4^{2-}$	-1584.954	-136.85 ^b	0	0	0	0	-556.77 ^b	0	0
NpO ₂ CO _{3(aq)}	-1404.5646	-36.00^{a}	0	0	0	0	-289.00^{a}	0	0
$NpO_2(CO_3)_2^{2-}$	-1967.267	116.10^{a}	0	0	0	0	-203.00^{a}	0	0

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Table 10 continued									
Species	$\Delta \overline{G}_f^o/kJ\cdot mol^{-1}$	$\overline{S}^{0}/J \cdot M^{-1} \cdot K^{-1}$	<i>a</i> HKF,1	<i>a</i> HKF,2	<i>a</i> HKF,3	aHKF,4	CHKF,1	CHKF,2	3
$\mathrm{NpO}_2(\mathrm{CO}_3)_3^{4-}$	-6.498	38.10^{a}	0	0	0	0	-535.00^{a}	0	0
Parameters were detern $J \cdot mol^{-1} \cdot K^{-1}$, $c_{HKF,2}$ in	nined in this study un J·K·mol ⁻¹ , ω in J·m	less otherwise noted. I ol ⁻¹	Jnits: a _{HKF,1} in J	$mol^{-1} \cdot bar^{-1}, a_{j}$	_{HKF,2} in J·mol ⁻¹	, a _{HKF,3} in J.K.mo	d^{-1} ·bar ⁻¹ , $a_{HKF,4}$	in J·K·mol ⁻¹ , c _H	KF,1 in
^a Values were taken fr	om literature [7]								
^b Values were estimate	d based on those of	the constituent ions							
^c Values were taken fr	om Guillaumont et ai	l. [2]							

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Solid phase	$\Delta G_{ m f}^{ m o} \ \Lambda { m J} \cdot { m mol}^{-1}$	$S^{\circ}/J \cdot mol^{-1} \cdot K^{-1}$	$C_p (J \cdot mol^{-1} \cdot K^-)$	$^{1}) = A + BT + C/T^{2}$	$+ DT^2 + ET^3$		1
			A	В	С	D	Ε
Am(OH) ₃ (am)	-1216.293	209.00^{a}	150.00^{a}	0	0	0	0
Am(OH) ₃ (cr)	-1226.565	116.00^{g}	150.00^{a}	0	0	0	0
Am(OH)CO ₃	-1417.828	87.60	102.00^{a}	0	0	0	0
$Am_2(CO_3)_3$	-3002.062	481.67	204.00^{a}	0	0	0	0
NaAm(CO ₃) ₂ .6H ₂ O	-3465.624	693.69	$326.36^{\rm b}$	0	0	0	0
Cm(OH) ₃ (am)	-1213.682	134.01 ^c	150.00^{d}	0	0	0	0
Cm(OH)CO ₃	-1414.887	87.60 ^d	102.00^{d}	0	0	0	0
$Cm_2(CO_3)_3$	-2996.321	481.67 ^d	204.00^{d}	0	0	0	0
NaCm(CO ₃) ₂ ·6H ₂ O	-3463.649	693.69 ^d	326.36^{d}	0	0	0	0
$UO_2(cr)^e$	-1029.682	71.13	96.5249	-0.028515	-2305401	1.6996e-5	0
U(OH) ₄ (am)	-1497.872	$160.67^{\rm b}$	146.44 ^b	0	0	0	0
$UO_2(OH)_2 \cdot H_2O$	-1636.986	486.03	182.84^{b}	0	0	0	0
$UO_2(OH)_2$ (s) ^e	-1377.687	543.73	41.80	0.20000	3530000	0	0
UO ₂ CO ₃ (s)	-1568.013	463.02	120.10 ^e	0	0	0	0
NaUO ₂ OOH·H ₂ O ^e	-1861.570	275.90	262.83	0.014653	-3549040	0	0
Na ₄ UO ₂ (CO ₃) ₃ (s)	-3713.923	590.76	311.68 ^b	0	0	0	0
$UO_2(NO_3)_2.2H_2O$	-1617.317	413.21	278.20^{f}	0	0	0	0
$UO_2(NO_3)_2^{-3}H_2O$	-1860.491	477.11	332.00^{f}	0	0	0	0
UO ₂ (NO ₃) ₂ .6H ₂ O	-2581.407	627.92	466.90^{f}	0	0	0	0
$Pu(OH)_3(am)$	-1206.293	92.00^{a}	105.00^{a}	0	0	0	0
$Pu(OH)_4(am)$	-1434.179	278.40	131.00^{a}	0	0	0	0
$Pu(NO_3)_4.5H_2O$	-2093.180	560.57 ^b	475.46 ^b	0	0	0	0
PuOH(NO ₃) ₃ ·5H ₂ O	-2235.930	391.50	438.39^{b}	0	0	0	0
PuO ₂ OH(am)	-1061.297^{a}	86.99^{a}	86.00^{a}	0	0	0	0

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Table 11 continued							
Solid phase	$\Delta G_{\mathrm{f}}^{\mathrm{o}} \ A \mathrm{J} \cdot \mathrm{mol}^{-1}$	$S^{\circ}/J \cdot mol^{-1} \cdot K^{-1}$	$C_p (J \cdot mol^{-1} \cdot \mathbf{k})$	$(^{-1}) = A + BT +$	$C/T^2 + DT^2 + ET^3$		
			A	В	С	D	Ε
Na ₂ PuO ₂ (OH) ₃ ·2H ₂ O	-2386.834	242.17 ^b	248.40 ^b	0	0	0	0
NaPuO ₂ (OH) ₂ (s)	-1503.361	119.49 ^b	121.63 ^b	0	0	0	0
$PuO_2(OH)_2 \cdot H_2O$	-1431.100	190.00^{g}	170.00^{g}	0	0	0	0
PuO ₂ (NO ₃) ₂ ·3H ₂ O	-1684.646	$345.14^{\rm b}$	$308.82^{\rm b}$	0	0	0	0
$PuO_2(NO_3)_2 \cdot 6H_2O$	-2399.926	484.59 ^b	419.82 ^b	0	0	0	0
PuO ₂ (NO ₃) ₂ ·HNO ₃ ·3H ₂ O	-1776.706	$433.17^{\rm b}$	382.88 ^b	0	0	0	0
$PuO_2CO_3(s)$	-1369.072	99.20^{b}	104.60^{b}	0	0	0	0
Np(OH) ₄ (am)	-1470.542	138.99^{a}	131.00^{a}	0	0	0	0
NpO ₂ OH(am)	-1130.634	101.00^{a}	85.98^{a}	0	0	0	0
$Na_3NpO_2(CO_3)_2(s)$	-2839.179	295.60^{b}	237.99 ^b	0	0	0	0
NaNpO ₂ CO ₃ ·3.5H ₂ O	-2603.783	314.01^{b}	268.82 ^b	0	0	0	0
NpO ₂ (OH) ₂ ·H ₂ O	-1499.462	159.83 ^b	153.85 ^b	0	0	0	0
$Na_2Np_2O_7(s)$	-2729.190	212.21 ^b	199.58^{b}	0	0	0	0
$NpO_2CO_3(s)$	-1433.748	116.11 ^b	104.60^{b}	0	0	0	0
Property values were determir	ned in this study unless of	herwise noted					

^a Values were taken from literature [2, 7]

^b Values were estimated [43-45] in this study

^c Values were taken from Konings et al. [5]

^d Values were set to be the same as those of corresponding Am compounds

 $^{\circ}$ Values of C_p coefficients were taken from Glushko et al. [202] and Grenthe et al. [3]

^f Values were taken from Wagman et al. [203]

^g Values were taken from Guillaumont et al. [2]

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range contribution resulting from intermolecular interactions. The activity coefficients of any aqueous species can be derived from the excess Gibbs energy by taking the derivative of G^{ex} with respect to the number of moles of a given species. The functional form of activity coefficients is summarized in Appendix 1. The long-range interaction contribution is calculated from the Pitzer–Debye–Hückel formula [24] expressed in terms of mole fractions and symmetrically normalized. The specific ion-interaction contribution is calculated from an ionic strength-dependent, symmetrical second virial coefficient-type expression [11]:

$$\frac{G_{\rm II}^{\rm ex}}{RT} = -\left(\sum_{i} n_i\right) \sum_{i} \sum_{j} x_i x_j B_{ij}(I_x) \tag{12}$$

where $B_{ii}(I_x) = B_{ii}(I_x)$, $B_{ii} = B_{ij} = 0$ and the ionic strength dependence of B_{ij} is given by

$$B_{ij}(I_x) = b_{ij} + c_{ij}exp(-\sqrt{I_x + a_1})$$
(13)

where b_{ij} and c_{ij} are adjustable parameters and a_1 is set equal to 0.01. The parameters b_{ij} and c_{ii} are represented as functions of temperature as

$$b_{ij} = b_{0,ij} + b_{1,ij}T + b_{2,ij}/T \tag{14}$$

$$c_{ij} = c_{0,ij} + c_{1,ij}T + c_{2,ij}/T$$
(15)

For most electrolyte systems, these three terms are sufficient for representing the variations of properties with temperature up to 573 K. Additional temperature-dependent terms and pressure-dependent parameters have been introduced for a limited number of systems [25] for which the additional complexity is justified by the availability of data over extended ranges of temperatures and pressures.

The short-range interaction contribution is calculated from the UNIQUAC equation [26]. When justified by experimental data, the temperature dependence of the UNIQUAC energetic parameters is expressed using a quadratic function:

$$a_{ij} = a_{ij}^{(0)} + a_{ij}^{(1)}T + a_{ij}^{(2)}T^2$$
(16)

For electrolyte systems encountered in nuclear waste treatment and nuclear fuel reprocessing, the ionic strength and the concentrations of actinide components can be large. Therefore, the specific ion-interaction contribution is the most important term for reproducing the properties of the solutions. When a chemical process occurs in solutions where undissociated inorganic acids or bases are present in significant amounts, the short-range contribution is introduced to account for molecular interactions between the undissociated acid (or base). It should be noted that the G_{II}^{ex} term can also be applied to non-ionic mixtures or weakly ionized systems, and has been found to improve the simultaneous fit to multiple properties in weak and/or associating electrolyte systems when B_{ij} is introduced between two neutral molecules [25, 27].

While the excess Gibbs energy model is used to calculate nonideality effects on solution properties, the chemical equilibrium is governed by the chemical potentials of all species that participate in various reactions, such as precipitation, hydrolysis, and complexation (cf. Eqs. 1-10). For aqueous species, the chemical potential of each ionic or neutral species

i in the liquid phase (L) is determined by its standard-state chemical potential, $\mu_i^{L,o,x}(T,p)$, and its activity coefficient, γ_i^x , i.e.,

$$\mu_i^{\mathcal{L}}(T, p, x) = \mu_i^{\mathcal{L}, o, x}(T, p) + RT \ln x_i \gamma_i^x \tag{17}$$

Here, the superscript ^o denotes the standard state and the superscript ^x indicates that the values of the properties (e.g., $\mu_i^{\text{L},o,x}(T,p)$ and γ_i^x) are expressed on the mole fraction basis. The standard-state chemical potentials are calculated as functions of temperature and pressure based on the Helgeson–Kirkham–Flowers (HKF) equation of state [28–30] using the standard partial molar Gibbs energy of formation ($\Delta \overline{G}_f^\circ$) and standard partial molar entropy (\overline{S}°) at a reference pressure (1 bar) and temperature (298.15 K), and 7 other species-specific parameters. The equation and the HKF parameters are summarized in Appendix 2. The parameters of the HKF model are available for various aqueous species including selected actinide species [31–33]. The standard-state properties calculated from the HKF model are based on the infinite dilution reference state and on the molality concentration scale. To make the equilibrium calculations consistent when the standard-state properties are combined with the mole fraction-based and symmetrically normalized activity coefficients, two conversions are performed [11]:

(1) The activity coefficients calculated from Eq. 11 are converted to those based on the unsymmetrical reference state, i.e., at infinite dilution in water:

$$\ln\gamma_i^{x,*} = \ln\gamma_i^x - \lim_{\substack{x_i \to 0 \\ x_w \to 1}} \ln\gamma_i^x \tag{18}$$

where the superscript * denotes the activity coefficient defined on the unsymmetrical basis and $\lim_{\substack{x_i \to 0 \\ x_w \to 1}} \ln \gamma_i^x$ is the value of the symmetrically-normalized activity coefficient

at infinite dilution in water, which is calculated by substituting $x_i = 0$ and $x_w = 1$ into the activity coefficient equations and

(2) The molality-based standard-state chemical potentials, $\mu_i^{L,o,m}(T,p)$, are converted to corresponding mole fraction-based quantities, $\mu_i^{L,o,x}(T,p)$ [11]:

$$\mu_i^{\text{L},\text{o},x}(T,p) = \mu_i^{\text{L},\text{o},m}(T,p) + RT \ln\left(\frac{1000}{M_{\text{H}_2\text{O}}}\right)$$
(19)

where $M_{\rm H_2O}$ is the molar mass of water. The values of $\ln \gamma_i^{x,*}$ and $\mu_i^{\rm L,o,x}$ from Eqs. 18 and 19 are then used in Eq. 17 to determine the chemical potential of each species for chemical equilibrium calculations. Thus, the calculations require the availability of parameters for both the standard-state properties and activity coefficients.

For the species in the vapor phase (g), the chemical potential of species *i* is given by the standard relation

$$\mu_i^{g} = \mu_i^{g,o}(T) + RT \ln\left(\frac{py_i\phi_i(T,p)}{p^o}\right)$$
(20)

where $\mu_i^{g,o}(T)$ is the chemical potential of pure component *i* in the ideal gas state, y_i is the mole fraction in the gas phase, $\phi_i(T,p)$ is the fugacity coefficient, *p* is the total pressure, and $p^o = 1$ bar. The $\mu_i^{g,o}(T)$ term is calculated from the ideal-gas Gibbs energy of formation, $\Delta G_f^{g,o}$, absolute entropy, $S^{g,o}$, at the reference temperature of 298.15 K, and heat

capacity as a function of temperature, $C_p^{g}(T)$, using standard thermodynamics [34]. For water, this term was obtained from the equation of state of Haar et al. [35] The fugacity coefficient was calculated from the Soave–Redlich–Kwong equation of state [36].

In the cases of solid phases (s), the chemical potential of the pure solids, $\mu_i^{s,o}(T)$, is calculated as a function of temperature from the solid-state standard-state Gibbs energy of formation, $\Delta G_{\rm f}^{\rm s,o}$, absolute entropy, $S^{\rm s,o}$, and heat capacity as a function of temperature, $C_p^{\rm s}(T)$.

2.3 Determination of Model Parameters

The MSE thermodynamic framework has been parameterized for actinide systems based on the analysis of extensive literature data on solubility, speciation, and vapor-liquid equilibrium. Experimental studies of radioactive actinides face a number of challenges. One of the challenges stems from the radiolytic effects and radioactive decay of actinides, which complicate the measurements of their concentrations in solutions and in solid phases. Also, the precipitates can be difficult to characterize because they are subject to aging and have variable water contents. In addition, the existence of multiple redox states can cause problems in designing experiments so that a certain oxidation state can be dominant under given conditions. For transplutonium elements such as Am and Cm, the trivalent oxidation state is by far the most stable one under most conditions. However, multiple oxidation states may coexist in a relatively wide range of conditions for other actinides considered in this study, especially for Pu [37-39]. This is due to the fact that the reduction potentials for the Pu⁴⁺/Pu³⁺, PuO₂⁺/Pu⁴⁺, PuO₂²⁺/Pu⁴⁺, and PuO₂²⁺/PuO₂⁺ couples lie relatively close to each other, making it easy for multiple oxidation states to coexist in solution [1]. Also, redox equilibria may be shifted by complexation, hydrolysis, and precipitation reactions. In such systems, species in specific oxidation states may exist only under carefully controlled redox conditions. Rard [40] summarized various challenges and difficulties in the interpretation of experimental solubility data and discussed the speciation of Np, Pu, and U in a comprehensive review and critical evaluation of the literature.

In view of the two application areas considered in this study and taking into account the complexities of the actinide systems, the model needs to be developed based on a combined analysis of different actinides at the same oxidation state, and, for a given actinide, at different redox states. Specifically, the analysis is focused on trivalent Am and Cm and the main oxidation states of Np, Pu, and U for which experimental solubility and/or speciation data are available, i.e.,

- A. Am(III)
- B. Cm(III)
- C. Np(IV), Np(V), Np(VI)
- D. Pu(III), Pu(IV), Pu(V), Pu(VI)
- E. U(IV), U(VI)

Considering the nature of the solubility and speciation data that are available, we analyze the solution chemistry of each of the actinide systems in two steps:

 The effects of acids, bases, and additional electrolyte components (i.e., NaCl, CaCl₂, MgCl₂, NaClO₄, and Na₂SO₄) on the solubility and speciation in CO₂/CO₃-free systems; 2. The effect of CO₂ and carbonates {i.e., (K/Na)₂CO₃, (K/Na)HCO₃} with or without acids/bases and extra salt components.

The first step lays the foundation for establishing the appropriate acid–base chemistry, the formation of hydroxide complexes, and the dependence of solubility on the solution pH and salt concentrations. On this basis, the additional effects of CO_2 are analyzed in step 2.

As isotopes of plutonium and uranium are the most important fissile materials for nuclear energy applications, these two actinides have also been investigated in concentrated nitric acid and/or nitrate salts mixtures that are encountered in nuclear fuel processing. Therefore, in addition to the above two steps, a third step is included for Pu and U:

 Solubilities in concentrated U(VI)–NO₃–HNO₃–H₂O, Pu(VI)–NO₃–HNO₃–H₂O, and Pu(IV)–NO₃–HNO₃–H₂O mixtures

Experimental thermodynamic data have been extensively reported in the literature for these mixtures. These data extend to high concentrations with respect to both the actinides and the acid (i.e., up to $x'_{HNO_3} = 0.7$, where the prime ' denotes the mole fraction on a salt-free basis, or equivalently $m_{HNO_3} = 127 \text{ mol} \cdot \text{kg}^{-1}$) and provide an excellent foundation to apply the MSE model. Modeling such systems would be difficult, if not impossible, using conventional electrolyte models, such as the Pitzer molality-based ion-interaction model [24], for which the maximum concentration limit is usually 6 mol·kg⁻¹. Tables 1, 2, 3, 4 and 5 summarize the primary literature sources that were used for developing the model, together with the conditions at which the experimental data were measured including the temperatures and the concentration ranges of salts, acids or bases.

Due to the presence of various salt components in the actinide solubility or speciation measurements, it is necessary to account for the effects of these components by incorporating the relevant model parameters that provide appropriate activity coefficients for the background electrolyte. In previous studies, the MSE model parameters have been established for binary, ternary, and multicomponent Na–K–Ca–Mg–H–NO₃–SO₄–Cl–CO₃/HCO₃/CO₂–OH systems to reproduce chemical and phase equilibria for such mixtures from the freezing point up to 573 K and from infinite dilution to solid saturation or the fused salt or pure acid/base limit. Parameters that determine the properties of individual species (i.e., the standard-state partial molar Gibbs energy of formation, entropy, and the HKF equation parameters) as well as the binary interaction parameters (Eqs. 4 and 5) have been reported previously [14, 17, 25, 27, 41].

In the present work, we determine the actinide-specific model parameters. In the first step, solubility and hydrolysis equilibria in CO_2/CO_3 -free systems were analyzed to evaluate the standard-state partial molar properties (i.e., $\Delta \overline{G}_f^\circ, \overline{S}^\circ$, and HKF coefficients) of various aqueous actinide hydroxide/oxide complexes and actinide-bearing solids ($\Delta G_f^\circ, S^\circ$, and C_p°). Based on the parameters established in the first step, systems with CO_2 and carbonates were examined in the second step and solubility data were regressed. In the third step, parameters were determined for U and Pu in mixtures with nitric acid. The parameters that were evaluated in the second and third steps include the standard-state molar properties for additional aqueous species, especially carbonate complexes, and solids that precipitate in the presence of CO_2 , carbonates, nitric acid, and nitrates. They also include the ion-interaction parameters between the actinide species and the prevailing ions in these solutions (e.g., CO_3^{2-} , NO_3^{-}). In the presence of other salt, acid or base components, ion-interaction parameters have also been introduced between actinides and the ions

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that result from the dissociation of the additional components (e.g., Na⁺, Cl⁻, OH⁻). This is necessary to reflect the non-ideality of concentrated actinide solutions.

For most systems that were studied in this work, experimental data were reported only at ambient conditions. Thus, the only standard-state thermochemical property that could be determined by regressing experimental data was the Gibbs energy of formation ($\Delta G_{\rm f}^{\circ}$ or $\Delta \overline{G}_{\rm f}^{\circ}$). For such systems, the standard partial molal entropy, \overline{S}° , and HKF coefficients for aqueous species as well as the S° and C_{p}° parameters for solids were taken from literature sources [2, 6, 7, 33], or estimated based on the methodology of Shock et al. [31, 42] or group contribution approaches [43–45]. For systems for which data are available over an extended range of temperature, the S° (or \overline{S}°) and C_{p}° (or HKF coefficients) values have been obtained by evaluating the temperature dependence of the speciation and solubility data.

The parameters that have been determined in the present work are collected in Tables 6, 7, 8, 9, 10, 11, 12, 13 and 14. These parameters, combined with those determined in our previous studies [14, 17, 25, 27, 41], provide a complete representation of chemical speciation and phase equilibria.

3 Results and Discussions

3.1 Trivalent Systems

Although trivalent species exist for all of the actinides studied here, they are prevalent only for americium and curium under the conditions of natural aqueous environments [46, 47]. Trivalent species of Np, Pu, and U are unstable as they can be readily oxidized and may exist only under carefully controlled reducing conditions. As a result, literature data are more abundant for Am(III) and Cm(III). For Pu(III), experimental solubility data have been obtained only at carefully managed conditions to ensure the stability of Pu(III) during the measurements [48]. In this section, we analyze the chemistry of Am(III), Cm(III), and Pu(III) based on the available experimental speciation and solubility data. The analysis is also supported by the chemical analogies among trivalent actinides and rare earth elements because marked similarities in various properties have been relied on in the development of thermochemical databases for missing thermodynamic data in actinide systems [1, 2, 4]. The trivalent actinides are grouped together in the thermodynamic analysis so that general trends in the chemical and phase behavior can be examined. It can be expected that such trends may be of interest in the study of other trivalent actinides.

3.1.1 Am(III)

The Am(III) system has been studied fairly extensively in the literature. Table 1 summarizes the reported experimental solubility data. The standard-state partial molal properties (i.e., $\Delta \overline{G}_{f}^{\circ}$, \overline{S}° , and $\overline{C_{p}}^{\circ}$) for Am³⁺ and the complexes of Am³⁺ with hydroxide, chloride, and carbonate ions are among the properties reported in the compilations of OECD-NEA [2] and Phillips et al. [7] Thermodynamic analysis has been first performed for CO₂/CO₃-free environments, in which americium hydroxide, Am(OH)_{3(s)}, is identified as the solid phase in equilibrium with solutions over a wide range of pH. Considerable

Table 12 Binary pai	rameters in the virial	interaction term (Eqs. 1	[4 and 15) determined	in this study for species pa	irs involving the Cm,	, Np, and Pu species	
Species i	Species j	$b_{0,ij}$	$b_{2,ij}$	Species i	Species j	$b_{0,ij}$	$b_{2,ij}$
Cm ³⁺	Cl ⁻	24.89529	0	CmCl_2^+	Na^+	-13.24650	0
$CmOH^{2+}$	Cl ⁻	24.89529	0	Cm^{3+}	SO_4^{2-}	72.88739	0
$Cm(OH)_2^+$	Cl_	24.89529	0	$\rm CmOH^{2+}$	SO_4^{2-}	72.88739	0
CmCl ²⁺	CI_	4.197485	0	CmSO_4^+	CI_	19.62042	0
$CmCl_2^+$	Cl ⁻	4.197485	0	CmSO_4^+	Na^+	-16.72136	0
Cm^{3+}	Na^+	-13.24650	0	$\operatorname{Cm}(\operatorname{SO}_4)^2$	Na^+	18.22998	0
CmCl ²⁺	Na^+	-13.24650	0	$\operatorname{Cm}(\operatorname{SO}_4)_3^{3-}$	Na^+	18.22998	0
$NpO_2CO_3^-$	Na^+	8.172669	0	$\mathrm{NpO}_2(\mathrm{CO}_3)_2^{3-}$	Cl ⁻	18.53955	0
$NpO_2(CO_3)_2^{3-}$	Na^+	8.172669	0	$NpO_2(CO_3)_3^{5-}$	Cl ⁻	18.53955	0
$NpO_2(CO_3)_3^{5-}$	Na^+	8.172669	0	NpO ₂ Cl _(aq)	HCO_3^-	30.36849	0
$NpO_2CO_3^-$	CO_3^{2-}	91.37748	0	NpO ₂ Cl _(aq)	CO _{2 (aq)}	30.36849	0
$NpO_2(CO_3)_2^{3-}$	CO_3^{2-}	91.37748	0	NpO ₂ Cl _(aq)	Cl ⁻	30.36849	0
$NpO_2(CO_3)_3^{5-}$	CO_3^{2-}	91.37748	0	NpO ₂ Cl _(aq)	Na^+	30.36849	0
$NpO_2CO_3^-$	HCO_3^-	57.82193	0	$NpO_2(OH)_3^-$	Na^+	17.26653	0
$NpO_2(CO_3)_2^{3-}$	HCO_3^-	57.82193	0	$NpO_2(OH)_4^{2-}$	Na^+	17.26653	0
$NpO_2(CO_3)_3^{5-}$	HCO_3^-	57.82193	0	$NpO_2(OH)_3^-$	-HO	38.71964	0
$NpO_2CO_3^-$	Cl ⁻	18.53955	0	$NpO_2(OH)_4^{2-}$	-HO	38.71964	0
Pu^{4+}	NO_3^-	-2.874251	-894.4466	$Pu(OH)_3(CO_3)_2^{3-}$	_HO	28.83416	0
PuOH ³⁺	NO_3^-	-2.299401	-715.5572	$Pu(OH)_6^{2-}$	-HO	6.562490	0
$Pu(OH)_2^+$	NO_3^-	-1.437125	-447.2233	$PuO_2(OH)_3^{2-}$	Na^+	31.41855	0
$Pu(OH)_3^+$	NO_3^-	-0.7185627	-223.6116	PuO_2^{2+}	NO_3^-	0.6285105	0
$Pu(OH)_{5}^{-}$	CO_3^{2-}	28.83416	0	PuO_2^{2+}	HNO _{3 (aq)}	2.302976	0
$Pu(OH)_6^{2-}$	CO_3^{2-}	28.83416	0	$PuO_2(CO_3)_2^{2-}$	NH^+_4	-31.82653	0

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. I	$j = b_{0,ij}$	$b_{2,ij}$	Species i	Species j	$b_{0,ij}$	$b_{2,ij}$
$Pu(OH)_2(CO_3)_2^{2-}$ CO_3^{2-}	28.83416	0	$PuO_2(CO_3)_3^{4-}$	NH_4^+	-377.5370	0
$Pu(OH)_3(CO_3)_2^{3-}$ CO_3^{2-}	28.83416	0	$PuO_2(CO_3)_3^{4-}$	Li ⁺	123.6782	0
$Pu(OH)_2(CO_3)_2^{2-}$ OH^-	28.83416	0				

			•				
Species i	Species j	$b_{0,ij}$	$b_{1,ij}$	$b_{2,ij}$	$c_{0,ij}$	$c_{1,ij}$	$c_{2,ij}$
HUO_3^-	CO_3^{2-a}	-35.35930	0	0	0	0	0
$UO(CO_3)_3^{4-}$	CO_3^{2-a}	69.15088	0	0	0	0	0
$UO(CO_3)_3^{4-}$	HCO_3^{-a}	210.6932	0	0	0	0	0
UO_2^{2+}	NO_3^{-b}	-30.50353	-0.0001058757	13627.33	0.2140163	0.0001687714	-20505.12
UO_2^{2+}	HNO ^b _{3 (aq)}	19.29809	0	-9270.832	-175.6417	0	54200.20
UO_2OH^+	NO_3^{-b}	-41.36595	0	340.9370	53.48925	0	-209.0866
$UO_2NO_3^+$	NO_3^{-b}	11.93504	0.003534430	-9645.152	3.670460	0	0
$UO_2NO_3^+$	HNO ^b _{3 (aq)}	-2.311574	0	-2107.953	0	0	0
^a Parameters we	re determined based	on experimental data a	t 298 K				
^b Parameters we	are determined based	on experimental data i	n a temperature range of 2	255–598 K			

 Table 13
 Binary parameters in the virial interaction term (Eqs. 14 and 15) for species pairs involving U species

Table 14 Binary parameters (Eqs. $14-16$) for species pairs in the HNO + H O system	Species i	Species j	$b_{0,ij}$	$b_{2,ij}$	$a_{ij}^{\left(0 ight)}$
$11100_3 + 11_20$ system	HNO _{3(aq)}	H_2O	-3.228640	1942.850	5334.530
	N ₂ O ^a _{5(aq)}	H ₂ O	-3.228640	1942.850	5334.530
Parameters were determined based on experimental data in a	HNO _{3(aq)} HNO _{3(aq)}	N_2O_5 (aq) NO_3^-	0 1.548040	508.5590 -1081.110	
temperature range of 225–554 K. Values of $b_{1,ij}$ and $c_{0,ij} - c_{2,ij}$ are set equal to zero for all pairs	$HNO_{3(aq)}$ $N_2O_{5(aq)}$ N_2O_{2}	H_3O^+ NO_3^- H_2O^+	1.548040 1.548040 1.548040	-1081.110 -1081.110 1081.110	
^a Values of $a_{ij}^{(1)}$ and $a_{ij}^{(2)}$ are set equal to zero	NO_3^-	H_3O^+	3.211300	-2127.870	

discrepancies exist between the reported $Am(OH)_{3(s)}$ solubility data. Analysis of the data has revealed that these discrepancies can be primarily attributed to the preparation methods, aging of the samples, and levels of crystallinity. In general, if the crystallinity was not established by means of analytical methods or not indicated by the authors, the solid is most likely amorphous. Additionally, the scatter of the data may also be due to radiolysis reactions, which can alter the redox potential of the solution and cause the oxidation of Am(III). In fact, increased solubilities have been observed for Am at higher oxidation states [49-51]. Regardless of the uncertainties in the experimental data, solubility products have been reported for two forms of solid americium hydroxide, i.e., the crystalline Am(OH)3(cr) and the amorphous Am(OH)3(am) [2]. These two forms of solid Am(OH)₃ generally define the limits of solid precipitation. The higher solubility results from the metastability of the amorphous phase, $Am(OH)_3(am)$, which would be converted into the stable, less soluble crystalline phase, $Am(OH)_{3(cr)}$, if the thermodynamic equilibrium was reached. Here, we take into consideration both of these solid forms in order to be able to predict the solubilities of the metastable as well as the stable phases. The experimental data and the calculated results are compared in Fig. 1 for non-complexing environments (Fig. 1a) and in the presence of substantial concentrations of Cl⁻ ions, which induce complexation (Fig. 1b). The lines in these figures are calculated using the model with parameters listed in Tables 6 and 11. These results also demonstrate how sensitive the model parameters (e.g., the standard molar Gibbs energies of formation, $\Delta G_{\rm f}^{\circ}$) are to the uncertainties of the data from which these parameters were determined. For example, in Fig. 1a, the differences between the higher solubility defined by the metastable solid Am(OH)3(am) and the lower solubility defined by Am(OH)3(cr) span nearly two orders of magnitude, which corresponds to a difference of 2.4 kJ·mol⁻¹ (or ca 0.8%) in $\Delta G_{\rm f}^{\circ}$ (cf. Table 11) between these two solid phases.

In Fig. 1b, the solubilities of $Am(OH)_{3(s)}$ in NaCl concentrations up to 5.6 mol·kg⁻¹ [49, 52, 53] are shown. These data were used for modeling the effect of the chloride ion on the solubility and for determining the properties of the $Am(III)-Cl^-$ complexes. The $Am(OH)_{3(s)}$ solubility is shown to increase with the chloride concentration as a result of the $Am(III)-Cl^-$ complex formation (Fig. 1b). This is illustrated by the differences between the baseline solubility in the absence of Cl^- (cf. the lowest line in Fig. 1b) and the solubilities in 0.6 and 5.6 mol·kg⁻¹ NaCl. This behavior is accurately reproduced by the model. The accelerated increase in the baseline solubility (i.e., in 0.1 mol·kg⁻¹ NaClO₄) with decreasing pH at pH < 6 causes it to converge with the solubility at 0.6 mol·kg⁻¹ NaCl. This is most likely due to activity coefficient effects for the different anions (e.g., Cl^- versus ClO_4^-) in that region; such an increase appears to be consistent with the trend of



the experimental data shown in Fig. 1a. The $\Delta \overline{G}_{f}^{\circ}$ values for the aqueous species (Table 6) and ΔG_{f}° for the two (crystalline and amorphous) solids (Table 11) were determined by regressing the literature solubility data (Table 1) while the S° and C_{p}° values were taken from the literature [2, 7]. A mixed complex, Am(OH)₃Cl⁻, has been introduced as it plays a key role in alkaline solutions at high Cl⁻ concentrations. In general, at high ionic concentrations, ambiguity exists between the formation of a physical entity (such as a complex) and the physical interactions between two (or more) species when they interact in close proximity. In this case, better results are obtained by explicitly considering this complex because the very small Am(III) concentrations in alkaline solutions render the physical interactions between Am(OH)_{3(aq)} and Cl⁻ insufficiently significant to reproduce the increase of solubility with increasing chloride concentration.

In the presence of carbonates and/or CO₂, solid-liquid equilibrium becomes more complicated due to the formation of additional Am-carbonate complexes and the

precipitation of multiple solids. At least three Am-bearing carbonate solids have been identified in the literature. Depending on conditions, the solubility in CO_2 or CO_3^{2-} -containing systems may be controlled by the formation of Am(OH)CO_{3(s)}, Am₂(CO₃)_{3(s)}, or NaAm(CO₃)₂·xH₂O [51], in addition to Am(OH)_{3(s)}. Standard-state thermochemical properties have been reported in the literature for all these solids [2, 7]. However, while the solubility data for Am(OH)CO_{3(s)} and Am₂(CO₃)_{3(s)} have been reported, the $\Delta G_{\rm f}^{\circ}$ value for $NaAm(CO_3)_2 xH_2O$ that is reported in the OECD-NEA compilation [2] is based on measurements that are not publicly accessible. Thus, the actinide-lanthanide analogy has led us to investigate the NaAm(CO₃)₂·xH₂O solubility on the basis of the available data for NaNd($(CO_3)_2$ ·6H₂O [54]. Therefore, a solid phase in the form of NaAm($(CO_3)_2$ ·6H₂O has been considered in the present work. Based on the literature solubility data listed in Table 1 and those reported for an analogous solid, NaNd(CO₃)₂·6H₂O [54], the standardstate thermochemical properties have been determined for the three Am carbonate solids, i.e., $Am(OH)CO_{3(s)}$, $Am_2(CO_3)_{3(s)}$, and $NaAm(CO_3)_2 \cdot 6H_2O$. The values of S° for these solids have been evaluated based on the solubility data at elevated temperatures [50]. These standard-state property values are listed in Table 11. Figure 2 shows how the model represents the literature solubilities at various partial pressure of CO_2 (Fig. 2a) and at different total carbonate concentrations (Fig. 2b). Both the experimental data and the calculated results indicate that an increase in pCO_2 causes a shift of the solubility curve toward lower pH. Similar trends have also been observed for lanthanide and other actinide systems [55, 56]. While the experimental identification of the solid phases can be cumbersome for these systems, the calculated results show clear trends. At higher pCO_2 (i.e., $pCO_2 \ge 0.1$ atm), the solid phase Am₂(CO₃)_{3(s)} precipitates whereas Am(OH)CO_{3(s)} forms at lower pCO_2 (i.e., $pCO_2 \le 0.01$ atm). Increased pH favors the precipitation of NaAm(CO₃)₂·6H₂O. In the presence of a carbonate salt (e.g., in 3×10^{-5} and 7×10^{-2} $mol kg^{-1} Na_2CO_3$ [57]), it is the Am(OH)CO_{3(s)} phase that precipitates at relatively low pH (e.g., pH < 11) whereas $Am(OH)_3(s)$ is the stable solid at elevated pH (i.e., pH > 11).

The data of Meinrath and Kim [58], which were measured at $pCO_2 = 10^{-2}$ bar show considerably higher solubilities and are shifted toward higher pH values compared to the data measured at $pCO_2 = 10^{-3}$ atm by Felmy et al. [57] and at atmospheric pCO_2 (i.e., $10^{-3.5}$ bar) by Bernkopf and Kim [59]. Thus, the Meinrath and Kim data are closer to those measured under CO_2 -free conditions and are inconsistent with the trend that is evident for Am(III) and other actinides and lanthanides [56]. Further analysis of these experiments indicates that the equilibrium time in the solubility measurements of Meinrath and Kim was only 2-3 days whereas Felmy et al. measured the solubilities from both oversaturation and undersaturation with an equilibration time up to 66 days. It has been noted that 36 days are about the right amount of time to reach equilibrium [46, 57] as prolonged equilibration time may result in a significant decrease of pH due to radiolysis-induced acidification of the samples. Also, the solid phase in the Meinrath and Kim experiments was identified as $Am_2(CO_3)_{3(s)}$ based on the XRD, DTA and TGA analysis performed on solid samples obtained from the Nd(III)-CO3 system under similar conditions whereas Felmy et al. confirmed the solid phase to be $Am(OH)CO_{3(s)}$ from direct XRD analysis of the Ambearing solid samples. Although Nd(III) provides a reasonable analogue for the analysis of Am(III) data, Meinrath and Kim [58] may have used insufficient equilibration time to precipitate the thermodynamically stable solid. Therefore, these data were not included in the determination of model parameters but are shown in Fig. 2a for comparison. In Fig. 2, the computed results for CO_3/CO_2 -free systems are also plotted as a baseline to show the solubility trends in the limit of $pCO_2 = 0$. The lower (dashed) curve in the CO_3/CO_2 -free



Fig. 2 Solubilities of Am(III) in the Am(III)–H–OH–CO₂/CO₃–H₂O system: **a** at various values of pCO₂, where 1 atm = 1.01325 bar; **b** at fixed total carbonate concentrations. Results at extended pCO₂ are also shown in (**b**) and compared with extrapolated solubilities at a total Na₂CO₃ = 0.07 mol·kg⁻¹ at lower pH. All results are at or near 298 K. The literature data are from sources listed in Table 1 as indicated in the legend; the *lines* are calculated using the model with parameters listed in Tables 6 and 11

system represents the thermodynamically stable crystalline $Am(OH)_{3(cr)}$ phase while the upper (solid) one denotes the amorphous $Am(OH)_3(am)$. In the case of the data of Ewart et al. [60, 61] (Fig. 2b), an improved fit may be obtained if mixed complexes (e.g., $Am(OH)_2CO_3^-$, $AmOH(CO_3)_2^{2-}$, etc.) are introduced, as in the work of these authors. However, considering the large discrepancies in experimental data among various sources (even from the same authors) within a range of comparable CO_2/CO_3 conditions, we omitted such mixed complexes and consider our model to represent the experimental results within their uncertainty. The results shown in Fig. 2 are consistent with those obtained by other authors [51, 62–64].

Due to low solubilities, only the standard-state thermochemical properties of the Am(III) aqueous species and solids are necessary to reproduce experimental results in Figs. 1 and 2. No ion interaction parameters have been introduced to model the Am(III) systems.

3.1.2 Cm(III)

Compared to Am(III), much less extensive solubility data have been published for Cm(III). The only available solubility data have been recently reported in alkaline solutions containing concentrated NaCl and CaCl₂ [65, 66]. These data have been measured in conjunction with spectroscopic studies of Cm(III) solutions. Compared to the solubility data, relatively extensive spectroscopic studies of Cm(III) solutions have been published, including measurements at temperatures up to 473 K [67]. Specifically, time resolved laser fluorescence spectroscopy (TRLFS) was used to investigate aqueous complexation and speciation of Cm(III). TRLFS has been proved to be highly sensitive and selective for studying the speciation of Cm(III) and enables the Cm(III) species concentrations to be measured at the trace level, which is not assessible by any other method [68]. The majority of the TRLFS studies have been reported during the past 20 years by Fanghänel and collaborators [67, 69–73] and are of great value in the development of the thermodynamic model for Cm(III) solutions.

As noted earlier, the solubilities of the hydroxides of Am(III), Pu(III), and Nd(III) are similar, resulting in similar solubility products and hydrolysis constants [74]. In view of the lack of comprehensive Cm(III) solubility data, chemical analogies between actinides and rare earth elements [75] have been utilized in conjunction with the TRLFS speciation results to establish hydrolysis equilibria for Cm(III) over a wide range of pH. The Cm(OH)₃(s) solubility data at higher pH [65] show trends as a function of pH that are consistent with those for Am(OH)₃(am) at lower pH values [76], when measured under otherwise identical conditions (e.g., all in 5.6 mol·kg⁻¹ NaCl solutions). Thus, the Cm(III) model parameters have been developed based on a combined analysis of (1) Cm(III) speciation results from TRLFS measurements, (2) Cm(III) solubility data, which are limited to the alkaline range at high chloride (e.g., NaCl and CaCl₂) concentrations, and (3) solubilities estimated from those for Am(III) solutions, including values computed using the Am(III) parameters for the CO₂ effect, which has not been investigated for Cm(III).

The TRLFS results provide the necessary speciation input for determining the standardstate thermochemical properties of the Cm(III) species. The solid phases are considered to be similar to those in the corresponding Am(III) systems, i.e., Cm(OH)_{3(s)}, Cm(OH)CO_{3(s)}, Cm₂(CO₃)_{3(s)}, and NaCm(CO₃)₂·6H₂O. The reported Cm(III) solubility data have been attributed to the formation of colloidal Cm(OH)₃(am) particles [65, 66], and thus only a single form of solid Cm(OH)₃(am) is considered in this work. The standard-state thermochemical properties for aqueous and solid species are listed in Tables 7 and 11. Additionally, the complex solubility and speciation behavior at high salt concentrations necessitates introducing the ion-interaction parameters for Cm(III) species. These parameters are listed in Table 12.

Figure 3 compares the experimental speciation with that calculated using the model. Figure 3a depicts the distribution (in mole fractions) of uncomplexed Cm^{3+} and various carbonate complexes as a function of the overall carbonate concentration. Figure 3b illustrates the distribution of Cm^{3+} and its chloride complexes as a function of CaCl_2 concentration. For the results shown in Fig. 3b, the pH of the solution has been adjusted to approximately 2 to avoid the hydrolysis in the determination of Cm–Cl complexation. Fig. 3 Comparison of experimental and calculated distribution (in mole fractions) of Cm(III) species: a Variation of Cm(III) and its carbonate complexes with carbonate concentration in aqueous solutions with equal molalities of Na₂CO₃ and NaHCO₃ at the ionic strength of 1.0 mol·kg $^{-1}$ (NaCl). Experimental results were obtained at pH 9.03-9.44 and the lines are calculated at an average pH of 9.38; b Variation in the distribution of Cm(III) and its chloride complexes with CaCl₂ concentration (pH \sim 2), where M denotes the molarity in mol·dm⁻³. All results are at 298 K. The literature data are from Fanghänel et al. [69, 72]; the lines are calculated using the model with parameters listed in Table 7



The Cm(OH)_{3(s)} solubilities are shown in Fig. 4, which compares the experimental data (solid symbols) and calculated results (solid lines). These solubilities were obtained in solutions containing concentrated NaCl or CaCl₂. In 5.6 mol·kg⁻¹ NaCl solutions, Cm(OH)₃(am) solubilities were reported at high NaOH concentrations at pH > 14 (cf. the solid triangles in Fig. 4). These results appear to be a continuation of the solubility curve for Am(OH)₃(am), which was determined at lower pH values at the same NaCl concentration (cf. the hollow triangles in Fig. 4). The speciation results that are listed in Table 2 and illustrated in Fig. 3 have been used, together with the solubility data, to determine the standard partial molar properties of Cm hydroxide (Cm(OH)_n³⁻ⁿ, n = 0-3) and Cm chloride (CmCl_n³⁻ⁿ, n = 1, 2) complexes. These complexes affect the solubility over wide ranges of pH and Cl⁻ concentration. As with Am(III), a mixed complex, Cm(OH)₃Cl⁻, has been assumed to account for the solubility in the alkaline range.

For the solubility data measured in concentrated alkaline CaCl₂ solutions (at pH 10–12), there is a substantial increase in the solubility with increasing pH. Such an increase is not observed in the NaOH–NaCl solutions and, thus, cannot be attributed to the formation of strong Cm(OH)_n²⁻ⁿ complexes. Examination of analogous systems of the type Ca–M–OH $\{M = Zr(IV) \text{ and Th}(IV)\}$ at similar CaCl₂ concentrations revealed the formation of ternary complexes of the stoichiometry Ca₃[Zr(OH)₆]⁴⁺ and Ca₄[Zr(OH)₈]⁴⁺ as determined by EXAFS [66, 77]. Therefore, three mixed complexes Ca[Cm(OH)₃]²⁺,





 $Ca_2[Cm(OH)_4]^{3+}$ and $Ca_3[Cm(OH)_6]^{3+}$ have been proposed for the CaCl₂–NaOH–Cm(III) mixtures [65]. These complexes are also included in the present model to represent the solubility behavior of Cm(OH)₃(am) in the presence of concentrated CaCl₂ in alkaline solutions. With these complexes, the model accurately represents the solubility trends as illustrated in Fig. 4. The Cm–Cl complexation causes an increase in solubility with CaCl₂ concentration. The effect of chloride concentration on the solubility of CmOH)₃(am) can be put into perspective by comparing the results obtained for concentrated NaCl and CaCl₂ solutions with a baseline calculated for a 0.1 mol·kg⁻¹ NaCl solution, in which complexation is negligible (cf. the lowest, dashed line in Fig. 4). The chloride complexation effect is similar to that observed for Am(III) solutions (cf. Fig. 1b). An additional comparison between trivalent actinides is included in Sect. 3.1.3.

3.1.3 Pu(III)

The only available solubility data for Pu(III) are those reported by Felmy et al. [48] at 298 K, measured under carefully controlled reducing conditions to ensure that Pu(III) is stable. The standard-state thermochemical properties of aqueous and solid species that are reported in the literature [2, 6, 7] were used as initial values in modeling the hydrolysis and solubility behavior of Pu(OH)₃(am) as a function of pH. For a quantitative representation of the solubility data, the values of ΔG_f^0 have been adjusted for aqueous Pu(III) hydroxide complexes and for solid Pu(OH)₃(am). The final values of these properties are given in Tables 8 (aqueous species) and 11 (solids). Figure 5 compares the data of Felmy et al. (open squares) with the model calculations (dotted line). To analyze the similarities in the solubility behavior of trivalent actinides, the solubilities of Am(OH)₃(am) (dashed line and crosses) and Cm(OH)₃(am) (solid line), all determined in 0.1 mol·kg⁻¹ NaClO₄ solutions, are also shown in Fig. 5. The calculated solubilities of these three actinide hydroxides fall in a relatively narrow concentration band, which is essentially within the scattering of experimental data.



3.2 Tetravalent Systems

Solubility data have been extensively reported in the literature for Np(IV), Pu(IV), and U(IV). For all of these tetravalent actinides, the effects of pH and varying concentrations of acids, bases and chloride, perchlorate and carbonate salts have been experimentally studied (cf. Tables 3, 4 and 5). In addition, solubilities were measured for Pu(IV) in nitrate salt solutions and in nitric acid up to high concentrations [78–80]. Although the majority of literature data were measured at ambient conditions, solubility data at temperatures as high as 373 K for Pu(IV) and 573 K for U(IV) have also been reported (cf. Tables 3 and 4). Boiling point data have also been reported for Pu(NO₃)₄ in concentrated nitric acid solutions [80–82]. The data at elevated temperatures, when combined with those measured at ambient conditions, make it possible to determine the temperature dependence of the thermodynamic parameters.

$3.2.1 \ U(IV)$

Standard-state partial molar properties of uranium species have been published based on a comprehensive analysis of literature data including solubilities [33]. These properties provide an excellent basis for the determination of model parameters for uranium(IV). Two solid forms of U(IV), i.e., UO₂(cr) and UO₂·*x*H₂O, have been identified [83] and solubility data have been reported for these phases [8]. However, a comparison of data from different sources reveals large discrepancies of nearly four orders of mangnitude at all pH values. As discussed earlier, the sources of such discrepancies may include inadvertent oxidation that may result in spuriously high solubilities. Also, a contributing factor may be a failure to distingush between $UO_2(cr)$ and $UO_2\cdot xH_2O$ (e.g., $U(OH)_4(am)$) most likely refer to a range of solid phases with different thermodynamic stabilities. In addition, errors may be due to measuring solubilities near the analytical detection limits and to difficulties in achieving reducing conditions.

For model development, data from solubility measurements under rigidly controlled redox conditions and with a careful characterization of solid phases using structural identification tools such as XRD are preferred. In general, considering various sources,

such data show a solubility difference of approximately 1-2 orders of magnitude between $UO_2(cr)$ and $UO_2 xH_2O$ at a fixed pH, with $UO_2(cr)$ being the stable (less soluble) phase. Based on the published standard-state thermochemical properties of aqueous U(IV) species and solids, the solubility behavior can be predicted for U(IV) solutions as a function of pH. chloride concentration, and temperature. However, large discrepancies between the predicted and experimental solubilities are obtained using the published thermochemical property values. In the paper of Neck and Kim [84], the solubility of $UO_2(cr)$ was estimated using a K_{sp} value derived from the standard state Gibbs energy of formation, $\Delta G_{\rm f}^{\circ}({\rm UO}_2({\rm cr}))$. With this $K_{\rm sp}$ value, the calculated solubility at neutral pH is several orders of magnitude ($\sim 10^{-15} \text{ mol·kg}^{-1}$) lower than the experimental data (10^{-10} - 10^{-8} $mol kg^{-1}$) [83, 85, 86]. In Neck and Kim's analysis of the data reported in neutral to alkaline solutions at 100–300 °C by Parks and Pohl [85], it was concluded that the solubilities obtained in these measurements did not refer to UO₂(cr), but rather to an amorphous surface layer. While this can be a possibility, we note that the K_{sn} value used in the work of Neck and Kim was derived from a $\Delta G_{f}^{\circ}(UO_{2}(cr))$ value that was calculated from the standard molar enthalpy of formation, $\Delta H_{\rm f}^{\circ}({\rm UO}_2({\rm cr}))$, and standard molar entropy, $S^{\circ}(UO_{2}(cr))$, which were obtained from the calorimetrically determined enthalpy of oxidation of $UO_2(cr)$ to $U_3O_8(cr)$ and low-temperature heat capacities of the solid $UO_2(cr)$ [3]. The derivation from these data (i.e., the enthalpy of oxidation and heat capacity) to obtain $\Delta H_{\rm f}^{\circ}({\rm UO}_2({\rm cr}))$ and $S^{\circ}({\rm UO}_2({\rm cr}))$ requires some numerical steps, including the integration of the heat capacity with respect to temperature, that may introduce additional errors besides those present in the direct measurements. It has been noted that calorimetric data often fail to reproduce the solubility products of many solids, with relevant examples given in a recent study of hydrothermal mobilization and mineral deposition of lanthanides, a group that is analogous to actinides [87]. The disagreement has been attributed to either erroneous values of the standard enthalpy of formation of the solids, or to a low accuracy of the determination of the entropy, or to both. Faced with a choice between the indirectly determined K_{sp} based on calorimetric data and the directly measured solubility data, we have decided to use the solubility data to establish the model parameters and to determine the values of $\Delta G_{\rm f}^{\circ}({\rm UO}_2({\rm cr}))$ and $S^{\circ}({\rm UO}_2({\rm cr}))$.

To achieve the optimum representation of solubility data, the thermochemical property values have been re-evaluated by regressing the experimental results. In this study, the $UO_2(cr)$ and $U(OH)_4(am)$ solid phases have been considered. Among the various sets of experimental measurements for U(IV) under CO_2/CO_3 -free conditions, the solubility data of Ryan and Rai [88], Rai et al. [89, 90], and Fujiwara et al. [91] for $U(OH)_4(am)$, and of Rai et al. [83], Yajima et al. [86], and Parks and Pohl [85] for $UO_2(cr)$ were used in the parameterization of the model because these measurements were performed under carefully controlled reducing conditions and used extra measures to remove or minimize carbonate contamination (e.g., under inert gas or by treating alkaline solutions with $Ba(OH)_2$ or $BaCl_2$). The solubilities from these sources are in general agreement for the corresponding solid phases. These data are shown as solid symbols in Fig. 6 as indicated in the legend. In chloride solutions, a chloride complex, UCl³⁺, has been taken into consideration as it has been identified in the literature [3]. This complex has been found to be most prominent in acidic environments, e.g., in aqueous HCl solutions when hydrochloric acid is used for pH adjustment whereas measurements at higher pH values reveal little effect of chlorides on solubility over wide ranges of chloride concentrations [90].

Several solubility data sets were reported in aqueous NaOH solutions up to concentrations of ca. 11 mol·kg⁻¹ [88, 92, 93]. These data, from different sources, show a

1.E+00

1.E-01

1.E-02

1.E-03

1.E-04 1.E-05 1.E-06 1.E-07 1.E-08 1.E-09 1.E-10

1 E-11

U(IV), mol·kg⁻





Fig. 6 Solubilities of $U(OH)_4(am)$ at 298 K and of $UO_{2(cr)}$ at 298, 373, 473, and 573 K. The *symbols* denote the literature data listed in Table 3 and as indicated in the legend; the *lines* are calculated using the model with parameters given in Tables 9 and 11. Data points at 298 K from different sources are not differentiated to avoid being overcrowded, but primary sources used to parameterize the model are shown as *filled symbols* with references indicated in the legend

consistent solubility increase with OH⁻ concentration. Measurements reported by Fujuwara et al. [91] in the pH range of approximately 12–14 also show a strong solubility increase with pH. The solubility results of Gayer and Leider [93] and Galkin and Stepanov [92] are significantly higher compared to other measurements [88, 91], which has been attributed to the oxidized U(VI) species [8, 84]. Although the increase in solubility with OH⁻ concentration has been suspected to be due to U(IV)–carbonate complexation [88], no details were provided to quantify such effects. At the same time, the increase in the solubility of U(IV) and a similar actinide, Pu(IV), with pH has been explained by the formation of hydrolyzed anionic species in a number of studies [91, 94–96]. In our data analysis, we have attributed such increase to the formation of the hydrolyzed anionic U(IV) species. The strong correlation between the solubility and the hydrolysis of the U⁴⁺ ion are represented by the formation of five hydroxide complexes, i.e., UOH³⁺, UO²⁺, HUO⁺₂, UO_{2(aq)}, and HUO⁻₃. In alkaline solutions, it is the anionic species HUO⁻₂ that plays a key role in the increased solubility at pH > 12. It should be noted that the forms of the hydrolyzed species are taken from Shock et al. [33], and can be reconciled, if necessary,

with the conventional forms, $U(OH)_n^{4-n}$, by adding an appropriate number of moles of H₂O. The differences in the thermodynamic properties between these species and their conventional forms can be determined by the addition of an appropriate number of moles of water, multiplied by the molar thermodynamic properties (e.g., ΔG_f°) of pure water, which are well known [35]. At higher temperatures, solubility data are reported for only the crystalline phase, i.e., UO₂(cr) [85, 96]. The solubilities shift toward lower pH values as the temperature increases. Among the two available sets of high-temperature measurements, the data of Tremaine et al. [96] are substantially higher than those reported later by Parks and Pohl [85]. The differences between these data have been analyzed in the latter study [85]. The model results at higher temperatures agree better with data of Parks and Pohl. Figure 6 compares the experimental and calculated solubilities of UO₂(cr) at 298, 373, 473, and 573 K and those of U(OH)₄(am) at 298 K.

The effects of carbonates on the $U(OH)_4(am)$ solubility have been examined in the second step of the analysis. A substantial increase in the U(IV) solubility with carbonate concentration is observed. This increase has been attributed to the formation of carbonate complexes [97, 98]. Although carbonate complexation has been reported in the literature, the composition of the complexes has been subject to debate [3]. In the present study, a complex of the form $UO(CO_3)_3^{4-}$ has been assumed and its standard-state thermochemical properties have been determined based on the analysis of experimental solubility data in carbonate and bicarbonate solutions [97, 98]. Since the data cover a substantial range of carbonate concentration, it was necessary to introduce ion-interaction parameters between the U(IV) species and the carbonate ions. These interactions parameters are listed in Table 13 and the relevant standard-state thermochemical properties are collected in Tables 9 and 11. The results of calculations for carbonate and bicarbonate systems are presented in Figs. 7 and 8, respectively, and are in a reasonable agreement with experimental data. For comparison, these figures also include the solubilities of other actinide hydroxides, i.e., $Np(OH)_4(s)$ and $Pu(OH)_4(s)$ in similar environments (cf. Sects. 3.2.2 and 3.2.3, respectively).

3.2.2 Np(IV)

All data that are available for this system have been reported at ambient conditions (see Table 5). Thus, the standard-state entropies and heat capacities (i.e., S° and C_{p}°) of Np(IV) species have been taken from the literature [7]. Only the values of the Gibbs energy of formation, $\Delta \overline{G}_{f}^{\circ}$ or ΔG_{f}° , of the aqueous and solid species have been adjusted to give the best fit to the experimental results. These properties are listed in Tables 10 and 11.

The calculated and experimental solubilities of Np(OH)₄(am) are compared in Fig. 9 as a function of pH in CO₂/CO₃-free systems. To minimize the complexity of the plot, literature data from different sources are not distingushed. In this system, the effects of different conditions (e.g., using different background electrolytes and/or reducing agents for maintaining the tetravalent oxidation state) can be ignored compared to the scattering of the data. Figure 9 also compares the results for U(OH)₄(am) and Pu(OH)₄(am) in order to illustrate the solubility trends among tetravalent actinide hydroxides under similar conditions. Compared to U(OH)₄(am) and Pu(OH)₄(am), the Np(OH)₄(am) solubility plateaus after the pH reaches ca. 7. No substantial solubility increase was observed in the alkaline region up to pH 14 as shown by several independent measurements in the pH 7–14 region [99–102] where solubilities from various authors are in general agreement. Although the data reported at high NaOH concentrations (0.5–16 mol·kg⁻¹) by Peretrukhin Fig. 7 Solubilities of An(OH)₄(am) (An = U, Pu) at 298 K in aqueous M₂CO₃ (M = K or Na) solutions as a funtion of M₂CO₃ molality in mol·kg⁻¹. The *symbols* are the literature data from Rai et al. [37, 97, 98] and Moskvin and Gelman [174]; the *lines* are calculated using the model with parameters given in Tables 8, 9, 10, 11, 12, and 13



et al. [95] show an increase in solubility with NaOH concentration, these data are significantly higher than those reported by Rai and Ryan [102] in an overlapping range $(0.5-2.1 \text{ mol}\cdot\text{L}^{-1})$ of NaOH concentration. In their measurements of the solubilities of hydroxides of Np(IV) and Pu(IV), Peretrukhin et al. [95] noted that Np(IV) was less stable with respect to oxidation compared to Pu(IV) in alkaline solutions and that the ineffectiveness of the reductant (hydrazine) and the poor purification from oxygen in their Np(IV) experiments had resulted in the oxidation of Np(IV) to the more soluble Np(V) species, leading to the appearance of Np(V) in the solid phase. Their data are thus considered unreliable and were not included in the parameterization in the present work.

The plateau of the solubility over a wide range of pH is primarily controlled by the properties of the uncharged hydroxide complex, Np(OH)₄(aq). Although the anionic complex Np(OH)₅ has been included in the model, it plays only a minor role in determining the solubility in the pH range around 14, where experimental data show a very slight and somewhat uncertain increase. The $\Delta \overline{G}_{f}^{\circ}$ value for Np(OH)₅, which has been determined in this study based on the experimental data within the pH range up to ca. 14, is significantly less negative ($-1578.07 \text{ kJ} \cdot \text{mol}^{-1}$) than the literature value [7] ($-1607.00 \text{ kJ} \cdot \text{mol}^{-1}$) and predicts a solubility increase at a considerably higher pH compared to the U(IV) and Pu(IV) systems. Nonetheless, the ΔG_{f}° values determined for the aqueous hydroxide complexes as well as for the solid Np(OH)₄(am) provide reasonable solubility predictions that are within the uncertainties of the data as shown in Fig. 9. Despite the overall similarity in the solubility behavior of the An(OH)₄(am) hydroxides (where An denotes Np, U, Pu), some differences can be expected due to the inherent differences in the properties of the cations. Compared to U(OH)₄(am) and Pu(OH)₄(am),



Fig. 8 Solubilities of An(OH)₄(am) (An = Pu, Np, U) at 298 K in aqueous MHCO₃ (M = K or Na) solutions as a funtion of the MHCO₃ concentrations. The *symbols* are the literature data from Rai et al. [38, 97, 98, 191] and Kitamura and Kohara [192] (in the presence of 2 mol·dm⁻³ NaClO₄); the *lines* are calculated using the model with parameters given in Tables 8, 9, 10, 11, 12, and 13

the solubility data for Np(OH)₄(am) are less extensive, especially in highly alkaline solutions. The data of Peretrukhin et al. [95], which were measured at high NaOH concentrations, are not adequate to provide quantitative support for the extrapolation of the model in the highly alkaline region, making it difficult to unequivocally confirm the reported solubility trends, which are used as the basis for model development. Clearly, more reliable experimental measurements are needed to further validate the model and to guide the extrapolation of the solubility in the range beyond pH 14.

As with U(IV), the presence of carbonates results in an increased solubility of Np(OH)₄(am). A detailed analysis of Np(IV)–carbonate complexation can be found in the reviews by Lemire et al. and Guillaumont et al. [1, 2]. Depending on experimental conditions, various forms of the Np(IV)–carbonate complexes have been proposed. The solubility behavior in carbonate and bicarbonate solutions appears to be consistent with the presence of two carbonate complexes, Np(OH)₂(CO₃)^{4–}₃ and Np(CO₃)^{6–}₅, with the former being more significant at higher pH in carbonate solutions, and the latter being more prominent in bicarbonate solutions at relatively low pH (e.g., pH ~ 8). Introducing these complexes enables the model to reproduce the solubility over wide ranges of carbonate and

An(OH)4, mol·kg⁻¹



 □
 Pu(OH)4(am), Pazukhin (1990)[104]
 ■
 Pu(OH)4(am), [61,78,95,165-170,172,175,176]

 ✓
 Pu(OH)4(am), Ewart[61]; Rai[38]; Lierse[103]
 →
 Pu(OH)4(am), calc.

 ○
 U(OH)4(am), [89,90,91,93]
 →
 Pu(OH)4(am), calc.

 △
 Np(OH)4(am), elo102,130,189,190]
 →
 ¬

Fig. 9 Solubilities of An(OH)₄(am) (An = Pu, Np, U) at 298 K as a function of pH. Data for Pu(OH)₄(am) measured in aqueous NaOH solutions are shown in the inserted plot. The *symbols* are the literature data from Tables 3, 4 and 5. Only the data in CO_2/CO_3 -free systems are included; the *lines* are calculated for 0.1 mol·kg⁻¹ NaCl solutions using the model with parameters given in Tables 8, 9, 10, 11 and 12

bicarbonate concentrations. The experimental and calculated solubilities in the Np(OH)₄(am)–MHCO₃ (M = Na, K) systems are compared in Fig. 8. This figure also includes analogous comparisons for U(OH)₄(am) and Pu(OH)₄(am). The results shown in Fig. 8 further illustrate the similarities between the actinides at the same oxidation state. The bicarbonate has a similar impact on the three actinide systems by causing their solubilities to increase with similar slopes versus the HCO₃⁻ concentration. Similar behavior is also shown in Fig. 7 for U(IV) and Pu(IV) in carbonate solutions.

3.2.3 Pu(IV)

Compared to U(IV) and Np(IV), data for Pu(OH)₄(am) show a deeper solubility minimum, which is approximately two orders of magnitude lower than those for Np(OH)₄(am) and U(OH)₄(am) (Fig. 9), with three sets of measurements (Lierse and Kim [103], Rai et al. [38], Ewart et al. [61]) being consistent in the pH range where the solubility minimum is shown (pH 8–12, half-filled squares). Notwithstanding the inherent uncertainties due to the

very low solubilities that may approach the detection limit, this seems to indicate that $Pu(OH)_4(am)$ is the most stable actinide tetrahydroxide solid in the moderately alkaline range (pH 8–12). As with U(OH)₄(am), considerable discrepancies in the solubility data are seen over the entire pH range. Critical evaluations of the published solubility data for Pu(OH)₄(am) have been provided by Hala and Miyamoto [8] and by Neck and Kim [84]. Several possible reasons have been identified [84] for the large discrepancies including the questionable redox states of the dissolved Pu species due to disproportionation and oxidation of Pu(IV) and different solid phases obtained in various measurements due to differences in particle size, degree of crystallinity or water content of the hydrated solids, thus affecting the Gibbs energy and solubility. The existence of Pu(IV) colloids also affects the measured solubilities if saturated solutions are not properly purified and filtrated, causing erroneously high Pu concentrations. This effect has been noted [8] in the Pazykhin and Kudryavtsev [104] data (cf. the open squares in Fig. 9), which are significantly higher than data from other sources, especially for pH > 7. These data are therefore excluded from the model parameterization.

The solubility of Pu(IV) hydroxide has been measured in highly alkaline solutions up to NaOH concentrations as high as ca. 18 mol·kg⁻¹ [78, 95]. The increased solubility of Pu(OH)₄ with increasing OH⁻ concentration has been explained by the formation of anionic hydroxide complexes, Pu(OH)₅⁻ and Pu(OH)₆²⁻, although the identification of these complexes by spectrophotometric measurements was unsuccessful because of their low extinction coefficients [95]. Thermochemical properties of Pu(OH)₅⁻ have been reported [6, 7]. In this work, both hydroxide complexes have been included in the model and their thermodynamic properties (i.e., $\Delta \overline{G}_{f}^{\circ}$ and \overline{S}°) have been taken from the literature, estimated from constituent ions, or adjusted ($\Delta \overline{G}_{f}^{\circ}$) to reproduce the solubility data in highly concentrated NaOH solutions, as shown in Fig. 9 (upper right).

The effects of carbonates and bicarbonates on the $Pu(OH)_4(am)$ solubility are shown in Figs. 7 and 8. As discussed in Sect. 3.2.2, similar trends as a function of carbonate/bicarbonate concentration are evident in the tetravalent actinide systems. In general, the agreement between the experimental and calculated results is within one order of magnitude. Compared to the experimental data, which span up to 2 orders of magnitude (from the same authors) or more (from different authors) under the same conditions due to factors such as different sample preparation and aging of the samples, the calculated results represent the solubility within the experimental uncertainties.

Solubilities of $Pu(OH)_4(am)$ have also been studied in relatively dilute nitric acid solutions (0–0.7 mol·kg⁻¹) at temperatures up to 373 K (Table 4). As shown in Fig. 10, a significant decrease in the solubility with increasing temperature is observed from the ambient temperature to 373 K. At a given temperature, solubility increases with the acid concentration. The dependence of the solubility on temperature and acid concentration is accurately reproduced by the model. The behavior of plutonium(IV) nitrate solubilities in nitric acid up to high concentrations were also studied. Experimental data have been reported for such systems at HNO₃ concentrations up to ca. 8 mol·kg⁻¹ [80]. These data are shown in Fig. 11 together with the calculated solubilities of plutonium nitrates. Although multiple solid nitrate phases have been reported in the literature [80], the available amount of quantitative data is limited and would not justify determining the properties of all of these solids. The observed solubilities are consistent with the precipitation of two solid phases, i.e., Pu(NO₃)₄·5H₂O and Pu(OH)(NO₃)₃·5H₂O, with Pu(OH)(NO₃)₃·5H₂O being favored at higher nitric acid concentrations and the basic salt Pu(OH)(NO₃)₃·5H₂O being stable in less concentrated nitric acid [80]. By considering

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these two solid phases, the model represents the solubilities within the scattering of experimental data, as shown in Fig. 11. This figure further compares the solubilities of nitrate-bearing Pu(IV) and Pu(VI) species, which will be discussed in Sect. 3.4.2.

3.3 Pentavalent Systems

For pentavalent actinide systems, solubility data have been reported for Pu(V) and Np(V) (Tables 4 and 5). However, Pu(V) is unstable, especially in acidic solutions and undergoes disproportionation in dilute acids or oxidation in concentrated oxidizing acids. Only very few solubility data points have been found for Pu(V). More extensive solubility data have been reported for Np(V) as pentavalent neptunium is the most stable oxidation state in aqueous solutions [105, 106].

3.3.1 Pu(V)

There is very little information on the hydrolysis of PuO_2^+ and on the solubility of PuO_2 OH(am). The standard molal thermochemical properties (e.g., $\Delta \overline{G}_{f}^{\circ}, \overline{S}^{\circ}$, and $\overline{C_{p}}^{\circ}$) for PuO₂⁺ have been reported and those for PuO₂OH(aq) and PuO₂OH(am) have been determined from the equilibrium constant for the formation of the neutral complex $PuO_2OH(aq)$ and the solubility product of PuO₂OH(am) [1, 2, 6, 7]. Alkalization of a solution containing the PuO_2^+ ions can lead to the precipitation of the hydrated oxyhydroxide $PuO_2OH \cdot xH_2O$. The amphoteric character of this compound is confirmed by the existence of salts such as MePuO₂(OH)₂·xH₂O or Me₂PuO₂(OH)₃·xH₂O [107]. In alkaline solutions, the increase in solubility has been attributed to formation of anionic hydroxide complexes, such as $PuO_2(OH)_2^-$, $PuO_2(OH)_3^{2-}$, or $PuO_2(OH)_4^{3-}$ [78, 107–109]. Unfortunately, there is a lack of data on the stability of these complexes and on the solubility of the oxyhydroxide in alkaline solutions. The solubility of $PuO_2OH(am)$ was reported in a slightly alkaline solution [108]. Peretrukhin et al. [95] reported solubility data in concentrated NaOH solutions prepared starting from the salt $Na_2PuO_2(OH)_3 \cdot xH_2O$. The solid phases that are in equilibrium with the solution were not identified, but were postulated to be $Na_2PuO_2(OH)_3 \cdot xH_2O$ and $NaPuO_2(OH)_2 \cdot xH_2O[95, 108]$. The oxidation states in both the solution and the solid phases have been spectrophotometrically determined to be consistent with Pu(V), although possible disproportionation of Pu(V) at NaOH concentrations below 6 mol·L⁻¹ has been indicated [95]. The disproportionation of Pu(V) can generally be represented by

$$2\operatorname{PuO}_2(\operatorname{OH})_n^{1-n} + 2\operatorname{H}_2\operatorname{O} \rightleftharpoons \operatorname{Pu}(\operatorname{OH})_n^{4-n} + \operatorname{PuO}_2(\operatorname{OH})_n^{2-n} + 4\operatorname{OH}$$
(21)

The reduction of Pu(V) also leads to the formation of PuO₂·xH₂O [78, 109], i.e.,

$$\operatorname{PuO}_{2}(\operatorname{OH})_{n}^{1-n} + x\operatorname{H}_{2}\operatorname{O} + e^{-} \rightleftharpoons \operatorname{PuO}_{2} \cdot x\operatorname{H}_{2}\operatorname{O} + n\operatorname{OH}^{-}$$
(22)

The extent of Pu(V) disproportionation has been shown to decrease with increasing NaOH concentration [109]. This information has provided a basis for the development of the Pu(V) model.

To quantify the solubility behavior in a relatively wide range of alkaline conditions, two fixed-composition sodium salts of Pu(V) in the form of NaPuO₂(OH)₂ and Na₂PuO₂ (OH)₃·2H₂O have been considered in this work in addition to the hydroxide PuO₂OH(am), which precipitates in weakly alkaline solutions when Pu is controlled to be at the pentavalent state. In the aqueous phase, the base species PuO₂⁺ and its hydrolyzed forms PuO₂OH(aq), PuO₂(OH)₂⁻, and PuO₂(OH)₃²⁻ have been taken into account. The standard molar thermochemical properties (e.g., $\Delta \overline{G}_{f}^{\circ}, \overline{S}^{\circ}, \overline{C_{p}^{\circ}}$) for the aqueous species, PuO₂⁺ and PuO₂OH(aq), and those ($\Delta G_{f}^{\circ}, S^{\circ}, C_{p}^{\circ}$) for the solid PuO₂OH(am) have been taken from the literature [2, 6, 7]. These standard molar properties for aqueous species, PuO₂(OH)₂⁻ and

PuO₂(OH)₃²⁻, and solids NaPuO₂(OH)₂ and Na₂PuO₂(OH)₃·2H₂O, were determined by regressing the solubility data [95]. These property values are listed in Tables 8 and 11. The parameters that quantify the temperature and pressure dependence in the HKF equation of state (i.e., a_1 to a_4 , c_1 , c_2 , and ω) for the aqueous Pu(V) species have been estimated based on Shock et al. [31, 42]. The values of S° were either taken from the literature [7] or estimated using those of the constituent ions. For the solids, the values of S° and C_p° were taken from the literature or estimated [7, 43–45].

As redox equilibria become important for the Pu(V) system due to disproportionation, the model parameters have been determined by taking into consideration the redox equilibria, i.e.,

$$PuO_2^+ + 4H_3O^+ + e^- \rightleftharpoons Pu^{4+} + 6H_2O$$
(23)

$$PuO_2^+ \rightleftharpoons PuO_2^{2+} + e^-$$
(24)

Calculations have also been performed by considering only the pentavalent state. Results with and without redox equilibria have been then compared to reveal how the redox equilibria affect the solubility. The results of these calculations for the Pu(V)-NaOH-H₂O system are shown in Fig. 12 as a function of pH. The pH values in the NaOH solutions have been calculated at the experimental NaOH concentrations using the activity coefficients determined from the model, thus leading to very high pH values at high NaOH concentrations. The solubility results are shown in Fig. 12a. The results obtained by including redox equilibria are represented by dotted lines whereas those obtained without redox are shown by dashed lines. Clearly, the solubility of Pu(V) in acidic solutions and up to low NaOH concentrations (less than 0.1 mol·L⁻¹, or pH < 12) is governed by the reductive precipitation of $Pu(OH)_4(am)$ (i.e., Eqs. 23). At higher pH, solids with the formula of NaPuO₂(OH)₂(s) (at pH 12-15.2, which corresponds to NaOH = 0.1-7 mol·kg⁻¹) and Na₂PuO₂(OH)₃·2H₂O (for pH > 15.2, which corresponds to NaOH > 7 mol·kg⁻¹) are in equilibrium with the solution. In the entire range of pH, the solutions are dominated by the Pu(V) species. This is illustrated in Fig. 12b. At the same time, when only pentavalent Pu is considered in the calculations, the calculated solubilities (dashed lines in Fig. 12a) are much higher and are controlled by the precipitation of PuO₂OH(am) below ca. pH 12. In this region, the calculated solubilities of PuO₂OH(am) are close to those of $NpO_2OH(am)$, which are also shown in Fig. 12a as the solid line. At higher pHs, the sodium salts of Pu(V) precipitate. As pH increases to ca. pH 13.5, the results with and without redox equilibria are identical, indicating that Pu(V) disproportionation becomes insignificant in more concentrated NaOH solutions, a result that is consistent with the spectrophotometric studies of Pu(V) and Pu(IV) [109]. The solubility data point reported at pH 8.3 [108] was not included in the parameterization, as no experimental details are provided with regard to the redox state in either the solution or the solid phase. This point is consistent with the model in which redox equilibria are not included. When only the pentavalent state is considered, the solubility in the pH < 12region is determined by the standard molar thermodynamic properties (e.g., Gibbs energy of formation) of PuO₂⁺, PuO₂OH(aq), and solid PuO₂OH(am), which are taken from the literature [2, 6, 7]. The model reproduces the experimental data, especially in highly alkaline solutions, with a good accuracy. It should be noted that when redox equilibria were included, all model parameters pertaining to oxidation states other than Pu(V) were kept unchanged in the process of determining the Pu(V) parameters.

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Fig. 12 Solubilities in the systems An(V)–H–Na–OH–H₂O (An = Pu and Np) as a function of pH at 298 K. **a** Only the data used in the fitting are shown for Np(V). The *lines* are calculated using the model with parameters given in Tables 8, 10, and 11. The *dotted lines* in (**a**) were calculated for the Pu(V) system by including the redox equilibria. Speciation in saturated solutions in the Pu(V) redox system is shown in (**b**)

In Fig. 12, the solubility results for the Pu(V) system are further compared with those for the Np(V) system without considering redox equilibria, as Np(V) is the most stable oxidation state in solution. This is discussed in the following section.

3.3.2 Np(V)

Solubility data for Np(V) in CO₂/CO₃-free system are reported in a number of sources (cf. Table 5). Although the experimental results are scattered, two extensive data sets by Neck et al. [110] and Lierse et al. [111] show a general agreement with each other and have been used as primary sources in model development. These data (cf. the open symbols in Fig. 12) cover an ionic strength range from 0.1 to 3.0 mol·kg⁻¹ and a pH range from 6.8 to 13.7. Within this pH range, only the solubilities of the amorphous NpO₂OH(am) phase were measured. Standard-state thermochemical properties for the dioxo species, i.e.,

NpO₂⁺, NpO₂OH(aq), and NpO₂(OH)₂⁻, as well as for the NpO₂OH(am) solid phase, have been reported in the literature [2, 7]. However, these values do not yield accurate solubility predictions. Thus, the $\Delta G_{\rm f}^{\circ}$ values have been determined based on an analysis and regression of the experimental data. A comparison between the experimental and calculated NpO₂OH(am) solubilities is shown in Fig. 12. The thermochemical properties that have been used to generate the calculated results are given in Tables 10 and 11. In view of the large uncertainties in the experimental data, the model provides reasonable solubility predictions over a wide range of pH. It is noteworthy that there is little effect of the ionic strength (varied via NaClO₄ concentration) on the experimental results and the curves calculated at the ionic strengths ranging from 0.1 to 3 mol·kg⁻¹ nearly fall on top of each other over the entire range of pH. Therefore, Fig. 12 shows the calculated results only at the ionic strength of 1.0 mol·kg⁻¹. Also, Fig. 12 compares the Np(V) results with those for Pu(V). Within the pH range in which the Np(V) data were measured (i.e., pH 6-14), the solid phases that are in equilibrium with the solutions are NpO₂OH(am) and PuO₂OH(am). The solubility trends shown for these two pentavalent actinide systems reflect the similarities between Np(V) and Pu(V) with respect to both solid formation and aqueous speciation. Such similarities may be useful for analyzing other, similar systems for which experimental data are missing.

In the presence of CO_2 and carbonates, extensive Np(V) solubility data have been reported near 298 K over wide ranges of pH, ionic strength, carbonate concentration, and pCO_2 . The solid phases that have been identified in the carbonate systems are NaNpO₂ $CO_3(s)$, $Na_3NpO_2(CO_3)_2(s)$, and their hydrates. The solubilities of these solids are affected by the concentration of carbonate ions due to the formation of carbonate complexes. The Np(V) complexation reactions are considered to be restricted to the formation of three complexes, i.e., $NpO_2CO_3^-$, $NpO_2(CO_3)_2^{3-}$, and $NpO_2(CO_3)_3^{5-}$ [112]. Based on the experimental data, two solids are considered: NaNpO₂CO₃·3.5H₂O and Na₃NpO₂ $(CO_3)_2(s)$. In contrast to the CO_2/CO_3 -free systems, the ionic strength has a marked effect on the solubility under otherwise identical conditions (i.e., at the same pH and pCO_2). Solubility results at varying ionic strengths (i.e., NaClO₄ concentrations) of 0.1, 1.0, 3.0, and 5.0 mol·L⁻¹ [112] are shown in Fig. 13. Under the atmospheric CO₂ partial pressure (i.e., $pCO_2 = 10^{-3.51}$ bar), NaNpO₂CO₃·3.5H₂O is found to be the stable solid phase over the whole carbonate concentration range (up to 0.03 mol·kg⁻¹) in 0.1 mol·L⁻¹ NaClO₄ solutions. However, at higher NaClO₄ concentrations, i.e., in 1, 3 and 5 mol·L⁻¹ solutions, $Na_3NpO_2(CO_3)_2(s)$ becomes the stable solid at higher pH, which requires higher carbonate concentrations at the fixed pCO₂. At these higher ionic strengths, NaNpO₂CO₃·3.5H₂O precipitates only at lower pH values and lower carbonate concentrations. It may continue to precipitate at carbonate concentrations as high as 0.5 mol·L⁻¹ (pH > 10) but has been found to convert to the less soluble solid $Na_3NpO_2(CO_3)_2(s)$ after equilibrium is reached. In 1.0 mol·L⁻¹ solutions, such conversion occurs at pH > 9.5 where the carbonate concentration exceeds ca. 0.01 mol·L⁻¹. As the NaClO₄ concentration increases to 3 and 5 mol·L⁻¹, the conversion of NaNpO₂CO₃·3.5H₂O to Na₃NpO₂(CO₃)₂(s) occurs at somewhat lower pH and carbonate concentrations. In Fig. 13, the hollow symbols and thin lines represent the solubilities of $NaNpO_2CO_3 \cdot 3.5H_2O$; metastable extensions of the solubilities of NaNpO₂CO₃·3.5H₂O to higher pH values are also shown as dashed lines. In the region of higher pH, the stable solid is $Na_3NpO_2(CO_3)_2(s)$ as represented by the solid symbols and thick lines. The thermodynamic model reproduces the solubilities of both the stable and metastable solids as illustrated in Fig. 13. The effect of pCO_2 on the



Np(V) solubility is similar to that observed in the Am–CO₃ system. Specifically, the solubility curves shift toward lower pH values with increasing pCO₂.

3.4 Hexavalent Systems

Hexavalent actinides are usually predominant under aerated conditions or in the presence of oxidizing agents. Extensive solubility data have been reported for Pu(VI), U(VI), and Np(VI). Literature values for the standard-state thermochemical properties of individual aqueous species and solids [2, 6, 7, 33] and the available solubility data (Tables 3, 4 and 5) provide a broad foundation for parameterizing the model.

In addition to the environments containing common acids, bases, and salts (i.e., those involving the H_3O^+ , OH^- , Na^+ , Cl^- , ClO_4^- , and CO_2/CO_3^{2-} species), the behavior of U(VI) and Pu(VI) has also been studied in concentrated nitric acid and nitrate salts. Solubility data in nitric acid environments are more extensive for hexavalent U(VI) and Pu(VI) than for tetravalent actinides, including the Pu(IV) system discussed in Sect. 3.2.3. The hexavalent uranium and plutonium are the most stable oxidation states in the presence of nitric acid due to the strongly oxidizing nature of the acid.

3.4.1 U(VI)

Hexavalent uranium has been extensively investigated in the literature. In CO_2/CO_3 -free system, the solubilities are controlled primarily by the solution pH. The presence of other cations that may contribute to the formation of solids (e.g., Na⁺) also plays an important role in determining the equilibrium concentrations of U(VI) and the solid phases that are in equilibrium with the solution. The literature solubility data collected in Table 3 cover extensive ranges of pH and salt concentrations and have been included in the evaluation of both the standard-state properties and ion interaction parameters. Among the various U(VI)

solid phases that have been studied in the literature, the phases that may precipitate in the $U(VI)-H-OH-Na-X-H_2O$ (X = Cl or ClO₄) system are reported to be schoepite, UO₂ (OH)₂·H₂O, and clarkeite, a sodium salt of U(VI). The chemical composition of clarkeite may vary depending on how the solid was crystallized. Frequently, clarkeite contains small amounts of elements that commonly exist in natural waters and minerals (e.g., Ca and Pb) and includes varying amounts of hydration water. In the present work, clarkeite with a chemical composition of NaUO₂O(OH)·H₂O is assumed. This composition has been identified by XRD analysis for a solid phase precipitated from alkaline NaCl solutions [113]. Speciation in U(VI) systems includes the uranyl ion, UO_2^{2+} , and its hydrolyzed forms: UO_2OH^+ , UO_3^0 , HUO_4^- , UO_4^{2-} , and UO_4OH^{3-} . If the published standard-state partial molar properties are used for these aqueous dioxouranium(VI) oxide and hydroxide species [33], the predicted solubilities are systematically lower than the measured values at pH below 5. Therefore, the properties of UO_2^{2+} and UO_2OH^+ have been adjusted to fit the experimental data in this region. This adjustment is also necessary for the systems where nitric acid is present up to high concentrations. Also, it has been necessary to include an additional hydrolyzed species, UO₄OH³⁻, to represent solubility data in highly alkaline solutions, especially those associated with the precipitation of clarkeite [114].

Figure 14 shows the results for the U(VI) system under CO₂-free conditions. There have been numerous reports on the solubilities of UO2(OH)2·H2O [113-126]. Most of these data were measured in acidic to weakly alkaline solutions (i.e., pH 3.3–9). The data reported by Krupka et al. [122] and Redkin and Wood [124] show considerably lower slopes at the lower pH values (i.e., pH 3–6) compared to most other measurements. Solubility data have also been reported for a sodium salt of U(VI), i.e., clarkeite (NaUO₂O(OH)·H₂O or Na₂ $U_2O_7 \cdot xH_2O_3$, at higher pH and/or elevated sodium ion concentrations [113, 114]. At higher pH (pH > 6), the solubilities reported by Krupka et al. [122], Redkin and Wood [124], Bruno and Sandino [115], and Gayer and Leider (in NaOH solutions) [118] are considerably higher than those reported by Fanghänel and Neck [113] and Altmaier et al. [114]. The solid phase in equilibrium with solutions has been reported to be $UO_2(OH)_2 \cdot H_2O$ in the Krupka et al. and Gayer and Leider measurements in the entire pH range of their experiments. On the other hand, the solids in the Altmaier et al. [114] and Fanghänel and Neck [113] measurements have been identified by XRD analysis as schoepite at lower pHs and as clarkeite (NaUO₂O(OH) \cdot H₂O) at elevated pHs and sodium ion concentrations. It is possible that the higher solubilities reported by these authors [115, 118, 122, 124] at higher pH values may have been due to presence of the metastable solid $UO_2(OH)_2 H_2O$, which would eventually be transformed to the more stable clarkeite when equilibrium is reached [113]. The solubilities reported for amorphous schoepite by Kim et al. [120] are significantly lower than other data sets in the pH range of 6-10. Thus, the Kim et al. data, together with those of Krupka et al. [122], Gayer and Leider [118], Redkin and Wood [124], and Bruno and Sandino [115] were not included in the model parameterization and have been excluded from Fig. 14, except for the Krupka et al. data at pH > 8 which give the highest solubilities among all data sets in this pH range and are shown to be consistent with the predicted solubility of the metastable phase $UO_2(OH)_2 H_2O$ (cf., the dotted lines). The calculated solubilities (lines) were obtained using the parameters listed in Tables 9 and 11. In relatively acidic solutions (i.e., for pH values below ca. 7), schoepite is the stable solid that is in equilibrium with the solutions. Clarkeite becomes the stable solid phase in more alkaline solutions. The solubility of clarkeite is much lower than that of schoepite and is influenced by NaCl concentration [114]. An increase in NaCl concentration results in clarkeite to start precipitating at lower pH (cf. the results for 0.5 and



Fig. 14 Solubilities of schoepite (UO₂(OH)₂·H₂O) and clarkeite (NaUO₂OOH·H₂O) in the U(VI)–H–Na–OH–H₂O system as a function of pH at 298 K, where m denotes the molality in mol·kg⁻¹. The symbols are the literature data as indicated. The *lines* are calculated using the model with parameters listed in Tables 9 and 11. Also shown are the experimental and calculated solubilities of PuO₂(OH)₂·H₂O (*solid black dots* and *thick black line*)

2.6 mol·kg⁻¹ NaCl in Fig. 14). The increase in the solubility as pH increases in alkaline solutions (cf. Fig. 14) results from the formation of negatively charged oxyhydroxides of U(VI). The model accurately reproduces these phenomena as shown in Fig. 14. The model also represents the solubility of metastable schoepite at high pH values (cf. the dotted lines in Fig. 14), at which clarkeite is the stable phase.

The solubility of U(VI) can be significantly affected by the presence of carbonates, bicarbonates, and CO₂. The solid phases that have been identified to precipitate in the U(VI)–H–OH–Na–CO₂/CO₃–H₂O system include rutherfordine (UO₂CO₃) and čejkaite (Na₄(UO₂)(CO₃)₃), in addition to schoepite (UO₂(OH)₂·H₂O) and clarkeite (NaUO₂ O(OH)·H₂O). Solubility data have been reported for this system at varying pCO₂, carbonate and bicarbonate concentrations, and with or without other salt components (cf. Table 3). In the presence of carbonates and/or CO₂, carbonate complexes including

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Fig. 15 Solubilities of schoepite (UO₂(OH)₂·H₂O) and rutherfordine (UO₂CO₃) in the U(VI)–H–Na–OH–CO₂–H₂O system as a function of pH at 298 K, where m denotes the molality in mol·kg⁻¹. The symbols are the literature data listed in Table 3 as indicated in the legend. The *lines* are calculated using the model with parameters given in Tables 9 and 11. Also shown in this figure are the experimental and calculated solubilities of PuO₂CO₃(s) at $pCO_2 = 1.01$ bar (*solid black triangles* and *thick black line*)

 $UO_2CO_3^0$, $UO_2(CO)_2^{2-}$, and $UO_2(CO_3)_3^{4-}$ have been experimentally identified in the literature [127]. Standard-state thermochemical property values have been reported for these complexes and for rutherfordine and čejkaite [2, 6, 7]. These values were used as initial estimates but have been adjusted to obtain the optimum representation of experimental solubility data. Figure 15 illustrates the solubility results in the U(VI)–H–OH–Na–CO₂– H₂O system as a function of pH at the partial pressures of CO₂ from 0–1.01325 bar. The calculated results have been obtained using the standard thermochemical properties listed in Tables 9 and 11. In the pH range shown in Fig. 15, schoepite is the stable solid at low pCO_2 (i.e., for $pCO_2 \ll 0.1$ bar) and rutherfordine precipitates at higher pCO_2 (i.e., at $pCO_2 \ge 0.1$ bar). As with other systems, the solubility curves shift toward lower pH values with increasing pCO_2 . The solubility results shown in Fig. 15 were obtained in salt (NaClO₄ or NaCl) solutions with concentrations up to 3.0 mol·kg⁻¹. However, the salt effect on the rutherfordine solubility is almost insignificant compared to that of pH and pCO_2 . A noticeable salt effect is observed only as the salt concentration increases from 0–0.1 mol·kg⁻¹ and is due to an appreciable change of activity coefficients in dilute

solutions. However, as shown in Fig. 15, the effect of salt concentration on the calculated solubilities is well within the experimental uncertainty.

For nitrate salts of uranium(VI), experimental solubility data (cf. Table 3) have been reported over a wide range of temperature (255-623 K), nitric acid concentration $(x'_{\rm HNO_3} = 0-0.7 \text{ or } m_{\rm HNO_3} = 0-127 \text{ mol}\cdot\text{kg}^{-1})$, and U(VI) nitrate concentrations (up to solid saturation). The experimentally identified solid phases that may precipitate from these solutions include UO₂(NO₃)₂·6H₂O, UO₂(NO₃)₂·3H₂O, UO₂(NO₃)₂·2H₂O, and UO₂(OH)₂ (or UO3·H2O). Although aqueous dioxouranium(VI) nitrate complexes have been reported in the literature, they appear to be weak, thus making it difficult to distinguish experimentally between complex formation and changes in the activity factor of the solutes as a function of concentration [3]. However, as the mixtures involve very high U(VI) nitrate and nitric acid concentrations, it is justifiable to take into account the formation of such complexes. Therefore, in this study, we consider only a 1:1 complex, $UO_2NO_3^+$, for which a $\Delta G_{\rm f}^{\circ}$ value has been reported [3]. The model parameters for U(VI) nitrates have been established by analyzing the experimental solubility data in the systems $UO_2(NO_3)_2-H_2O_3$ UO₃-HNO₃-H₂O, UO₃-UO₂(NO₃)₂-H₂O, and UO₂(NO₃)₂-HNO₃-H₂O. Modeling such concentrated solutions necessitates introducing ion-interaction parameters between aqueous species. These parameters have been determined together with the standard-state property values for the aqueous complex species $(UO_2NO_3^+)$ and the solid phases $\{UO_2(NO_3)_2 \cdot 6H_2O, UO_2(NO_3)_2 \cdot 3H_2O, UO_2(NO_3)_2 \cdot 2H_2O, and UO_3 \cdot H_2O\}$. The values of these parameters are given in Tables 9, 11, and 12. The solubility results in the UO_{3-} HNO₃-H₂O system at temperatures ranging from 298 to 332 K are shown in Fig. 16. All four solid phases can precipitate from the solutions depending on the composition range and temperature. At relatively low acid concentrations (i.e., below 25 mass%), the stable solid is UO₃·H₂O. The uranyl nitrate hydrates UO₂(NO₃)₂·nH₂O start to precipate as the acid concentration increases and the hydration water in the solid phase decreases with acid concentration. The stability range of the hexahydrate, $UO_2(NO_3)_2 \cdot 6H_2O$, shrinks as the temperature increases so that only $UO_2(NO_3)_2 \cdot 3H_2O$ and $UO_2(NO_3)_2 \cdot 2H_2O$ precipitate



Fig. 16 Solubility in the UO_3 -HNO₃-H₂O system at various temperatures. The *symbols* are the literature data from Lacher et al. [161]. The concentrations are shown in weight percent. The *lines* are calculated using the model with the parameters listed in Tables 9, 11, and 12

at 332 K. These transitions are very accurately represented by the model. It should be noted that a single consistent set of model parameters (cf. Tables 8, 11, and 12) reproduces the behavior of all U(VI) systems, i.e., those with and without CO_3/CO_2 or HNO_3/NO_3 . A comparison of the behavior of U(VI) and Pu(VI) in concentrated nitric acid mixtures will be discussed in the next section.

3.4.2 Pu(VI)

The Pu(VI) systems have been modeled using a methodology that is similar to that adopted for U(VI) systems. Based on the reported solubility experiments, the solid phase that is in equilibrium with CO_3/CO_2 -free solutions has been identified as plutonium(VI) oxide hydrate, $PuO_3 \cdot xH_2O$, over the entire pH range. The solubilities were measured in solutions with ionic strengths from 0.1 to 1.0 mol·kg⁻¹ NaClO₄ but show little effect of background electrolyte concentration. When compared with the corresponding U(VI) system, the equilibrium concentrations of Pu(VI) show a similar trend. This is illustrated in Fig. 14, where the solubilities of Pu(VI) are shown as solid black circles. In the present study, a solid phase that is similar to schoepite has been assumed, i.e., $PuO_2(OH)_2 \cdot H_2O$ (which is equivalent to $PuO_3 \cdot 2H_2O$). As with the U(VI) system, the standard-state partial molar properties have been evaluated for a series of hydrolyzed forms of PuO_2^{2+} and for the $PuO_2(OH)_2 \cdot H_2O$ solid (cf. Tables 8 and 11).

The solubilities of PuO_2CO_3 have been reported at various pCO_2 and carbonate concentrations and in different ionic media (Table 4). These data were analyzed to develop the parameters for the Pu(VI)-CO3/CO2-H2O system. The carbonate complexes that have been identified for Pu(VI) are similar to those for U(VI), i.e., $PuO_2CO_3^0$, $PuO_2(CO_3)_3^{2-}$, and $PuO_2(CO_3)_3^{4-}$ [1] and have been adopted in this study. As with the U(VI) systems, the ionic strength has much less effect on solubilities compared to that of pH and pCO_2 . While it is interesting that, in the CO₂-free systems, the stability range of $PuO_2(OH)_2 H_2O$ extends to higher pH values compared to $UO_2(OH)_2 \cdot H_2O_1$, it is equally interesting to note that the stability range of $PuO_2CO_3(s)$ also extends to higher pH compared to that for $UO_2CO_3(s)$. This is shown in Fig. 15 where the solubility results at $pCO_2 = 1$ atm (1.01325 bar) are shown for PuO₂CO₃(s) as solid black triangles (experimental data) and the thick solid line (calculated). The solubilities at other pCO_2 values show similar trends. In the lower pH region (pH < 4), PuO₂CO₃(s) and UO₂CO₃(s) behave similarly as a function of pH. At higher pHs, the solubility of $PuO_2CO_3(s)$ is about one order of magnitude lower than that of $UO_2CO_3(s)$ under the same conditions and extends to much higher pH values before it increases due to the formation of competing carbonate and hydroxide complexes. These results are indicative of appreciable differences in the effects of carbonate complexation on the precipitation of $PuO_2CO_3(s)$ and $UO_2CO_3(s)$. The solubility behavior at lower pH is primarily controlled by the properties of positively charged species such as PuO_2^{2+} and $PuO_2(OH)^+$ in the Pu(VI) system and UO_2^{2+} and $UO_2(OH)^+$ in the U(VI) system and is not affected by carbonate complexation. As the pH increases, higher solubilities in the U(VI) system indicate the formation of relatively strong carbonate complexes. Carbonate complexation is weaker in the Pu(VI) system, which causes a lower solubility of $PuO_2CO_3(s)$ compared to that of $UO_2CO_3(s)$. However, the carbonate complexation becomes much stronger with a further increase in pH at a constant pCO_2 due to increased carbonate concentration, thus causing increases in solubilities in both systems.

Plutonium(VI) nitrate exists as the anhydrous salt $PuO_2(NO_3)_2$ or as the hexa-, tetra-, tri-, or dihydrates [80]. An acidic solid phase, $PuO_2(NO_3)_2 \cdot HNO_3 \cdot nH_2O$, has also been

reported in highly concentrated (ca. 19 mol·kg⁻¹) HNO₃ solutions [128]. The published solubility data span a wide range of nitric acid concentrations (up to ca. 19 mol·kg⁻¹) and show considerable scattering among different sources. Three solid phases have been considered to represent these limited data: PuO₂(NO₃)₂·6H₂O, PuO₂(NO₃)₂·3H₂O, and PuO₂(NO₃)₂·HNO₃·3H₂O. The $\Delta G_{\rm f}^{\circ}$ values for these solids have been determined from the solubility data together with the activity coefficient ion-interaction parameters. The values of S° and C_{p}° were estimated using a group contribution approach [43–45]. These parameters are collected in Tables 11 and 12.

It is interesting to compare the solubility trends for Pu(IV) and Pu(VI) in nitric acid environments, i.e., in the Pu(NO₃)₄–HNO₃–H₂O and PuO₂(NO₃)₂–HNO₃–H₂O systems. Such a comparison is shown in Fig. 11. In the Pu(IV) system, solubility increases significantly with the HNO₃ concentration, with a break point at ~5 mol·kg⁻¹ HNO₃, where the precipitated solid changes from Pu(OH)(NO₃)₃·5H₂O to Pu(NO₃)₄·5H₂O. In contrast, for the Pu(VI) system, the solubility decreases sharply with the HNO₃ concentration up to ~5 mol·kg⁻¹ HNO₃ and appears to level off at higher concentrations. Pu(VI) nitrate is less soluble than Pu(IV) nitrate in concentrated HNO₃ solutions. This solubility difference makes it possible to separate Pu(VI) from Pu(IV) as Pu(VI) nitrate can crystallize first from nitric acid solutions.

It is also of interest to compare the solubility behavior of the $PuO_2(NO_3)_2$ -HNO₃-H₂O and $UO_2(NO_3)_2$ -HNO₃-H₂O mixtures. This comparison is provided in Fig. 17. To emphasize the results at lower acid concentrations, the x-axis is expressed as the square root of the nitric acid mole-fraction (on salt-free basis), $(x'_{HNO_3})^{0.5}$. Complex solubility behavior is evident in these mixtures. In both systems, sharp solubility decreases are observed when the acid is initially added. Similar solid phases precipitate in the two systems at lower acid concentrations, i.e., hexahydrates followed by trihydrates as the acid concentration increases. The $UO_2(NO_3)_2 \cdot 6H_2O$ solid phase exhibits a much deeper solubility minimum compared to that of $PuO_2(NO_3)_2 \cdot 6H_2O$. At the highest nitric acid concentrations, the solid phases that are in equilibrium with the acid solutions are different. In





the U(VI) system, the stable solid is $UO_2(NO_3)_2 \cdot 2H_2O$ whereas a mixed solvate, PuO_2 (NO₃)₂·HNO₃·3H₂O, precipitates in the Pu(VI) system. Both, however, reflect the progressive depletion of water molecules from the solid phases compared to the solids that form at lower acid concentrations. In addition, the hydrates of $PuO_2(NO_3)_2$ shows a markedly lower solubility than those of $UO_2(NO_3)_2$ at any acid concentration.

3.4.3 Np(VI)

Solubility data in the system Np(VI)–OH–H–Na–Cl–CO₂–H₂O have been measured in CO₂-free systems [129, 130] and at varying partial pressures of CO₂ [131, 132]. These data span wide ranges of pH (3–14.6), pCO₂ (0.0003–0.8 bar), and NaCl concentration (0.1–5.6 mol·kg⁻¹) and provide an excellent basis for establishing the thermodynamic model for the Np(VI) system.

It has been noted that Np(VI) is unstable in aqueous solutions in the region near and below neutral pH as it can be easily reduced to Np(V) and Np(IV) depending on the redox potential [129]. Among the published solubility data, those reported by Gaona et al. [129] and Kato et al. [131, 132] were measured under carefully controled and monitored redox conditions to ensure the hexavalent state for Np. The oxidizing conditions required for stablizing Np(VI) in the measurements of Gaona et al. were maintained by using 5×10^{-3} mol·L⁻¹ NaClO. However, Np(V) species have been detected at near-neutral pH after a prolonged equilibration time due to the degradation of NaClO, thus causing a decreased redox potential. At near-neutral pH conditions (pH 7–9), Gaona et al. confirmed the predominance of the pentavalent species, NpO₂⁺, in the aqueous phase. At the same time, the solid phase was identified to remain as Np(VI) in the form of NpO₂(OH)₂·H₂O or $Na_2Np_2O_7(s)$. The solid-liquid equilibrium was characterized as reductive dissolution of Np(VI) solid phases in the near-neutral pH region [129]. Meanwhile, the measurements of Kato et al. were made in acidic solutions (pH 3–7) under varying pCO_2 conditions, in which a much stronger oxidizing agent, ozone, was used for stablizing Np(VI) so that the redox potentials were maintained within the stability range of Np(VI), i.e., $E \sim 1.3$ V at pH 3 and $E \sim 1.1$ V at pH 7 [131, 132]. The Np(V) concentration in the experiments of Kato et al. was determined to be less than 2% of the total Np by absorption spectrophotometry and liquid scintillation counting. In the case of Moskvin's data [130], no oxidizing agent was specified for maintaining the hexavalent state of Np during the solubility measurements and the equilibrium constants were derived on the assumption that only Np(VI) species were present in the aqueous solution.

Based on the available literature data, the model parameters for Np(VI) have been determined concurrently using two different chemistry definitions. In the first definition, redox equilibria are allowed in the analysis of the data of Gaona et al. Thus, the following redox equilibria have been taken into consideration, together with all acid to base and complexation equilibria for the corresponding oxidation states, i.e., Np(III–VI):

$$NpO_2^{2+} + 4H_3O^+ + 3e^- \Rightarrow Np^{3+} + 6H_2O$$
 (25)

$$NpO_2^{2+} + 4H_3O^+ + 2e^- \Longrightarrow Np^{4+} + 6H_2O$$
 (26)

$$NpO_2^{2+} + e^- \rightleftharpoons NpO_2^+$$
(27)

In the second chemistry definition, only the Np(VI) state is included in the analysis of the data of Kato et al. Standard-state thermochemical properties (i.e., $\Delta \overline{G}_{f}^{\circ}$ and ΔG_{f}°) for the

aqueous and solid Np(VI)–carbonate species were determined based on the data of Kato et al., which were also used to validate the properties of the hydrolyzed Np(VI) species that are important in acidic solutions (e.g., NpO₂²⁺ and NpO₂(OH)⁺). At the same time, the data of Gaona et al. provided the basis for the determination of the properties of NpO₂(OH)₂· H₂O(s), Na₂Np₂O₇(s), and the aqueous species that are important at neutral to alkaline pHs (i.e., NpO₂(OH)₃⁻ and NpO₂(OH)₄²⁻). Also, they were used to determine the ion interaction parameters (i.e., for Na⁺ and OH⁻ with NpO₂(OH)₃⁻ and NpO₂(OH)₄²⁻, respectively). It should be noted that when redox equilibria are allowed, all model parameters pertaining to Np(V) and the lower oxidation states discussed in previous sections were kept unchanged when those for Np(VI) were determined. The model parameters for this system are collected in Tables 10, 11 and 12. With these parameters, solubility curves have been calculated and compared with experimental data in Fig. 18.

At relatively low pH values and in the presence of CO₂ (Fig. 18a), the solubility is controlled by the precipitation of NpO₂CO₃(s) at $pCO_2 \ge 0.1$ bar, which is analogous to UO₂CO₃(s) and PuO₂CO₃(s) in the U(VI) and Pu(VI) systems, respectively. As with UO₂CO₃(s) and PuO₂CO₃(s), the solubility of NpO₂CO₃(s) shifts toward lower pH as pCO_2 increases. As discussed above, only Np(VI) aqueous species are included in the calculations shown as lines in Fig. 18a because the corresponding data of Kato et al.



Fig. 18 Solubilities of Np(VI) solids as a function of pH at 298 K: **a** at various pCO_2 (1 atm = 1.01325 bar), Kato et al. [131, 132], with *lines* calculated with only Np(VI) species included; **b** at various NaCl concentrations (CO₂ free), Gaona et al. [129], with *lines* calculated with redox equilibria included (see text); **c** in CO₂ free solutions, Moskvin [130], with lines calculated with (*solid line*) and without (*dashed line*) redox equilibria; and **d** speciation in saturated solutions for 1 mol·kg⁻¹ NaCl corresponding to (**b**). All *lines* are calculated using the model with parameters listed in Tables 10, 11 and 12

[131, 132] were measured by maintaining an appropriate redox potential so that Np(VI) dominates in the solution. Figure 18b shows a comparison of the calculated solubilities with the data of Gaona et al. [129]. The model results were calculated by including redox equilibria as discussed above. The calculated speciation is illustrated in Fig. 18d for 1.0 mol·kg⁻¹ NaCl solutions and is limited to species with the highest concentrations. In solutions at near-neutral pH (pH 7–9), it is the Np(V) species (i.e., NpO₂⁺) that are predominant. At higher pH, the speciation is dominated by Np(VI) species (i.e., NpO₂(OH)₃⁻¹ and NpO₂(OH)₄²⁻¹). In the entire pH region, Np(VI) solid phases precipitate in the form of NpO₂(OH)₂·H₂O(s) (at near-neutral pH and lower NaCl concentrations) and Na₂Np₂O₇ (s) (at higher pH and NaCl concentrations). These results are consistent with the experimental observations of Gaona et al. [129]. The data of Moskvin [130] are inconsistent with the results of either Gaona et al. or Kato et al. and were not included in the fitting. However, the Moskvin data have been compared with the calculations with and without including redox equilibria, as shown in Fig. 18c. Clearly, the Moskvin data are more consistent with the calculations in which redox is included (solid line) where NpO₂

 $(OH)_2 \cdot H_2O(s)$ is in equilibrium with solutions dominated by Np(V).

In CO_2 -free systems, it has been noted that the Np(VI) solubility trends are similar to those for U(VI) when measured under similar conditions [129], especially in alkaline solutions (pH > 9). This similarity can be due to the formation of similar aqueous species. The solid precipitate obtained by Gaona et al. [129] in alkaline solutions and at high NaCl concentrations (e.g., $Na_2Np_2O_7(s)$) is analogous to clarkeite in the U(VI) system. The solubility of $Na_2Np_2O_7(s)$ is affected by the NaCl concentration in the same way as clarkeite. An increase in NaCl concentration results in a decreased solubility of this solid. At lower pH and lower NaCl concentrations (below 0.1 mol·kg⁻¹), the solid phase, NpO₂(OH)₂·H₂O, is analogous to UO₂(OH)₂·H₂O and PuO₂(OH)₂·H₂O. This underscores the similarities among the hexavalent actinide systems with respect to solid phase formation. The solubility difference between Np(VI) and U(VI) in the near-neutral pH region (pH 7–9) has been observed in experiments [129] where Np(VI) solids have markedly higher solubility that decreases more rapidly with pH compared to the corresponding U(VI) solids. This difference is due to different equilibrium reactions that control the solubility in this region. The solubilities of Np(VI) solids are governed by reductive dissolution, in which the solids are in equilibrium with solutions dominated by Np(V) species, whereas U(VI) is more stable in aqueous solution and the solubilities of U(VI) solids are controlled by simple dissolution, in which the solids are in equilibrium with aqueous solutions dominated by U(VI).

As shown in Fig. 18, the model accurately reproduces the behavior of the Np(VI) system with respect to both the concentrations at solid–liquid equilibrium and the identity of the precipitated solids.

4 Conclusions

The previously developed Mixed-Solvent Electrolyte (MSE) model has been applied to calculate phase equilibria and chemical speciation for selected aqueous actinide systems. Specifically, the solution chemistry of Am(III), Cm(III), Np(IV, V, VI), Pu(III, IV, V, VI), and U(IV, VI) has been analyzed to develop thermodynamic model parameters. The model reproduces the complexities of the solubility behavior as a function of critical factors including pH, partial pressure of CO₂, concentration of carbonates and the presence of

other salt components. In addition, redox effects on the solubility and speciation have also been taken into consideration, as demonstrated by the reductive and oxidative dissolutions of Np(VI) and Pu(IV) solids, respectively. Thus, it can be used to elucidate how these radionuclides behave in natural aquatic systems or in nuclear waste repositories and to predict how their solubility behavior can be affected by changing environmental conditions. In addition, particular emphasis has been placed on analyzing systems relevant to nuclear fuel processing, in which nitric acid and nitrate salts of plutonium and uranium are present at high concentrations. The model has been shown to reproduce speciation and solubility behavior in highly concentrated systems that are difficult to handle with classical electrolyte models. It should be noted that for many systems investigated in the present work, the models have been established on the basis of experimental data under ambient conditions. In such systems, parameters used for calculating the thermodynamic properties at higher temperatures and pressures (e.g., the standard molal entropy, heat capacity, and HKF equation of state parameters for aqueous species) were either taken from calorimetric measurements reported in the literature or estimated using indirect methodologies, and have not been validated against experimental phase equilibrium and speciation data due to the lack of relevant measurements. Extrapolation of the properties of such systems to higher temperatures and pressures may be subject to larger uncertainties and lead to inaccurate predictions. Thus, some parameters are reported only to provide an estimate when extended ranges of conditions are considered. More reliable results can be obtained only when the parameters are calibrated using experimental data that were directly measured in broad ranges of conditions. In general, the model predicts the solubility and speciation behavior as a function of pH (from concentrated acids going through moderate pH ranges all the way to concentrated alkaline solutions) at temperatures up to 573 K. However, the degree of confidence in model predictions varies for different systems depending on the availability of underlying experimental data. Specifically, the predicted solubility behavior of U(IV) and U(VI) has been extensively validated up to 573 K. The behavior of Pu(IV) and U(VI) in dilute to concentrated acid solutions has been demonstrated to be accurately reproduced up to ca. 393 K. For Am(III), the model is supported by experimental solubility data up to 343 K in total carbonate concentration up to 1 mol kg⁻¹. The speciation behavior of Cm(III) has been validated up to 473 K in the mixed aqueous solutions of Na_2SO_4 and $NaClO_4$. For the remaining systems, the model has been largely validated against data at or near room temperature. Beyond the ranges of data availability, the model predictions can be treated as reasonable estimates that rely on a combination of moderate temperature phase equilibrium and speciation data, calorimetric measurements for solids and prediction techniques for aqueous species properties. Further improvements of the model are expected as more experimental information becomes available.

5 Supplementary Material

Thermodynamic values reported in the tables this article are given in units of $kJ \cdot mol^{-1}$ or $J \cdot K^{-1} \cdot mol^{-1}$. However, since the original Helgeson–Kirkham–Flowers (HKF) equation of state was formulated in units of kcal·mol⁻¹ and cal·K⁻¹·mol⁻¹, and many scientists still use it in that form, the corresponding values of Tables 6, 7, 8, 9, 10 and 11 are converted in these units in the supplementary Tables S6–S11.

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Appendix 1: Activity Coefficients in the MSE Model

The activity coefficients of an aqueous species k can be derived from the excess Gibbs energy, G^{ex} , (Eq. 11) by taking the derivative of G^{ex} with respect to the number of moles of k [11]. The functional forms are summarized here. As with the excess Gibbs energy, the activity coefficient, γ , consists of contributions due to long-range electrostatic effects (LR), specific ionic interactions (II), and a short range effect resulted from molecular interactions (SR), i.e.,

$$\ln\gamma_k = \ln\gamma_k^{\rm LR} + \ln\gamma_k^{\rm II} + \ln\gamma_k^{\rm SR} \tag{28}$$

The long-range electrostatic contribution term in the activity coefficient is derived from a symmetrical Pitzer–Debye–Hückel formulation for G_{LR}^{ex} [11] and is expressed as

$$\ln \gamma_{k}^{LR} = -A_{x} \left[\frac{2z_{k}^{2}}{\rho} \ln \frac{1 + \rho I_{x}^{1/2}}{\sum_{i} x_{i} \left[1 + \rho \left(I_{x,i}^{0} \right)^{1/2} \right]} + \frac{I_{x}^{1/2} \left(z_{k}^{2} - 2I_{x} \right)}{1 + \rho I_{x}^{1/2}} \right] - \frac{4A_{x}I_{x}}{\rho} \left\{ 1 - \frac{1 + \rho \left(I_{x,k}^{0} \right)^{1/2}}{\sum_{i} x_{i} \left[1 + \rho \left(I_{x,i}^{0} \right)^{1/2} \right]} \right\}$$
(29)

where the sum is over all of the species (ionic and neutral) and I_x is the mole fraction-based ionic strength defined by

$$I_x = -\frac{1}{2} \sum_i x_i z_i^2 \tag{30}$$

 $I_{x,i}^0$ represents the ionic strength when the system composition reduces to a pure component *i*, i.e., $I_{x,i}^0 = \frac{1}{2} z_i^2$; ρ is related to a hard-core collision diameter and is assigned a value of 14.0. The A_x parameter is given by

$$A_{x} = \frac{1}{3} (2\pi N_{\rm A} d_{\rm s})^{1/2} \left(\frac{e^2}{4\pi\epsilon_0 \epsilon_{\rm s} k_{\rm B} T}\right)^{3/2}$$
(31)

where N_A is the Avogadro number (6.022137 × 10²³ mol⁻¹), d_s is the molar density of the solvent (mol·m⁻³), e is the electron charge (1.602177 × 10⁻¹⁹ C), $\pi = 3.14159$, ε_0 is the permittivity of vacuum (8.8541878 × 10⁻¹² C²·J⁻¹·m⁻¹), ε_s is the dielectric constant of the solvent, k_B is the Boltzmann constant (1.38066 × 10⁻²³ J·K⁻¹) and *T* is temperature in K.

The specific ion-interaction contribution is calculated from an ionic strength-dependent, symmetrical second virial coefficient-type expression:

$$\ln \gamma_k^{\mathrm{II}} = \sum_i \sum_j x_i x_j B_{ij}(I_x) - \left(\sum_l n_l\right) \sum_i \sum_j x_i x_j \frac{\partial B_{ij}(I_x)}{\partial n_k} - 2\sum_i x_i B_{ik}(I_x)$$
(32)

where $B_{ij}(I_x) = B_{ji}(I_x)$, $B_{ii} = B_{jj} = 0$ and the ionic strength dependence of B_{ij} is given by

$$B_{ij}(I_x) = b_{ij} + c_{ij}exp(-\sqrt{I_x + a_1})$$
(33)

where b_{ij} and c_{ij} are adjustable parameters and a_1 is set equal to 0.01. The parameters b_{ij} and c_{ij} are calculated as functions of temperature as shown in Eqs. 14 and 15.

The short-range interaction contribution is calculated using the UNIQUAC equation [26]

$$\ln \gamma_{k}^{\text{UNIQUAC}} = \ln \left(\frac{\varphi_{k}}{x_{k}}\right) + \frac{Z}{2} q_{k} \ln \left(\frac{\theta_{k}}{\varphi_{k}}\right) + l_{k} - \frac{\varphi_{k}}{x_{k}} \sum_{j} x_{j} l_{j}$$
$$+ q_{k} \left[1 - \ln \left(\sum_{j} \theta_{j} \tau_{jk}\right) - \sum_{j} \frac{\theta_{j} \tau_{kj}}{\sum_{i} \theta_{i} \tau_{ij}}\right]$$
(34)

where

$$l_{j} = \frac{Z}{2} (r_{j} - q_{j}) - (r_{j} - 1)$$
(35)

 q_i and r_i are surface and size parameters, respectively, for species *i*, *Z* is a constant with a value of 10, while a_{ij} is the binary interaction parameter between species *i* and *j* ($a_{ij} \neq a_{ji}$) with a temperature dependence expressed by Eq. 16.

Appendix 2: The Helgeson–Kirkham–Flowers (HKF) Equation of State

The standard-state partial molal thermodynamic properties of aqueous species are calculated from the HKF equation of state using seven parameters that are specific to each species. These seven parameters (a_1 to a_4 , c_1 , c_2 and ω) are integration constants for volume (a), heat capacity (c) and temperature and pressure properties of water (ω). Details of the HKF equations of state are available in the literature [28–31]. Here, only the equation for calculating the standard partial molar Gibbs energy of formation is given, which is used to determine the equilibrium constant in chemical speciation calculations.

$$\Delta \overline{G_{P,T}^{\circ}} = \Delta \overline{G_{f}^{\circ}} - \overline{S_{pr,Tr}^{\circ}}(T - T_{r}) - c_{1} \left[T \ln \left(\frac{T}{T_{r}} \right) - T + T_{r} \right] + a_{1}(p - p_{r}) + a_{2} \ln \left(\frac{\Psi + p}{\Psi + p_{r}} \right) \\ + \left[a_{3}(p - p_{r}) + a_{4} \ln \left(\frac{\Psi + p}{\Psi + p_{r}} \right) \right] \left(\frac{1}{T - \Theta} \right) \\ - c_{2} \left[\left(\left(\frac{1}{T - \Theta} \right) - \left(\frac{1}{T_{r} - \Theta} \right) \right) \left(\frac{\Theta - T}{\Theta} \right) - \frac{T}{\Theta^{2}} \ln \left(\frac{T_{r}(T - \Theta)}{T(T_{r} - \Theta)} \right) \right] \\ + \omega \left(\frac{1}{\varepsilon} - 1 \right) - \omega_{pr,Tr} \left(\frac{1}{\varepsilon_{pr,Tr}} - 1 \right) + \omega_{pr,Tr} Y_{pr,Tr} (T - T_{r})$$
(36)

In this equation, $\Delta \overline{G_{f}^{\circ}}$ and $\overline{S_{pr,Tr}^{\circ}}$ represent the standard partial molal Gibbs energy of formation and entropy, respectively, at reference temperature (T_r , 298.15 K) and pressure (p_r , 1 bar), $\Theta = 228$ K and $\Psi = 2600$ bar, ε is the dielectric constant of water, and ω is the Born coefficient representing the temperature and pressure dependence for electrostatic nature of the electrolyte solutions. More details can be found in Tanger and Helgeson [133].

- Lemire, R.J., Fuger, J., Nitsche, H., Potter, P., Rand, M.H., Rydberg, J., Spahiu, K., Sullivan, J.C., Ullman, W.J., Vitorge, P., Wanner, H.: Chemical Thermodynamics of Neptunium and Plutonium. Chemical Thermodynamics, vol. 4. OECD Nuclear Energy Agency, Elsevier, Amsterdam (2001)
- Guillaumont, R., Fanghänel, T., Neck, V., Fuger, J., Palmer, D.A., Grenthe, I., Rand, M.H.: Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium. Chemical Thermodynamics, vol. 5. OECD Nuclear Energy Agency, Elsevier, Amsterdam (2003)
- 3. Grenthe, I., Fuger, J., Konings, R.J.M., Lemire, R.J., Nguyen-Trung, C., Wanner, H.: Chemical Thermodynamics of Uranium. OECD Nuclear Energy Agency, Elsevier, Amsterdam (2004)
- 4. Silva, R.J., Bidoglio, G., Rand, M.H., Robouch, P.B., Wanner, H., Puigdomenach, I.: Chemical Thermodynamics of Americium. OECD Nuclear Energy Agency, Elsevier, Amsterdam (2004)
- Konings, R.J.M., Morss, L.R., Fuger, J.: Thermodynamic properties of actinides and actinide compounds. In: Morss, L.R., Edelstein, N.M., Fuger, J. (eds.) The Chemistry of the Actinide and Transactinide Elements, pp. 2113–2224. Springer, Amsterdam (2006)
- Lemire, R.J., Tremaine, P.R.: Uranium and plutonium equilibria in aqueous solutions to 200 °C. J. Chem. Eng. Data 25, 361–370 (1980)
- Phillips, S.I., Hale, F.V., Silvester, L.F., Siegel, M.D.: Thermodynamic Tables for Nuclear Waste Isolation, Vol. 1. Aqueous Solutions Database, p. 181. Lawrence Berkeley Laboratory report LBL-22860 (1988)
- Hala, J., Miyamoto, H.: IUPAC-NIST Solubility Data Series. 84. Solubility of inorganic actinide compounds. J. Phys. Chem. Ref. Data 36, 1417–1736 (2007)
- Hala, J., Navratil, J.D.: IUPAC-NIST Solubility Data Series. 74. Actinide carbon compounds. J. Phys. Chem. Ref. Data 30, 531–698 (2001)
- Anderko, A., Wang, P., Rafal, M.: Electrolyte solutions: from thermodynamic and transport property models to the simulation of industrial processes. Fluid Phase Equilib. 194, 123–142 (2002)
- Wang, P., Anderko, A., Young, R.D.: A speciation-based model for mixed-solvent electrolyte systems. Fluid Phase Equilib. 203(1–2), 141–176 (2002)
- Wang, P., Springer, R.D., Anderko, A., Young, R.D.: Modeling phase equilibria and speciation in mixed-solvent electrolyte systems. Fluid Phase Equilib. 222, 11–17 (2004). doi:10.1016/j.fluid.2004. 06.008
- Wang, P., Anderko, A., Springer, R.D., Young, R.D.: Modeling phase equilibria and speciation in mixed-solvent electrolyte systems: II. Liquid–liquid equilibria and properties of associating electrolyte solutions. J. Mol. Liq. 125(1), 37–44 (2006)
- Wang, P., Kosinski, J.J., Anderko, A., Springer, R.D., Lencka, M.M., Liu, J.: Ethylene glycol and its mixtures with water and electrolytes: thermodynamic and transport properties. Ind. Eng. Chem. Res. 52, 15968–15987 (2013)
- Azimi, G., Papangelakis, V.G., Dutrizac, J.E.: Modelling of calcium sulphate solubility in concentrated multi-component sulphate solutions. Fluid Phase Equilib. 260, 300–315 (2007)
- Azimi, G., Papangelakis, V.G., Dutrizac, J.E.: Development of an MSE-based chemical model for the solubility of calcium sulphate in mixed chloride–sulphate solutions. Fluid Phase Equilib. 266, 172–186 (2008)
- Gruszkiewicz, M.S., Palmer, D.A., Springer, R.D., Wang, P.M., Anderko, A.: Phase behavior of aqueous Na–K–Mg–Ca–Cl–NO₃ mixtures: isopiestic measurements and thermodynamic modeling. J. Solution Chem. **36**(6), 723–765 (2007)
- Kosinski, J.J., Wang, P.M., Springer, R.D., Anderko, A.: Modeling acid–base equilibria and phase behavior in mixed-solvent electrolyte systems. Fluid Phase Equilb. 256(1–2), 34–41 (2007)
- Liu, H., Papangelakis, V.G.: Thermodynamic equilibrium of the O2–ZnSO4–H2SO4–H2O system from 25 to 250 °C. Fluid Phase Equilib. 234, 122–130 (2005)
- Liu, H., Papangelakis, V.G.: Solubility of Pb(II) and Ni(II) in mixed sulfate-chloride solutions with the mixed solvent electrolyte model. Ind. Eng. Chem. Res. 45, 39–47 (2006)
- Wang, P., Anderko, A., Springer, R.D., Kosinski, J.J., Lencka, M.M.: Modeling chemical and phase equilibria in geochemical systems using a speciation-based model. J. Geochem. Explor. 106(1–3), 219–225 (2010). doi:10.1016/j.gexplo.2009.09.003
- Wang, P., Anderko, A.: Modeling chemical equilibria, phase behavior, and transport properties in ionic liquid systems. Fluid Phase Equilib. 302(1-2), 74–82 (2011)
- Zemaitis Jr., J.F., Clark, D.M., Rafal, M., Scrivner, N.C.: Handbook of Aqueous Electrolyte Thermodynamics. American Institute of Chemical Engineers, New York (1986)
- 24. Pitzer, K.S.: Activity Coefficients in Electrolyte Solutions, 2nd edn. CRC Press, Boca Raton (1991)

- Wang, P., Kosinski, J.J., Lencka, M.M., Anderko, A., Springer, R.D.: Thermodynamic modeling of boric acid and selected metal borate systems. Pure Appl. Chem. 85(11), 2117–2144 (2013)
- Abrams, D.S., Prausnitz, J.M.: Statistical thermodynamics of liquid mixtures—new expressions for excess Gibbs energy of partly or completely miscible systems. AIChE J. 21(1), 116–128 (1975)
- Springer, R.D., Wang, Z., Anderko, A., Wang, P., Felmy, A.R.: A Thermodynamic model for predicting mineral reactivity in supercritical carbon dioxide: I. Phase behavior of carbon dioxide-waterchloride salt systems across the H₂O-rich to the CO₂-rich regions. Chem. Geol. **322–323**, 151–171 (2012)
- Helgeson, H.C., Kirkham, D.H., Flowers, G.C.: Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressures and temperatures. I. Summary of the thermodynamic/electrostatic properties of the solvent. Am. J. Sci. 274, 1089–1198 (1974)
- Helgeson, H.C., Kirkham, D.H., Flowers, G.C.: Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressures and temperatures. III. Equation of state for aqueous species at infinite dilution. Am. J. Sci. 276, 97–240 (1976)
- Helgeson, H.C., Kirkham, D.H., Flowers, G.C.: Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressures and temperatures. IV. Calculation of activity coefficients, osmotic coefficients, and apparent molal and standard and relative partial molal properties to 5 kb and 600 °C. Am. J. Sci. 281, 1241–1516 (1981)
- 31. Shock, E.L., Helgeson, H.C.: Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: correlation algorithms for ionic species and equation of state predictions to 5 kb and 1000 °C. Geochim. Cosmochim. Acta 52, 2009–2036 (1988)
- Sverjensky, D.A., Shock, E.L., Helgeson, H.C.: Prediction of the thermodynamic properties of aqueous metal complexes to 1000 °C and 5 kb. Geochim. Cosmochim. Acta 61, 1359–1412 (1997)
- Shock, E.L., Sassani, D.C., Betz, H.: Uranium in geologic fluids: Estimates of standard partial molal properties, oxidation potentials, and hydrolysis constants at high temperatures and pressures. Geochim. Cosmochim. Acta 61(20), 4245–4266 (1997)
- 34. Pitzer, K.S.: Thermodynamics, 3rd edn. McGraw-Hill, New York (1995)
- Haar, L., Gallagher, J.S., Kell, G.S.: NBS/NRC Steam Tables: Thermodynamic and Transport Properties and Computer Programs for Vapor and Liquid States in SI Units. Hemisphere Publishing, Washington, DC (1984)
- Soave, G.: Equilibrium constants from a modified Redlich–Kwong equation of state. Chem. Eng. Sci. 27(6), 1197–1203 (1972)
- Nitsche, H., Roberts, K., Xi, R., Prussin, T., Becraft, K., Al Mahamid, I., Silber, H.B., Carpenter, S.A., Gatti, R.C., Novak, C.F.: Long term plutonium solubility and speciation studies in a synthetic brine. Radiochim. Acta 66(67), 3–8 (1994)
- Rai, D., Hess, N.J., Felmy, A.R., Moore, D.A., Yui, M., Vitorge, P.: A Thermodynamic model for the solubility of PuO₂(am) in the aqueous K⁺–HCO₃⁻–CO₃^{2–}–OH⁻–H₂O system. Radiochim. Acta 86(3–4), 89–99 (1999)
- Choppin, G.R., Bond, A.H., Hromadka, P.M.: Redox speciation of plutonium. J. Radioanal. Nucl. Chem. 219(2), 203–210 (1997)
- Rard, J.A.: Potential for Radionuclide Immobilization in the EBS/NFE: Solubility Limiting Phases for Neptunium, Plutonium, and Uranium. UCRL-ID-128950, Lawrence Livermore National Laboratory, Livermore, California (1997)
- Springer, R.D., Wang, P., Anderko, A.: Modeling the properties of H₂S–CO₂-salt-water systems in wide ranges of temperature and pressure. SPE J. **20**(5), 1120–1134 (2015)
- Shock, E.L., Sassani, D.C., Willis, M., Sverjensky, D.A.: Inorganic species in geologic fluids: correlations among standard molal thermodynamic properties of aqueous ions and hydroxide complexes. Geochim. Cosmochim. Acta 61(5), 907–950 (1997)
- Hurst, J.E., Harrison, B.K.: Estimation of liquid and solid heat capacities using a modified Kopp's rule. Chem. Eng. Commun. 112, 21–30 (1992)
- Kubaschewski, O., Ünal, H.: An empirical estimation of the heat capacities of inorganic compounds. High Temp. High Press. 9, 361–365 (1977)
- 45. Latimer, W.M.: Methods of estimating the entropies of solid compounds. J. Am. Chem. Soc. **73**(4), 1480–1482 (1951)
- Rai, D., Strickert, R.G., Moore, D.A., Ryan, J.L.: Am(III) hydrolysis constants and solubility of Am(III) hydroxide. Radiochim. Acta 33, 201–206 (1983)
- Lumetta, G.J., Thompson, M.C., Penneman, R.A., Eller, P.G.: Curium. In: Morss, L.R., Edelstein, N.M., Fuger, J., Katz, J.J. (eds.) The Chemistry of the Actinide and Transactinide Elements, vol. 3, pp. 1397–1443. Springer, Dordrecht (2008)

- Felmy, A.R., Rai, D., Schramke, J.A., Ryan, J.L.: The solubility of plutonium hydroxide in dilute solution and in high-ionic-strength chloride brines. Radiochim. Acta 48(1–2), 29–35 (1989)
- Stadler, S., Kim, J.I.: Chemisches Verhalten von Americium in natürlichen wässrigen Lösungen: Hydrolyse, Radiolyse und Redox-Reaktionen. RCM 01188, Institut für Radiochemie, Technische Universität München (1988)
- Giffaut, E.: Influence des ions chlorure sur la chimie des actinides: Effets de la radiolyse et de la température. Ph.D thesis, Universite de Paris-Sud (1994)
- Giffaut, E., Vitorge, P.: Evidence of radiolytic oxidation of ²⁴¹Am in Na⁺/Cl⁻/HCO₃⁻/CO₃²⁻ media. Mater. Res. Soc. Symp. Proc. 294, 747–751 (1993)
- Runde, W., Kim, J.I.: Chemisches Verhalten von drei- und fünfwertigem Americium in Salinen NaCl-Lösungen, p. 236. Technische Universitat Munchen, Germany (1994)
- 53. Stadler, S., Kim, J.I.: Hydrolysis reactions of Am(III) and Am(V). Radiochim. Acta 44(45), 39–44 (1988)
- Rao, L., Rai, D., Felmy, A.R., Fulton, R.W., Novak, C.F.: Solubility of NaNd(CO₃)₂·6H₂O(c) in concentrated Na₂CO₃ and NaHCO₃ solutions. Radiochim. Acta 75, 141–147 (1996)
- Meinrath, G., Kim, J.I.: Solubility products of different Am(III) and Nd(III) carbonates. Eur. J. Solid State Inorg. Chem. 28, 383–388 (1991)
- Runde, W., Meinrath, G., Kim, J.I.: A study of solid–liquid phase equilibria of trivalent lanthanide and actinide ions in carbonate systems. Radiochim. Acta 58(59), 93–100 (1992)
- 57. Felmy, A.R., Rai, D., Fulton, R.W.: The solubility of AmOHCO₃(c) and the aqueous thermodynamics of the system Na⁺−Am³⁺−HCO₃⁻−CO₃⁻−OH⁻−H₂O. Radiochim. Acta **50**, 193–204 (1990)
- Meinrath, G., Kim, J.I.: The carbonate complexation of the Am(III) ion. Radiochim. Acta 52(53), 29–34 (1991)
- Bernkopf, M.F., Kim, J.I.: Hydrolysereaktionen und Karbonatkomplexierung von dreiwertigem Americium im natürlichen aquatischen System. Report RCM-02884, Technische Universität München (1984)
- Ewart, F.T., Howse, R.M., Thomason, H.P., Williams, S.J., Cross, J.E.: The solubility of actinides in the near-field. Mater. Res. Soc. Symp. Proc. 50, 701–708 (1985)
- Ewart, F.T., Smith-Briggs, J.L., Thomason, H.P., Williams, S.J.: The solubility of actinides in a cementitious near-field environment. Waste Manag. 12, 241–252 (1992)
- Keum, D.-K., Baik, M.-H., Hahn, P.-S.: Speciation and solubility of major actinides under the deep groundwater conditions of Korea. J. Korean Nucl. Soc. 34(5), 517–531 (2002)
- Vitorge, P.: Am(OH)₃(s), AmOHCO₃(s), Am ₂(CO₃)₃ stabilities in environmental conditions. Radiochim. Acta 58(59), 105–107 (1992)
- 64. Neck, V., Fanghänel, T., Kim, J.I.: Aquatische Chemie und thermodynamische Modellierung von trivalenten Actiniden. vol. FZKA-6110, p. 115. Forschungszentrum Karlsruhe GmbH Technik und Umwelt, Institut für Nukleare Entsorgungstechnik, Germany (1998)
- Neck, V., Altmaier, M., Rabung, T., Lützenkirchen, J., Fanghänel, T.: Thermodynamics of trivalent actinides and neodymium in NaCl, MgCl₂, and CaCl₂ solutions: Solubility, hydrolysis, and ternary Ca–M(III)–OH complexes. Pure Appl. Chem. 81(9), 1555–1568 (2009)
- Rabung, T., Altmaier, M., Neck, V., Fanghänel, T.: A TRLFS study of Cm(III) hydroxide complexes in alkaline CaCl₂ solutions. Radiochim. Acta 96, 551–559 (2008)
- 67. Skerencak, A., Panak, P.J., Fanghänel, T.: Complexation and thermodynamics of Cm(III) at high temperatures: the formation of $[Cm(SO_4)n]^{3-2n}$ (n = 1, 2, 3) complexes at t = 25 to 200 °C. Dalton Trans. **42**, 542–549 (2013)
- Edelstein, N.M., Klenze, R., Fanghänel, T., Hubert, S.: Optical properties of Cm(III) in crystals and solutions and their application to Cm(III) speciation. Coord. Chem. 250, 948–973 (2006)
- Fanghänel, T., Kim, J.I., Klenze, R., Kato, Y.: Formation of Cm(III) chloride complexes in CaCl₂ solutions. J. Alloys Compd. 225, 308–311 (1995)
- Fanghänel, T., Kim, J.I., Paviet, P., Klenze, R., Hauser, W.: Thermodynamics of radioactive trace elements in concentrated electrolyte solutions: hydrolysis of Cm³⁺ in NaCl-solutions. Radiochim. Acta 66(67), 81–87 (1994)
- Fanghänel, T., Konnecke, T., Weger, H., Paviet-Hartmann, P., Neck, V., Kim, J.I.: Thermodynamics of Cm(III) in concentrated salt solutions: carbonate complexation in NaCl solution at 25° C. J. Solution Chem. 28(4), 447–462 (1999)
- Fanghänel, T., Weger, H.T., Konnecke, T., Neck, V., Paviet-Hartmann, P., Steinle, E., Kim, J.I.: Thermodynamics of Cm(III) in concentrated electrolyte solutions. Carbonate complexes at constant ionic strength (1 m NaCl). Radiochim. Acta 82, 47–53 (1998)
- Paviet, P., Fanghänel, T., Klenze, R., Kim, J.I.: Thermodynamics of Cm(III) in concentrated electrolyte solutions: formation of sulfate complexes in NaCl/Na₂SO₄ solutions. Radiochim. Acta 74, 99–103 (1996)

- Felmy, A.R., Rai, D.: Application of Pitzer's equations for modeling the aqueous thermodynamics of actinide species in natural waters: a review. J. Solution Chem. 28(5), 533–553 (1999)
- Altmaier, M., Gaona, X., Fanghänel, T.: Recent advances in aqueous actinide chemistry and thermodynamics. Chem. Rev. 113, 901–943 (2013)
- Runde, W., Kim, J.I.: Chemisches Verhalten von drei- und fünfwertigem Americium in Salinen NaCl-Lösungen. Technische Universität München, Report RCM 01094 (1994)
- 77. Brendebach, B., Altmaier, M., Rothe, J., Neck, V., Denecke, M.A.: EXAFS study of aqueous Zr^{IV} and Th^{IV} complexes in alkaline CaCl₂ solutions: Ca₃[Zr(OH)₆]⁴⁺ and Ca₄[Zr(OH)₈]⁴⁺. Inorg. Chem. 46, 6804–6810 (2007)
- Delegard, C.H.: Solubility of PuO₂·xH₂O in alkaline Hanford high-level waste solution. Radiochim. Acta 41(1), 11–21 (1985)
- Gray, J.H., Swanson, J.L.: Properties of concentrated plutonium nitrate solutions. American Nuclear Society; Back End of the LWR Fuel Cycle. Held in Savannah, Georgia, 19–22 March 1978 (1978)
- Clark, S.B., Delegard, C.H.: Plutonium in concentrated solutions. In: Hoffman, D.C. (ed.) Advances in Plutonium Chemistry 1967–2000. American Nuclear Society and University Research Alliance, La Grange Park (2002)
- Pugh, R.A.: Notes pertaining to recuplex product evaporation, HW-32100. Hanford Atomic Products Operation, Richland (1954)
- Glazyrin, S.A., Rodchenko, P.Y., Sokhina, L.P.: Oxidation of plutonium(IV) on heat treatment of concentrated nitric acid solutions. Sov. Radichem. (English transl.) 31(4), 407–410 (1989)
- Rai, D., Yui, M., Moore, D.A.: Solubility and solubility product at 22 °C of UO₂(c) precipitated from aqueous U(IV) solutions. J. Solution Chem. 32(1), 1–17 (2003)
- Neck, V., Kim, J.I.: Solubility and hydrolysis of tetravalent actinides. Radiochim. Acta 89, 1–16 (2001)
- Parks, G.A., Pohl, D.C.: Hydrothermal solubility of uraninite. Geochim. Cosmochim. Acta 52, 863–875 (1988)
- Yajima, T., Kawamura, Y., Ueta, S.: Uranium(IV) solubility and hydrolysis constants under reduced conditions. In: Scientific Basis for Nuclear Waste Management XVIII. Materials Research Society Symposium Proceedings vol. 353, pp. 1137–1142 (1995)
- Migdisov, A., Williams-Jones, A.E., Brugger, J., Caporuscio, F.A.: Hydrothermal transport, deposition, and fractionation of the REE: Experimental data and thermodynamic calculations. Chem. Geol. 439, 13–42 (2016)
- Ryan, J.L., Rai, D.: The solubility of uranium(IV) hydrous oxide in sodium hydroxide solutions under reducing conditions. Polyhedron 2(9), 947–952 (1983)
- Rai, D., Felmy, A.R., Ryan, J.L.: Uranium(IV) hydrolysis constants and solubility product of UO₂ ·xH₂O(am). Inorg. Chem. 29(2), 260–264 (1990)
- Rai, D., Felmy, A.R., Sterner, S.M., Moore, D.A., Mason, M.J., Novak, C.F.: The solubility of Th(IV) and U(IV) hydrous oxides in concentrated NaCl and MgCl₂ solutions. Radiochim. Acta 79, 239–247 (1997)
- Fujiwara, K., Yamana, H., Fujii, T., Kawamoto, K., Sasaki, T., Moriyama, H.: Solubility of uranium(IV) hydrous oxide in high pH solution under reducing condition. Radiochim. Acta 93, 347–350 (2005)
- Galkin, N.P., Stepanov, M.A.: Solubility of uranium(IV) hydroxide in sodium hydroxide. Sov. J. At. Energy 8, 231–233 (1960)
- Gayer, K.H., Leider, H.: The solubility of uranium(IV) hydroxide on solutions of sodium hydroxide and perchloric acid at 25 °C. Can. J. Chem. 35, 5–7 (1957)
- Kertes, A.S., Guillaumont, R.: Solubility of UO₂. A comparative review. Nucl. Chem. Waste Manag. 5, 215–219 (1985)
- Peretrukhin, V.F., Kryutchkov, S.V., Silin, V.I., Tananaev, I.G.: Determination of the solubility of Np(IV)–(VI), Pu(III)–(VI), Am(III)–(VI) and Tc(IV),(V) hydroxo compounds in 0.5–14 *M* NaOH solutions. WHC-EP-0987, Westinghouse Hanford Company, Richland, WA (1996)
- Tremaine, P.R., Chen, J.D., Wallace, G.J., Boivin, W.A.: Solubility of uranium(IV) oxide in alkaline aqueous solutions to 300 °C. J. Solution Chem. 10(3), 221–230 (1981)
- 97. Rai, D., Felmy, A.R., Hess, N.J., Moore, D.A., Yui, M.: A thermodynamic model for the solubility of UO₂(am) in the aqueous K⁺−Na⁺−CO²₃−−OH[−]−H₂O system. Radiochim. Acta 82, 17–25 (1998)
- Rai, D., Felmy, A.R., Moore, D.A., Mason, M.: The solubility of Th(IV) and U(IV) hydrous oxides in concentrated NaHCO₃ and Na₂CO₃ solutions, In Scientific Basis for Nuclear Waste Management XVIII. Materials Research Society Symposium Proceedings, vol. 353, pp. 1143–1150 (1995)
- Eriksen, T.E., Ndalamba, P., Cui, D., Bruno, J., Caceci, M., Spahiu, K.: Solubility of the redoxsensitive radionuclides ⁹⁹Tc and ²³⁷Np under reducing conditions in neutral to alkaline solutions.

Effect of carbonate. Department of Nuclear Chemistry, Royal Institute of Technology, Stockholm (Sweden); MBT Technologia Ambiental, Cerdanyola (Spain), Sweden (1993)

- Ewart, F.T., Gore, S.J.M., Williams, S.J.: The Solubility of Neptunium(IV) at High pH. U.K. Atomic Energy Research Establishment, Report AERE-R 11975 (1985)
- Nakayama, S., Yamaguchi, T., Sekine, K.: Solubility of neptunium(IV) hydrous oxide in aqueous solutions. Radiochim. Acta 74, 15–19 (1996)
- Rai, D., Ryan, J.L.: Neptunium(IV) hydrous oxide solubility under reducing and carbonate conditions. Inorg. Chem. 24(3), 247–251 (1985)
- 103. Lierse, C.H., Kim, J.I.: Chemisches Verhalten von Plutonium in Naturlichen Aquatischen System. In: Hydrolyse, Carbonatkomplexierung und Redoxreaktionen, Report RCM-02286, Inst. fur Radiochemie, Technischen Universitat Munchen, (1986)
- Pazukhin, E.M., Kudryavtsev, Y.G.: Stability constants of hydrolysis forms of plutonium(IV) and solubility product of its hydroxide. Radiokhimiya 32(4), 18–25 (1990)
- Yoshida, Z., Johnson, S.G., Kimura, T., Krsul, J.R.: Neptunium. In: The Chemistry of the Actinide and Transactinide Elements, pp. 699–812. Springer, Netherlands (2006)
- 106. Baes, C.F., Mesmer, R.E.: The Hydrolysis of Cations. Wiley, New York (1976)
- 107. Tananaev, I.G.: Hydroxide compounds of Pu(V). Radiochem. 34(2), 161-163 (1992)
- Barney, G.S., Delegard, C.H.: Chemical species of plutonium in Hanford radioactive tank waste, HNF-SA-3181-FP. Paper presented at the American Chemical Society Symposium, Orlando, Flordia, 25–30 August 1996 (1997)
- Delegard, C.H., Jones, S.A.: Chemical disposition of plutonium in Hanford site tank wastes. Pacific Northwest National Laboratory Richland, Washington, PNNL-23468 Rev. 1, WTP-RPT-234 Rev. 1 (2015)
- Neck, V., Kim, J.I., Kanellakopulos, B.: Solubility and hydrolysis behaviour of neptunium(V). Radiochim. Acta 56(1), 25–30 (1992)
- Lierse, C.H., Treiber, W., Kim, J.I.: Hydrolysis reactions of neptunium(V). Radiochim. Acta 38(1), 27–28 (1985)
- Neck, V., Runde, W., Kim, J.I.: Solid–liquid equilibria of neptunium(V) in carbonate solutions of diffrent ionic strengths: II. Stability of the solid phases. J. Alloys Compd. 225, 295–302 (1995)
- Fanghänel, T., Neck, V.: Aquatic chemistry and solubility phenomena of actinide oxides/hydroxides. Pure Appl. Chem. 74(10), 1895–1907 (2002)
- 114. Altmaier, M., Neck, V., Metz, V., Müller, R., Schlieker, M., Fanghänel, T.: Solubility of U(VI) in NaCl and MgCl₂ solution. In: Migration Conference. Gyeongju, Korea (2003)
- 115. Bruno, J., Sandino, A.: The solubility of amorphous and crystalline schoepite in neutral to alkaline aqueous solutions. In: Scientific Basis for Nuclear Waste Management XII. Materials Research Society Symposium Proceedings, vol. 127, pp. 871–878 (1989)
- Diaz Arocas, P., Grambow, B.: Solid–liquid phase equilibria of U(VI) in NaCl solutions. Geochim. Cosmochim. Acta 62(2), 245–263 (1998)
- 117. Fujiwara, K., Yamana, H., Fujii, T., Kawamoto, K., Sasaki, T., Moriyama, H.: Solubility product of hexavalent uranium hydrous oxide. J. Nucl. Sci. Tech. 42(3), 289–294 (2005)
- 118. Gayer, K.H., Leider, H.: The Solubility of uranium trioxide, UO₃·H₂O, in solutions of sodium hydroxide and perchloric acid at 25 °C. J. Am. Chem. Soc. **77**, 1448–1450 (1955)
- 119. Gorman-Lewis, D., Fein, J.B., Burns, P.C., Szymanowski, J.E.S., Converse, J.: Solubility measurements of the uranyl oxide hydrate phases metaschoepite, compreignacite, Na-compreignacite, becquerelite, and clarkeite. J. Chem. Thermodyn. 40, 980–990 (2008)
- 120. Kim, W.H., Choi, K.C., Park, K.K., Eom, T.Y.: Effects of hypochlorite ion on the solubility of amorphous schoepite at 25 °C in neutral to alkaline aqueous solutions. Radiochim. Acta 66(67), 45–49 (1994)
- 121. Kramer-Schnabel, U., Bischoff, H., Xi, R.H., Marx, G.: Solubility products and complex formation equilibria in the systems uranyl hydroxide and uranyl carbonate at 25 °C and I = 0.1 M. Radiochim. Acta 56(4), 183–188 (1992)
- 122. Krupka, K.M., Rai, D., Fulton, R.W., Strickert, R.G.: Solubility data for U(VI) hydroxide and Np(IV) hydrous oxide: application of MCC-3 methodology. Mater. Res. Soc. Symp. Proc. 44, 753–760 (1985)
- Nikitin, A.A., Sergeeva, Z.I., Khodakovsky, I.L., Naumov, G.B.: Uranyl hydrolysis in a hydrothermal region. Geokhimiya 3, 297–307 (1972)
- 124. Redkin, A.F., Wood, S.A.: Uranium(VI) in aqueous solutions at 25 °C and a pressure of 1 bar: Insight from experiements and calculations. Geochem. Int. 45(11), 1111–1123 (2007)
- 125. Torrero, M.E., Casas, I., de Pablo, J., Sandino, M.C.A., Grambow, B.A.: Comparison between unirradiated UO₂(s) and schoepite solubilities in 1 *M* NaCl medium. Radiochim. Acta 66(67), 29–35 (1994)

- Valsami-Jones, E., Ragnarsdöttir, K.Y.: Solubility of uranium oxide and calcium uranate in water, and Ca(OH)₂-bearing solutions. Radiochim. Acta **79**(4), 249–257 (1997)
- 127. Götz, C., Geipel, G., Bernhard, G.: The influence of the temperature on the carbonate complexation of uranium(VI): a spectroscopic study. J. Radioanal. Nucl. Chem. **287**(3), 961–969 (2011)
- 128. Siekierski, S., Phillips, S.L.: Actinide Nitrates, vol. 55. Solubility Data Series (1994)
- Gaona, X., Fellhauer, D., Altmaier, M.: Thermodynamic description of Np(VI) solubility, hydrolysis, and redox behavior in dilute to concentrated alkaline NaCl solutions. Pure Appl. Chem. 85(11), 2027–2049 (2013)
- 130. Moskvin, A.I.: Hydrolytic behavior of neptunium(IV, V, VI). Radiokhimiya 13, 681-687 (1971)
- 131. Kato, Y., Kimura, T., Yoshida, Z., Nitani, N.: Solid–liquid phase equilibria of Np(VI) and of U(VI) under controlled CO₂ partial pressures. Radiochim. Acta **74**(1), 21–25 (1996)
- 132. Kato, Y., Kimura, T., Yoshida, Z., Nitani, N.: Carbonate complexation of neptunyl(VI) ion. Radiochim. Acta 82, 63-68 (1998)
- 133. Tanger, J.C., Helgeson, H.C.: Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: revised equations of state for the standard partial molal properties of ions and electrolytes. Am. J. Sci. 288, 19–98 (1988)
- 134. Silva, R.: The Solubilities of Crystalline Neodymium and Americium Trihydroxides. LBL-15055, Lawrence Berkeley National Laboratory, Berkeley, California (1982)
- 135. Kim, J.I., Bernkopf, M., Lierse, C.H., F., K.: Hydrolysis reactions of Am(III) and Pu(VI) ions in nearneutral solutions. In: Geochemical Behavior of Disposed Radioactive Waste. ACS Symposium Series, pp. 115–134. American Chemical Society, Washington DC (1984)
- Nitsche, H., Edelstein, N.M.: Solubilities and speciation of selected transuranium ions. A comparison of a non-complexing solution with a groundwater from Nevada Tuff site. Radiochim. Acta 39, 23–33 (1985)
- 137. Edelstein, N., Bucher, J., Silva, R., Nitsche, H.: Thermodynamic Properties of Chemical Species in Nuclear Waste. Report ONWI-399, LBL-15055. Lawrence Berkeley Laboratory, California (1983)
- Nitsche, H.: Solubility of AmOHCO₃ in aqueous solution under atmospheric conditions. Report LBL-21237. Lawrence Berkeley Laboratory, California (1987)
- Nitsche, H.: Effects of temperature on the solubility and speciation of selected actinides in near-neutral solution. Inorg. Chim. Acta 127, 121–128 (1987)
- 140. Silva, R.: The behavior of americium in aqueous carbonate systems. Mater. Res. Soc. Symp. Proc. 26, 875–881 (1984)
- 141. Robouch, P.: Contribution à la prévision du comportement de l'américium, du plutonium et du neptunium dans la géosphèr; données géochimiques. PhD thesis, Université Louis Pasteur, Strasbourg (1987)
- 142. Casas, I., De Pablo, J., Gimenez, J., Torrero, M.E., Bruno, J., Cera, E., Finch, R.J., Ewing, R.C.: The role of pe, pH, and carbonate on the solubility of UO₂ and uraninite under norminally reducing conditions. Geochim. Cosmochim. Acta 62(13), 2223–2231 (1998)
- 143. Bruno, J., Casas, I., Lagerman, B., Munoz, M.: The determination of the solubility of amorphous UO₂(s) and the mononuclear hydrolysis constants of uranium(IV) at 25 °C. In: Scientific Basis for Nuclear Waste Management X. Materials Research Society Symposium Proceedings, vol. 84, pp. 153–160 (1987)
- 144. Aguilar, M., Casas, I., de Pablo, J., Torrero, M.E.: Effect of chloride concentration on the solubility of amorphous uranium dioxide at 25 °C under reducing conditions. Radiochim. Acta 52/53(1), 13–16 (1991)
- 145. Torrero, M.E., Casas, I., Aguilar, M., De Pablo, J., Gimenez, J., Bruno, J.: The solubility of unirradiated UO₂ in both perchlorate and chloride test solutions. Influence of the ionic medium. In: Scientific Basis for Nuclear Waste Management XIV. Materials Research Society Symposium Proceedings, vol. 212, pp. 229–234 (1991)
- 146. Jang, J.-H., Dempsey, B.A., Burgos, W.D.: Solubility of schoepite: comparison and selection of complexation constants for U(VI). Water Res. 40, 2738–2746 (2006)
- 147. Meinrath, G., Kimura, T.: Behaviour of U(VI) solids under conditions of natural aquatic systems. Inorg. Chim. Acta 204(1), 79–85 (1993)
- Meinrath, G., Kato, Y., Kimura, T., Yoshida, Z.: Solid–aqueous phase equilibria of uranium(VI) under ambient conditions. Radiochim. Acta 75, 159–167 (1996)
- Meinrath, G., Kimura, T.: Carbonate complexation of the uranyl(VI) ion. J. Alloys Compd. 202, 89–93 (1993)
- 150. Yamamura, T., Kitamura, A., Fukui, A., Nishikawa, S., Yamamoto, T., Moriyama, H.: Solubility of U(VI) in highly basic solutions. Radiochim. Acta 83, 139–146 (1998)

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- 151. Grenthe, I., Ferri, D., Salvatore, F., Riccio, G.: Studies on metal carbonate equilibria. Part 10. A solubility study of the complex formation in the uranium(VI)-water-carbon dioxide(g) system at 25 °C. J. Chem. Soc. Dalton Trans. 11, 2439–2443 (1984)
- Giammar, D., Hering, J.G.: Influence of dissolved sodium and cesium on uranyl oxide hydrate solubility. Environ. Sci. Technol. 38, 171–179 (2004)
- 153. Pashalidis, I., Runde, W., Kim, J.I.: A study of solid–liquid phase equilibria of Pu(VI) and U(VI) in aqueous carbonate systems. Radiochim. Acta **61**, 141–146 (1993)
- 154. Pashalidis, I., Czerwinski, K.R., Fanghänel, T., Kim, J.I.: Solid–liquid phase equilibria of Pu(VI) and U(VI) in aqueous carbonate systems. Determination of stability constants. Radiochim. Acta 76(1–2), 55–62 (1997)
- Sergeyeva, E.I., Nikitin, A.A., Khodakovskiy, I.L., Naumov, G.B.: Experimental investigation of equilibria in the system UO₃-CO₂-H₂O in 25–200 °C temperature interval. Geochem. Int. 9, 900–910 (1972)
- 156. Pirozhkov, A.V., Nikolaeva, N.M.: Determination of UO₂CO₃ formation constant at temperature from 25° to 150°. Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk 5, 55–59 (1976)
- 157. Blake, C.A., Coleman, C.F., Brown, K.B., Hill, D.G., Lowrie, R.S., Schmitt, J.M.: Studies in the carbonate-uranium system. J. Am. Chem. Soc. **78**, 5978–5983 (1956)
- Brown, K.B., Schmitt, J.M.: Studies in the carbonate-uranium system. Part II, The solubility of sodium uranyl tricarbonate in solutions of certain sodium salts, p. 27. U.S. Atomic Energy Commission, Technical Information Service. AECD-3229 (1950)
- 159. Korolev, K.G., Rumyantseva, G.V., Golikova, G.A.: To the problem of uranium translocation in hydrothermal environment (from experimental data). Izv. Akad. Nauk SSSR, Ser. Geologiche. 10, 102–113 (1974)
- 160. Marshall, W.L., Slusher, R.: Aqueous systems at high temperature—VIII. The solubility of UO3 hydrates in HNO₃–H₂O solutions 25–350 °C, 10–4–6 molal nitrate. J. Inorg. Nucl. Chem. 25, 283–290 (1963)
- 161. Lacher, J.R., Ensley, K., Park, J.D.: Phase relation in the system uranium trioxide–nitric acid–water at various temperatures. Inorg. Chem. 1(4), 944–945 (1962)
- 162. Efimova, V.S., Gromov, B.V.: Investigation of the system UO₃–UO₂(NO₃), 2–H₂O. Atomic Energy 35(1), 676–677 (1973)
- 163. Cordfunke, E.H.P.: The system UO₂(NO₃)₂-UO₃-H₂O. J. Inorg. Nucl. Chem. 34, 531-534 (1972)
- 164. Linke, F., Seidell, A.S. (eds.): Solubilities of Inorganic and Metal-Organic Compounds, 4th edn. American Chemical Society, Washington, D.C. (1965)
- 165. Rai, D., Serne, R.J., Moore, D.A.: Solubility of plutonium compounds and their behavior in soils. Soil Sci. Soc. Am. J. 44, 490–495 (1980)
- 166. Pérez-Bustamante, J.A.: Solubility product of tetravalent plutonium hydroxide and study of the amphoteric character of hexavalent plutonium hydroxide. Radiochim. Acta 4(2), 67–75 (1965)
- 167. Fujiwara, K., Yamana, H., Fujii, T., Moriyama, H.: Solubility product of plutonium hydrous oxide. J. Nucl. Fuel Cycle Environ. 7(1), 17–23 (2001)
- 168. Efurd, D.W., Runde, W., Banar, J.C., Janecky, D.R., Kaszuba, J.P., Palmer, P.D., Roensch, F.R., Tait, C.D.: Neptunium and plutonium solubilities in a Yucca Mountain groundwater. Environ. Sci. Technol. 32, 3893–3900 (1998)
- 169. Rothe, J., Walther, C., Denecke, M.A., Fanghänel, T.: XAFS and LIBD Investigation of the formation and structure of colloidal Pu(IV) hydrolysis products. Inorg. Chem. 43(15), 4708–4718 (2004)
- 170. Krot, N.N., Silov, V.P., Yusov, A.B., Tananaev, I.G., Grigoriev, M.S., Garnov, A.Y., Perminov, V.P., Astafurova, L.N.: Plutonium(IV) precipitation formed in alkaline media in the presence of various anions. PNNL-11901, Pacific Northwest National Laboratory, Richland, Washington (1998)
- 171. Delegard, C.H.: Literature review of plutonium(IV) hydrous oxide solubility in dilute sodium hydroxide and dilute nitric acid solutions. Battelle—Pacific Northwest Division, Richland, Washington, WTP-RPT-149, Rev. 0 (2006)
- Shilov, V.P., Fedoseev, A.M.: Solubility of Pu(IV) in weakly alkaline solutions (pH 9–14) containing silicate anions. Radiochem. 45(5), 491–494 (2003)
- 173. Yamaguchi, T., Sakamoto, Y., Ohnuki, T.: Effect of the complexation on solubility of Pu(IV) in aqueous carbonate system. Radiochim. Acta **66**(67), 9–14 (1994)
- 174. Moskvin, A.I., Gelman, A.D.: Determination of the composition and instability constants of oxalate and carbonate complexes of plutonium IV. Zh. Neorg. Khim. 3, 962–974 (1958)
- 175. Brunstad, A.: Polymerization and precipitation of plutonium(IV) in nitric acid. Ind. Eng. Chem. 51(1), 38–40 (1959)
- 176. Rai, D.: Solubility product of Pu(IV) hydrous oxide and equilibrium constants of Pu(IV)/Pu(V), Pu(IV)/Pu(VI), and Pu(V)/Pu(VI) couples. Radiochim. Acta **35**(2), 97–106 (1984)

- 177. Boehm, M.: Zur Plutoniumchemie in wässriger Salpetersäure. Thesis, München University (1992)
- 178. Budantseva, N.A., Tananaev, I.G., Fedoseev, A.M., Delegard, C.H.: Behavior of plutonium(V) in alkaline media. J. Alloys Compd. 271–273, 813–816 (1998)
- 179. Pashalidis, I., Kim, J.I., Ashida, T., Grenthe, I.: Spectroscopic study of the hydrolysis of PuO₂²⁺ in aqueous solution. Radiochim. Acta 68(2), 99–104 (1995)
- Fujiwara, K., Yamana, H., Fujii, T., Moriyama, H.: Solubility product of Pu(VI) hydrous oxide. Radiochim. Acta 91, 81–85 (2003)
- Reilly, S.D., Runde, W., Neu, M.P.: Solubility of plutonium(VI) cabonate in saline solutions. Geochim. Cosmochim. Acta 71, 2672–2679 (2007)
- Wittenberg, L.J., Steinmeyer, R.H.: The solubility of plutonium(VI) carbonate in lithium acid carbonate. J. Inorg. Nucl. Chem. 24, 1015–1016 (1962)
- 183. Robouch, P., Vitorge, P.: Solubility of PuO₂(CO₃). Inorg. Chim. Acta 140, 239-242 (1987)
- 184. Neu, M.P., Reilly, S.D., Runde, W.H.: Plutonium solubility and speciation to be applied to the separation of hydrothermal waste treatment effluent. Mater. Res. Soc. Symp. Proc. 465, 759–765 (1997)
- Drabkina, L.E.: Determination of the solubility of ammonium-plutonyl carbonate in various aqueous solutions. Radiokhimiya 2, 337–338 (1960)
- Gelman, A.D., Moskvin, A.I., Aitseva, V.P.: Carbonate compounds of plutonyl. Sov. Radichem. (Engl transl.) 4, 138–145 (1962)
- Krevinskaia, M.Y., Nikol'skii, V.D., Pozharskii, B.G., Zastenker, Y.Y.: The properties of nitric acid solutions of the plutonyl ion. 1. Hydrolysis of plutonyl nitrate. Radiokhimiya 1, 562–566 (1959)
- 188. Fellhauer, D., Neck, V., Altmaier, M., Lützenkirchen, J., Fanghänel, T.: Solubility of tetravalent actinides in alkaline CaCl₂ solutions and formation of Ca₄[An(OH)₈]⁴⁺ complexes: a study of Np(IV) and Pu(IV) under reducing conditions and the systematic trend in the An(IV) series. Radiochim. Acta **98**, 541–548 (2010)
- Neck, V., Kim, J.I., Seidel, B.S., Marquardt, C.M., Dardenne, K., Jensen, M.P., Hauser, W.: A spectroscopic study of the hydrolysis, colloid formation and solubility of Np(IV). Radiochim. Acta 89, 439–446 (2001)
- 190. Rai, D., Swanson, J.L., Ryan, J.L.: Solubility of NpO₂·xH₂O(am) in the presence of Cu(I)/Cu(II) redox buffer. Radiochim. Acta 42(1), 35–41 (1987)
- 191. Rai, D., Hess, N.J., Felmy, A.R., Moore, D.A., Yui, M.: A Thermodynamic model for the solubility of NpO₂(am) in the aqueous K⁺-HCO₃-CO₃-OH-H₂O system. Radiochim. Acta 84(3), 159–169 (1999)
- Kitamura, A., Kohara, Y.: Solubility of neptunium(IV) in carbonate media. J. Nucl. Sci. Tech. Supplement 3, 294–297 (2002)
- 193. Kim, S.S., Baik, M.H., Kang, K.C.: Solubility of neptunium oxide in the KURT (KAERI Underground Research Tunnel) groundwater. J. Radioanal. Nucl. Chem. 280(3), 577–583 (2009)
- 194. Yamaguchi, T., Pratopo, M.I., Moriyama, H., Higashi, K.: Adsorption of cesium and neptunium(V) on bentonite. In: Third International Conference on Nuclear Fuel Reprocessing and Waste Management, RECOD'91, Sendai, Japan, pp. 999–1004. Atomic Energy Society of Japan, Tokyo (Japan), Japan Atomic Industrial Forum, Inc., Tokyo (1991)
- Sevostyanova, E.P., Khalturin, G.V.: Hydrolytic behavior of dioxoneptunium(V). Radiokhimiya 18, 870–876 (1976)
- Nakayama, S., Arimoto, H., Yamada, N., Moriyama, H., Higashi, K.: Column experiments on migration behaviour of neptunium(V). Radiochim. Acta 44(45), 179–182 (1988)
- 197. Ueno, K., Saito, A.: Solubility and absorption spectra of a carbonato complex of prentavalent neptunium. Radiochem. Radioanal. Lett. 22, 127–133 (1975)
- Maya, L.: Hydrolysis and carbonate complexation of dioxoneptunium(V) in 1.0 M NaClO4 at 25 °C. Inorg. Chem. 22, 2093–2095 (1983)
- Meinrath, G.: Np(V) carbonates in solid state and aqueous solution. J. Radioanal. Nucl. Chem. 186(3), 257–272 (1994)
- Al Mahamid, I., Novak, C.F., Becraft, K.A., Carpenter, S.A., Hakem, N.: Solubility of Np(V) in K– CI–CO₃ and Na–K–Cl–CO₃ solutions to high concentrations: measurements and thermodynamic model predictions. Radiochim. Acta 81, 93–101 (1998)
- 201. Simakin, G.A.: Actual oxidation potentials of the AmO₂²⁺-AmO₂⁺, NpO₂²⁺-NpO₂⁺ pairs in the solutions of potassium and sodium carbonates. Radiokhimiya **19**(4), 518–521 (1977)
- 202. Glushko, V.P., Gurvich, L.V., Bergman, G.A., Veyts, I.V., Medvedev, V.A., Kchachkurusov, G.A., Yungman, B.S.: Thermodynamic Properties of Individual Substances, vol. 4. Nauka, Moscow (1982)
- 203. Wagman, D.D., Evans, W.H., Parker, V.B., Schumm, R.H., Halow, I., Bailey, S., Churney, K.L., Nuttal, R.L.: The NBS tables of chemical thermodynamic properties. Selected values for onorganic and C1 and C2 organic substances in SI units, Supplement 2. J. Phys. Chem. Ref. Data 11, 2-1–2-392 (1982)