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CHEMICAL THERMODYNAMICS 2

Chemical Thermodynamics of Americium

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Figure V.1: Electrode potentials (in units of V) for some americium redox couples. The species Am^{2+} is italicized to stress the fact that it is only a transient species, *cf.* Section V.2.1.

$$\begin{tikzcd}
\mathrm{AmO_2^{2+}} \arrow[r, "\substack{1.60\\ \pm0.09}"] \arrow[rr, bend right, "\substack{1.217\\ \pm0.054}"'] & \mathrm{AmO_2^{+}} \arrow[r, "\substack{0.84\\ \pm0.11}"] \arrow[rr, bend left, "\substack{1.727\\ \pm0.041}"] & \mathrm{Am^{4+}} \arrow[r, "\substack{2.62\\ \pm0.11}"] \arrow[rrr, bend right, "\substack{-0.897\\ \pm0.023}"'] & \mathrm{Am^{3+}} \arrow[r, "\substack{-2.30\\ \pm0.15}"] \arrow[rr, bend left, "\substack{-2.068\\ \pm0.016}"] & Am^{2+} \arrow[r, "\substack{-1.95\\ \pm0.08}"] & \mathrm{Am(cr)}
\end{tikzcd}$$

Fuger and Oetting [76FUG/OET] and Martinot and Fuger [85MAR/FUG] have discussed the evidence for the formation of the heptavalent aquaion in 3 to 5 M NaOH by oxidising Am(VI) solutions using γ-irradiation in the presence of N_2O or $K_2S_2O_8$. It is also claimed (Nikolaevskii *et al.* [75NIK/SHI]) that AmO_2^{2+} disproportionates to Am(VII) and Am(V) in alkaline solutions with concentrations above 10 M NaOH. There are no quantitative thermodynamic data for the Am(VII) aquaion, and the species will not be considered further.

V.2.1. Am^{2+}

As discussed by Martinot and Fuger [85MAR/FUG], there is evidence for the transient formation of Am^{2+} in aqueous perchlorate media in pulse radiolysis experiments [76SUL/GOR, 78GOR/MUL] the half life was reported to be approximately $5 \mu s$. Radiopolarography (*cf.* the review by David *et al.* [90DAV/MAS]) shows fairly unambiguosly that Am^{2+} is *not* an intermediate species in the reduction of Am^{3+} to the metal in non-complexing media, although its formation has been suggested in molten salts [83MIK] and organic solvents [69MUS/MJA, 76FRI/STO, 92KUL/KAM]. Nugent *et at.* [73NUG/BAY] estimated the Am^{3+}/Am^{2+} potential to be −2.3 V from a systematic study of the properties of the lathanide and actinide chlorocomplexes in relation to their M(II)/M(III) potentials. A similar value of −2.4 V has been estimated by Bratsch and Lagowski [86BRA/LAG]. The value of $E^\circ = -(2.3 \pm 0.15)$ V, and the standard Gibbs energy of formation of Am^{3+} selected below gives

$$\Delta_f G^\circ_m(\mathrm{Am^{2+}, aq, 298.15\,K}) = -(377 \pm 15)\ \mathrm{kJ \cdot mol^{-1}}.$$

Morss and Morss and McCue [76MOR, 76MOR/MCC] and David [86DAV] have suggested two similar equations expressing $S^\circ_m(\mathrm{M^{2+}, aq, 298.15\ K})$ in terms of the relative atomic mass, charge, ionic radius and total angular momentum quantum number. These equations give the same estimated value,

$$S^\circ_m(\mathrm{Am^{2+}, aq, 298.15\,K}) = -(1 \pm 15)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$$

where the uncertainty is estimated in this review (the slightly earlier estimate of $-9.3\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ [85DAV/FOU] was presumably superseded by that of [86DAV]).

Combination with the standard Gibbs energy of formation gives the following estimated standard enthalpy of formation:

$$\Delta_f H^\circ_m(\mathrm{Am^{2+}, aq, 298.15\,K}) = -(355 \pm 16)\ \mathrm{kJ \cdot mol^{-1}}.$$

V.2.2. Am^{3+}

The first values of the enthalpy of solution of americium in hydrochloric acid, reported by Lohr and Cunningham [51LOH/CUN] and Westrum and Eyring [51WES/EYR], were carried out before the details of the allotropy were well defined, and the crystalline structure of the metal used in these investigations is not known. Both these values correspond to a value of $\Delta_f H^\circ_m(\mathrm{Am^{3+}, aq, 298.15K}) = -670$ to $-680\ \mathrm{kJ \cdot mol^{-1}}$ for the standard enthalpy of formation of Am^{3+} with an uncertainty of about $15\ \mathrm{kJ \cdot mol^{-1}}$. Later, Morss [69MOR] made some preliminary measurements which indicated an appreciably more positive value of about $-625\ \mathrm{kJ \cdot mol^{-1}}$. Subsequently, Fuger, Spirlet and Müller [72FUG/SPI] measured the enthalpy of solution of two samples of Am(α, dhcp) in hydrogen-saturated 1 M, 1.5 M and 6 M HCl solutions. Their americium samples, which contained mainly ^{241}Am, were characterised for non-metallic (H, N, O) and metallic elements. Their values for $\Delta_f H^\circ_m(\mathrm{Am^{3+}, aq, 298.15\,K})$ in 1 M, 1.5 M and 6 M HCl were $-(616.1 \pm 0.8)$, $-(615.4 \pm 0.8)$ and $-(613.1 \pm 1.4)\ \mathrm{kJ \cdot mol^{-1}}$, respectively. More recently, Mondal *et al.* [87MON/RAS] have found the enthalpy of dissolution of essentially isotopically pure ^{243}Am(α, dhcp), containing < 50 ppm by weight of metallic impurities, in hydrogen saturated 1 M HCl to be $-(620.6 \pm 1.3)\ \mathrm{kJ \cdot mol^{-1}}$. Since the samples used by Fuger *et al.* [72FUG/SPI] were characterised for both metallic and non-metallic impurities, and since Fuger *et al.* carried out consistent measurements in 1, 1.5 and 6 M HCl, their values are preferred in the present assessment. Extrapolation of these values to zero ionic strength leads to the selected value of

$$\Delta_f H^\circ_m(\mathrm{Am^{3+}, aq, 298.15\,K}) = -(616.7 \pm 1.5)\ \mathrm{kJ \cdot mol^{-1}}.$$

The reason for the large discrepancy with the early measurements is not clear. It is too large to be attributable to the presence of β- or γ-phases of americium in the earlier material. Undetected impurities in the rather small samples used could of course be a contributing factor. The close agreement of the value by [87MON/RAS] based on dissolution of ^{243}Am suggests that the effect of the radioactivity of americium (such as radiation damage of the metal) is probably negligible. It may be noted that similar discrepancies have been found in the enthalpies of solution of uranium and (to a lesser extent) plutonium metals; for these elements, however, there are problems of the formation of unwanted oxidation states (U^{3+} and Pu^{4+}, respectively), which is not the case with americium. Some Am(V) is slowly formed by radiolysis in Am^{3+} solutions in the presence of Cl^-, *cf.* Sections V.3.1.2 and V.3.2.5, but this effect will not be significant in the short time (∼ 1 h) taken for the calorimetric dissolution, in the presence of both dissolved and evolving hydrogen.

However, the careful measurements of Fuger, Spirlet and Müller [72FUG/SPI] are confirmed by the study in Ref. [87MON/RAS], as well as the earlier preliminary work of Morss [69MOR] already mentioned. The systematic relationships between the enthalpies of formation of the aqua ions and the enthalpy of sublimation of the monoatomic gas in actinide and lanthanide metals noted by Nugent, Burnett and Morss [73NUG/BUR] also suggest the enthalpy of formation of Am^{3+} is close to the value selected here.

As noted previously, the entropy of Am^{3+} was estimated by Fuger and Oetting [76FUG/OET] from the interrelationship of the ionic radii and the known thermodynamic properties of lanthanide and actinide ions. Their value of

$$S^\circ_m(\mathrm{Am^{3+}, aq, 298.15\,K}) = -(201 \pm 15)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$$

is accepted. David [85DAV/FOU, 86DAV] has estimated the very similar value of $-199\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$.

The Gibbs energy of formation is calculated from the selected values for the enthalpy of formation and the entropy.

$$\Delta_f G^\circ_m(\mathrm{Am^{3+}, aq, 298.15\,K}) = -(598.7 \pm 4.8)\ \mathrm{kJ \cdot mol^{-1}}.$$

V.2.3. Am^{4+}

As noted in Section V.2, this species is never found in any appreciable amount in tetravalent americium solutions, which are only stable in the presence of strongly complexing anions. Nevertheless, good estimates of its thermodynamic properties are of interest.

A fairly precise estimate of its enthalpy of formation was given by Morss and Fuger [81MOR/FUG]. They pointed out that the enthalpy of the hypothetical solution process,

$$M\mathrm{O_2(cr)} + 4\,\mathrm{H^+} \rightleftharpoons M^{4+} + 2\,\mathrm{H_2O(l)} \qquad \text{(V.5)}$$

is an excellent linear function of the lattice parameter of the dioxide where M is a lanthanide (Ce and Pr) or actinide (Th, U, Np, Pu) element. Only the values for terbium are discrepant. In the same paper, Morss and Fuger [81MOR/FUG] present a careful calorimetric determination of the enthalpy of formation of two samples of $AmO_2(cr)$, one containing ^{241}Am, the other ^{243}Am. With a lattice parameter of $a = 0.53743$ nm for $AmO_2(cr)$, the correlation noted above indicates that the enthalpy of the above hypothetical reaction for $M = \mathrm{Am}$ is $-(45 \pm 5)\ \mathrm{kJ \cdot mol^{-1}}$, which combined with $\Delta_f H^\circ_m(\mathrm{AmO_2, cr, 298.15\,K})$ (*cf.* Section V.3.2.3) finally gives

$$\Delta_f H^\circ_m(\mathrm{Am^{4+}, aq, 298.15\,K}) = -(406 \pm 6)\ \mathrm{kJ \cdot mol^{-1}}$$

Although there have been a number of estimates for the electrode potential of the Am^{3+}/Am^{4+} couple, the most reliable value for this is probably from an estimate of $S^\circ_m(\mathrm{Am^{4+}, aq})$. Following Fuger and Oetting [76FUG/OET], we take the difference in entropy of Am^{4+} and Am^{3+} to be the same as that for the plutonium ions, namely $-(205 \pm 21)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, giving for Am^{4+}

$$S^\circ_m(\mathrm{Am^{4+}, aq, 298.15\,K}) = -(406 \pm 21)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}.$$

in agreement with the estimate of David [85DAV/FOU, 86DAV] of $-402\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$. When combined with the enthalpy of formation, the selected value of the entropy gives

$$\Delta_f G^\circ_m(\mathrm{Am^{4+}, aq, 298.15\,K}) = -(346 \pm 9)\ \mathrm{kJ \cdot mol^{-1}}.$$

The assessed values for the Gibbs energies of formation of Am^{3+} and Am^{4+} correspond to a reduction potential of $E^\circ = (2.62 \pm 0.11)$ V. This is in reasonable agreement with the following values extrapolated from measurements in phosphate and carbonate solutions:

- $E^\circ = (2.50 \pm 0.06)$ V calculated by Marcus *et al.* [72MAR/YAN] from the measured value of $E^\circ = (1.75 \pm 0.03)$ V in 11.5 M phosphoric acid [70YAN/GIV]. However, given the uncertainties in the speciation in such concentrated solutions, the uncertainty of ±0.06 V in the inferred E° value is almost certainly too low.
- $E^\circ = (2.6 \pm 0.1)$ V from measurements in carbonate solutions by Hobart, Samhoun and Peterson [82HOB/SAM].
- $E^\circ = (2.34 \pm 0.22)$ V extrapolated by Nugent*et al.* [71NUG/BAY] from their value of $E = 1.78$ V measured in 10 M H_3PO_4.
- $E^\circ = 2.4$ V, with an unknown uncertainty, estimated by Bratsch and Lagowski [86BRA/LAG].

These measurements are discussed in more detail in Sections V.6.2.1.2, *p.*142, and V.7.1.2.1.d, *p.*157. The correlation with spectroscopic values proposed by Nugent *et al.* [73NUG/BAY] leads to the appreciably lower value of $E^\circ = (2.2 \pm 0.2)$ V.

V.2.4. AmO_2^+

The enthalpy of reduction of AmO_2^+ to Am^{3+} by the Fe^{2+} ion

$$\mathrm{AmO_2^+} + 2\,\mathrm{Fe^{2+}} + 4\,\mathrm{H^+} \rightleftharpoons \mathrm{Am^{3+}} + 2\,\mathrm{Fe^{3+}} + 2\,\mathrm{H_2O(l)}, \qquad \text{(V.6)}$$

was measured by Gunn and Cunningham [57GUN/CUN] in 1 M $HClO_4$ to be $\Delta_r H^\circ_m(\mathrm{V.6, 298.15\,K, 1\,M\,HClO_4}) = -(302.1 \pm 4.0)\ \mathrm{kJ \cdot mol^{-1}}$. If this value is assumed to hold at infinite dilution (since the correction will be both small and uncertain), combination with the current best CODATA compatible value for the enthalpy of the Fe^{3+}/Fe^{2+} reduction [95PAR/KHO], $(41.0 \pm 1.5)\ \mathrm{kJ \cdot mol^{-1}}$, gives a value of

$$\Delta_r H^\circ_m(\mathrm{V.7, 298.15\,K}) = (384.1 \pm 5.2)\ \mathrm{kJ \cdot mol^{-1}}$$

for the reaction

$$\mathrm{Am^{3+}} + 2\,\mathrm{H_2O(l)} \rightleftharpoons \mathrm{AmO_2^+} + 4\,\mathrm{H^+} + 2\,\mathrm{e^-}. \qquad \text{(V.7)}$$

From this and the previously assigned enthalpy of formation of Am^{3+}, the selected enthalpy of formation is obtained:

$$\Delta_f H^\circ_m(AmO_2^+, aq, 298.15\,K) = -(804.3 \pm 5.4)\ kJ \cdot mol^{-1}.$$

Following Fuger and Oetting [76FUG/OET] this review accepts

$$S^\circ_m(AmO_2^+, aq, 298.15\,K) = -(21 \pm 10)\ J \cdot K^{-1} \cdot mol^{-1},$$

based on the same value for NpO_2^+ from the (corrected) work of Brand and Cobble [70BRA/COB]. Corrections could be made in an attempt to take account of the differing magnetic contributions to the entropies of these ions, but since the overall sign of these (small) corrections is not known with certainty, they are ignored and deemed to be included in the (increased) overall uncertainty.

Hence, the following Gibbs energy value is obtained:

$$\Delta_f G^\circ_m(AmO_2^+, aq, 298.15\,K) = -(739.8 \pm 6.2)\ kJ \cdot mol^{-1}.$$

V.2.5. AmO_2^{2+}

The enthalpy of reduction of AmO_2^{2+} to Am^{3+} by the Fe^{2+} ion in 1 M $HClO_4$ was also measured by Gunn and Cunningham [57GUN/CUN]. For the reaction

$$AmO_2^{2+} + 3\,Fe^{2+} + 4\,H^+ \rightleftharpoons Am^{3+} + 3\,Fe^{3+} + 2\,H_2O(l) \qquad (V.8)$$

they obtained $\Delta_r H^\circ_m(V.8, 298.15\,K, 1\,M\,HClO_4) = -(414.6 \pm 1.0)\ kJ \cdot mol^{-1}$. If this value is assumed to hold at infinite dilution (since the correction will be both small and uncertain), combination with the current best CODATA compatible value for the enthalpy of the Fe^{3+}/Fe^{2+} reduction [95PAR/KHO], $(41.0 \pm 1.5)\ kJ \cdot mol^{-1}$, gives a value of

$$\Delta_r H^\circ_m(V.9, 298.15\,K) = (537.6 \pm 4.6)\ kJ \cdot mol^{-1}$$

for the reaction

$$Am^{3+} + 2\,H_2O(l) \rightleftharpoons AmO_2^{2+} + 4\,H^+ + 3\,e^-. \qquad (V.9)$$

From this, the selected enthalpy of formation is obtained:

$$\Delta_f H^\circ_m(AmO_2^{2+}, aq, 298.15\,K) = -(650.8 \pm 4.8)\ kJ \cdot mol^{-1}.$$

Penneman and Asprey [50PEN/ASP] measured the potentials of the AmO_2^{2+}/AmO_2^+ couple to be $E(1M\,HClO_4) = (1.600 \pm 0.0005)$ V and $E(0.3M\,HClO_4) = (1.614 \pm 0.001)$ V. Brand and Cobble [70BRA/COB] suggested that the difference of 0.100 V they found between the potential of the NpO_2^+/NpO_2^{2+} couple in 1 M $HClO_4$ and the value extrapolated to infinite dilution should also be applied to the similar couples in other actinides. However, it is now clear from more recent data for the dioxoneptunium ions (see Fuger and Oetting [76FUG/OET]) and the dioxouranium ions (see Grenthe *et al.* [92GRE/FUG]) that this correction is far too large. Following Fuger and Oetting, we do not apply any correction to the "formal" potentials of Penneman and Asprey [50PEN/ASP], but increase somewhat the uncertainty limits. The small change in the potential due to the change in standard state pressure from 1 atm to 1 bar is entirely negligible in the present case. Thus, for the reaction

$$AmO_2^+ + H^+ \rightleftharpoons AmO_2^{2+} + 0.5\,H_2(g) \qquad (V.10)$$

this review obtains $\Delta_r G^\circ_m(V.10, 298.15\,K) = (154.3 \pm 5.0)\ kJ \cdot mol^{-1}$. When combined with the enthalpy of the same reaction $\Delta_f H^\circ_m(AmO_2^{2+}) - \Delta_f H^\circ_m(AmO_2^+) = (153 \pm 2.5)\ kJ \cdot mol^{-1}$ and the standard entropy of AmO_2^+ selected in Section V.2.4, this gives $S^\circ_m(AmO_2^{2+}, aq, 298.15\,K) = -(91 \pm 20)\ J \cdot K^{-1} \cdot mol^{-1}$. This is in excellent agreement with the value estimated from the entropy NpO_2^{2+} from the (corrected) work of Brand and Cobble [70BRA/COB]. According to the method used to correct for the difference in the magnetic contributions to the entropy of these ions, the estimate for the entropy of AmO_2^{2+} is -86.2 or $-88.7\ J \cdot K^{-1} \cdot mol^{-1}$, with uncertainties of $\approx 10\ J \cdot K^{-1} \cdot mol^{-1}$.

The selected value is

$$S^\circ_m(AmO_2^{2+}, aq, 298.15\,K) = -(88 \pm 10)\ J \cdot K^{-1} \cdot mol^{-1}$$

from which one obtains

$$\Delta_f G^\circ_m(AmO_2^{2+}, aq, 298.15\,K) = -(585.8 \pm 5.7)\ kJ \cdot mol^{-1}.$$

V.3. Oxygen and hydrogen compounds and complexes

V.3.1. Aqueous americium hydroxide complexes

V.3.1.1. Aqueous Am(III) hydroxide complexes

Thermodynamic data on Am(III) hydrolysis have been compiled or reviewed by a number of authors [76SCH, 78RAI/SER, 80BEN/TEA, 82ALL, 84KER, 85PHI/PHI, 86KER/SIL, 86KIM, 88MOU/ROB, 89ROB, 92FUG/KHO, 94JUN/EDE]. Only a few of them, however, attempted a critical examination of the existing information [86KER/SIL, 89ROB, 92FUG/KHO, 94JUN/EDE]. Table V.4 shows the wide variability and uncertainties of the reported values of Am(III) hydrolysis constants. They refer to the reaction

$$Am^{3+} + n\,H_2O(l) \rightleftharpoons Am(OH)_n^{(3-n)} + n\,H^+. \qquad (V.11)$$

A re-evaluation of the published data is made by this review in cases where discrepancies or results of doubtful interpretation were reported. In general, there is no unique statistical procedure for selecting the best regression equation of experimental data. A great deal of personal judgement is often a necessary part of the method. Possibilities of bias in the estimates may arise in the case of very high intercorrelation among the predictor variables. This review has used the *same* procedure to select the best hydrolysis model from *all* sets of experimental data reported by the different authors. The procedure first involved the fitting of all possible hydrolysis models using the nonlinear regression programme NLIN of the SAS/STAT software package [88SAS] on a mainframe computer. This was then followed by a series of internal comparisons to find the best cutoff point for the number of predictor variables. The partial F-test and the residual mean square were used as criteria for the assessment. The values of the hydrolysis constants recalculated by this review from the original experimental data are given in Table V.5, where the reported error limits represent this review's estimate of the 95% confidence level.

Major difficulties in the experimental determination of equilibrium constants for Am(III) hydroxide complexes generally come from its great ease of adsorption and precipitation. Most of the experimental work was carried out in the pH region where the first and the second hydroxo species are present, while only a few data have been reported on the neutral $Am(OH)_3(aq)$. By analogy with neodymium [76BAE/MES], Allard [82ALL] and Phillips *et al.* [85PHI/PHI] proposed also the existence of $Am(OH)_4^-$. The formation of this negatively charged species would increase the Am(III) solubility in the high pH region. A number of experimental studies [83RAI/STR, 84BER/KIM, 84KIM/BER, 88STA/KIM, 88STA/KIM2] have shown that such a solubility increase does not occur at $pH \leq 13$. The observations by Vitorge and Tran The [91VIT/TRA] are not considered because of the great variation of the ionic strength during their experiments. Thus, there is no experimental evidence for anionic hydrolysis complexes of Am(III). Although polynuclear hydroxo- or oxo-complexes could be formed in the region immediately before precipitation, there is no evidence of their existence. Spectroscopic results [84BER/KIM, 84KIM/BER, 88STA/KIM] suggesting the absence of polynuclear complexes were inconclusive since these species are not expected to appreciably affect spectral shapes. This review has excluded the presence of polynuclear species on a statistical basis during the computer refinement of experimental data [82SIL, 84BER/KIM, 84KIM/BER].

No systematic studies have been made with the ionic strength varied to allow extrapolation to thermodynamic conditions. Corrections for activity coefficients should be possible with the equation derived from the specific ion interaction equations (see Appendix B, Eqs. (B.5) and (B.8)). Eq. (B.5) predicts a linear ionic strength dependence. Figures V.2 and V.3 show, however, that the equilibrium data from Table V.4, rearranged according to Eq. (B.5), cluster in two distinct regions of the graphs. According to Korotkin [73KOR2, 74KOR], the contradictory data might be explained with a different effect of the cations H^+, Li^+, Na^+,K^+ and NH_4^+ of the background electrolyte on Am(III) hydrolysis. However, the difference between the $\log_{10}{}^*\beta_n^\circ$ values, obtained using the specific ion interaction equations (Eq. (B.5) in Appendix B), is too large to be accounted for by a medium effect.

A kinetic method of analysis was used in Refs. [69MAR/KIK, 72SHA/STE, 73KOR2], with Am species moving in the solution either under the influence of an electric field or because of the solvent flow. Assuming a slow rate of equilibration between the various Am species, the formation of distinct Am peaks was entirely attributed to hydrolysis reactions. This review rejects this assumption because the rate of hydrolysis reactions, which involve only dissociation of protons from bound water molecules is expected to be rapid. Furthermore, it is likely that adsorption-

Table V.4: Literature values of equilibrium constants (in logarithmic units) for the reactions

$$Am(OH)_3(s) + 3\,H^+ \rightleftharpoons Am^{3+} + 3\,H_2O(l)$$

and

$$Am^{3+} + n\,H_2O(l) \rightleftharpoons Am(OH)_n^{(3-n)} + n\,H^+.$$

$Am(OH)_3(s)$	$AmOH^{2+}$	$Am(OH)_2^+$	$Am(OH)_3(aq)$	t (°C)	Medium	Method	Reference
	-5.92 ± 0.11			23	0.1 M (H, Li) ClO_4	dis	[69DES/HUS]
	-3.05 ± 0.05			15	5×10^{-3} M (H,K)Cl	em	[69MAR/KIK]
	-3.13 ± 0.1	-6.76		25	5×10^{-3} M NH_4ClO_4	em	[72SHA/STE]
	-5.3 ± 0.1			?	0.1 M (H, Li) ClO_4	dis	[73HUS/HUB, 76HUB/HUS]
	-2.5	-6.6		19	0.1 M $LiNO_3$	chr, em	[73KOR2]
		-14.7		25	0.2 M $NaClO_4$	dis	[82BID]
	-7.5 ± 0.3			25	1 M $NaClO_4$	dis	[82LUN]
	-7.03 ± 0.04			25	1 M $NaClO_4$	pot	[82NAI/CHA]
16.6 ± 0.4	$-7.7 \pm 0.3^{(a)}$	-16.7 ± 0.7	$-25.0 \pm 0.3^{(b)}$	25	0.1 M $NaClO_4$	sol	[82SIL]
	-7.54 ± 0.2			21	0.7 M NaCl	dis	[83CAC/CHO]
17.5 ± 0.3				25	0.1 M $NaClO_4$	sol	[83EDE/BUC]
17.5 ± 0.3	≤ -8.2	-17.1 ± 0.5	≤ -27.0	22	corr. to 0	sol	[83RAI/STR]
13.85 ± 0.11	-7.93 ± 0.35	-14.77 ± 0.25	-24.71 ± 0.11	25?	0.1 M $NaClO_4$	sol	[84BER/KIM]
(c)	-7.93 ± 0.13	-14.95 ± 0.13	-24.82 ± 0.11				
14.18 ± 0.47	-6.34 ± 0.83	-13.64 ± 0.63	-22.87 ± 0.52	25?	0.1 M $NaClO_4$	sol	[84KIM/BER]
(c)	-4.96	-12.88	-22.34				
	-6.8 ± 0.3			25	0.5 M $NaClO_4$	dis	[87RAO/MAH]
15.6 ± 0.3	-7.5 ± 0.3	-15.4 ± 0.4	-26.9 ± 0.5	25	0.1 M $NaClO_4$ ($\leq$ 3.7 GBq/l)	sol	[88STA/KIM, 88STA/KIM2]
16.3 ± 0.3	-7.5 ± 0.2	-15.4 ± 0.3	-26.9 ± 0.2	25	0.1 M $NaClO_4$ (44 - 185 GBq/l)		
16.2 ± 0.5	-7.8 ± 0.4	-15.4 ± 0.5	-26.9 ± 0.5	25	0.1 M NaCl (74 - 185 GBq/l)		
16.1 ± 0.1	-8.1 ± 0.3	-15.8 ± 0.4	-27.0 ± 0.5	25	0.6 M NaCl (74 - 185 GBq/l)		
$-25.0^{(d)}$			$14.4^{(e)}$	25	5 M $NaClO_4$		
14.60 ± 0.11	-6.40 ± 0.11	-13.40 ± 0.16	-20.31 ± 0.17	25	3 M $NaClO_4$	sol	[89PAZ/KOC]
	-6.9 ± 0.2		$-23.8 \pm 0.9^{(f)}$	25	0.1 M ClO_4^-	em	[89ROS/REI]

Table V.4 (continued)

$Am(OH)_3(s)$	$AmOH^{2+}$	$Am(OH)_2^+$	$Am(OH)_3(aq)$	t (°C)	Medium	Method	Reference
			≤ -28.6	?	corr. to 0	sol	[90FEL/RAI]
$-27.35^{(d)}$				?	diluted	pot	[90PER/SAP]
			$-11.1^{(g,h)}$	?	diluted	sol	[91VIT/TRA]

(a) Silva kept $\log_{10}{}^*\beta_1$ constant (= −7.7) in the least-squares fitting of his solubility data. The value of $\log_{10}{}^*\beta_1$ was taken from a previous work, [83EDE/BUC] where the first hydrolysis constant of Cm(III) was measured by potentiometry (*cf.* Appendix A).

(b) For $Am(OH)_4^-$, Silva reported $\log_{10}{}^*\beta_4 < -34.9$.

(c) Data obtained from solubility measurements of $AmO_2(s)$.

(d) Equilibrium constant $\log_{10}K_{s,0}$ for the reaction: $Am(OH)_3(s) \rightleftharpoons Am^{3+} + 3\,OH^-$.

(e) Stability constant $\log_{10}\beta_3$ for the reaction: $Am^{3+} + 3\,OH^- \rightleftharpoons Am(OH)_3(aq)$.

(f) For $Am(OH)_4^-$, Rösch *et al.* reported $\log_{10}{}^*\beta_4 \leq -38 \pm 1$.

(g) Equilibrium constant $\log_{10}K_{s,3}$ for the reaction: $Am(OH)_3(s) \rightleftharpoons Am(OH)_3(aq)$.

(h) Vitorge and Tran The reported $\log_{10}K_4 = -0.2$ for the equilibrium: $Am(OH)_3(aq) + OH^- \rightleftharpoons Am(OH)_4^-$.

desorption processes of americium species on the stationary phase interfered with the measurements.

Americium hydrolysis equilibria were studied using a solvent extraction technique by both Désiré, Hussonnois and Guillaumont [69DES/HUS] and Hussonnois *et al.* [73HUS/HUB] below pH 5.9 in 0.1 M $LiClO_4$ solutions. They assumed the presence of $AmOH^{2+}$ in quantities large enough to produce measurable deviations from the pH dependence of distribution coefficients expected in the presence of Am^{3+} only. Reanalysis of the data by this review excluded this for statistical reasons.

The values of $\log_{10}{}^*\beta_n$ for $n = 1$ and 2 at 0.1 M ionic strength reported by the same research group for distinct solubility experiments [84BER/KIM, 84KIM/BER, 88STA/KIM] cover nearly three orders of magnitude (see Figures V.2 and V.3). However, a reanalysis of the data [84BER/KIM, 84KIM/BER] made by this review indicated that a major disagreement exists only for $\log_{10}{}^*\beta_3$. This discrepancy appears to be related to a change of the solid phase with pH, *cf.* Appendix A. Model calculations below pH 8 were insensitive to ${}^*\beta_1$, suggesting a small concentration of $AmOH^{2+}$ overwhelmed with the predominant $Am(OH)_2^+$ (*cf.* Table V.5). Solubility measurements using $AmO_2(s)$ cannot be used for a quantitative evaluation of hydrolysis constants because the dissolution reactions could not be identified.

Silva [82SIL] analysed the pH dependence of $Am(OH)_3(cr)$ solubility in 0.1 M $NaClO_4$ in terms of four hydroxide complexes. The claim for the species $Am(OH)_3(aq)$ and $Am(OH)_4^-$ is refuted by this review because the experimental points above pH 8.5, influential in fitting the chosen model, were improperly overweighted.

Table V.5: Values of equilibrium constants (logarithmic units) for the reactions

$$Am(OH)_3(s) + 3\,H^+ \rightleftharpoons Am^{3+} + 3\,H_2O$$

and

$$Am^{3+} + n\,H_2O(l) \rightleftharpoons Am(OH)_n^{(3-n)} + n\,H^+$$

as recalculated by this review from the original experimental data (see Appendix A).

$Am(OH)_3(s)$ (phase)	$AmOH^{2+}$	$Am(OH)_2^+$	$Am(OH)_3(aq)$	t (°C)	Medium	Reference
	-7.3 ± 0.4	-15.0 ± 0.2		25	1 M ($NaClO_4$)	[82LUN]
	-7.2 ± 0.2	-15.0 ± 0.3		25	1 M ($NaClO_4$)	[82NAI/CHA]
17.5 ± 0.6(am)				22	corr. to 0	[83RAI/STR]
15.9 ± 0.6(cr)	-6.9 ± 0.6	-15.1 ± 0.6		25	0.1 M ($NaClO_4$)	[82SIL]
13.7 ± 0.2(?)		-14.7 ± 0.2		25?	0.1 M ($NaClO_4$)	[84BER/KIM]
13.9 ± 0.2(?)		-14.3 ± 0.3		25?	0.1 M ($NaClO_4$)	[84KIM/BER]
15.5 ± 0.4(?)	-7.0 ± 0.4	-15.1 ± 0.4	-26.4 ± 0.5	25	0.1 M ($NaClO_4$)	[88STA/KIM]

The publication by Stadler and Kim [88STA/KIM] is the major contribution to the study of $^{241}Am(OH)_3(s)$ solubility at high pH. Measurements were made in various ionic media (0.1 M and 5 M $NaClO_4$; 0.1 M, 0.6 M and 3 M NaCl), and at increasing radiation fields. The α-radiation damage affected the particle size of the precipitates without changing the chemical nature of the solution species. Formation of Am(V) only occurred in 3 M NaCl because of the presence of oxidising radicals. The analysis of the data obtained in 0.1 M $NaClO_4$ used ${}^*\beta_1$, ${}^*\beta_2$, and ${}^*\beta_3$ as best predictor variables (Table V.5).

Rai *et al.* [83RAI/STR], working with an amorphous solid in 1.5×10^{-3} M $CaCl_2$, reported a much higher americium solubility. Although the curve fitting analysis was insensitive to the first hydrolysis constant, an upper limit was assigned to the value of ${}^*\beta_1$. The proposed values for ${}^*\beta_2$ and ${}^*\beta_3$ are lower than selected in this review. The difference may be attributed to a pH dependent change of the solubility controlling solid phase in Ref. [83RAI/STR].

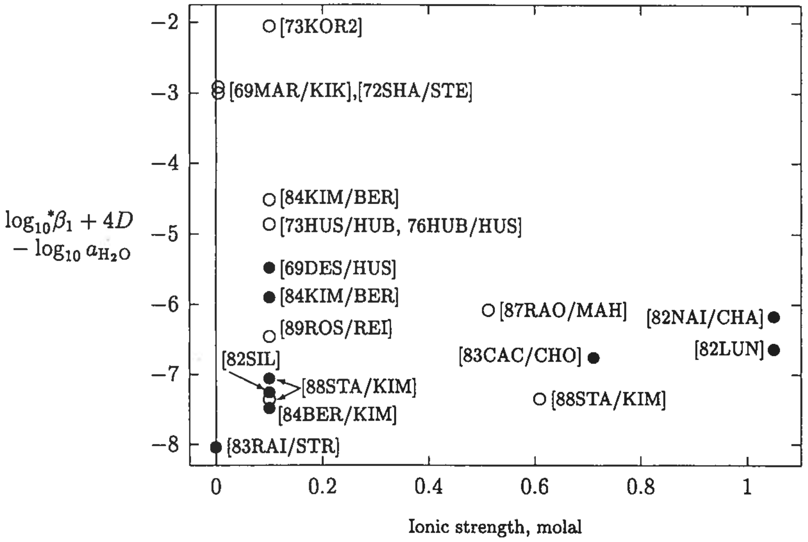
Values for ${}^*\beta_1$ in 0.7 M NaCl [83CAC/CHO] and in 0.5 M $NaClO_4$ [87RAO/MAH], and for ${}^*\beta_2$ in 0.2 M $NaClO_4$ [82BID] were obtained by solvent extraction. Although they are of the correct order of magnitude, they have not been included in the set of data used to calculate thermodynamic constants, because of experimental shortcomings (*cf.* Appendix A on discussion of selected references).

Hydrolysis equilibria in 1 M $NaClO_4$ were investigated by Lundqvist [82LUN] and by Nair, Chander and Joshi [82NAI/CHA] using, respectively, solvent extraction and potentiometry. In both cases, model calculations assumed only the formation of $AmOH^{2+}$. However, reinterpretation of the data by this review finds statistically significant evidence also for $Am(OH)_2^+$ (*cf.* Table V.5).

The results of Pazukhin and Kochergin [89PAZ/KOC] are not considered in this review for the reasons specified in Appendix A.

Thermodynamic data can be derived from the selected set of hydrolysis constants

Figure V.2: Literature data (*cf.* Table V.4) for the equilibrium
$$Am^{3+} + H_2O(l) \rightleftharpoons AmOH^{2+} + H^+$$
plotted according to Eq. (B.5). Filled circles denote the original equilibrium constants in experimental studies that are re-evaluated in the present review as described in the text and in Appendix A. For the sake of clarity, the constant from [89PAZ/KOC] at 3.5 m $NaClO_4$ ($\log_{10}{}^*\beta_1 + 4D - \log_{10} a_{H_2O} = -5.28$) is not presented in this graph.

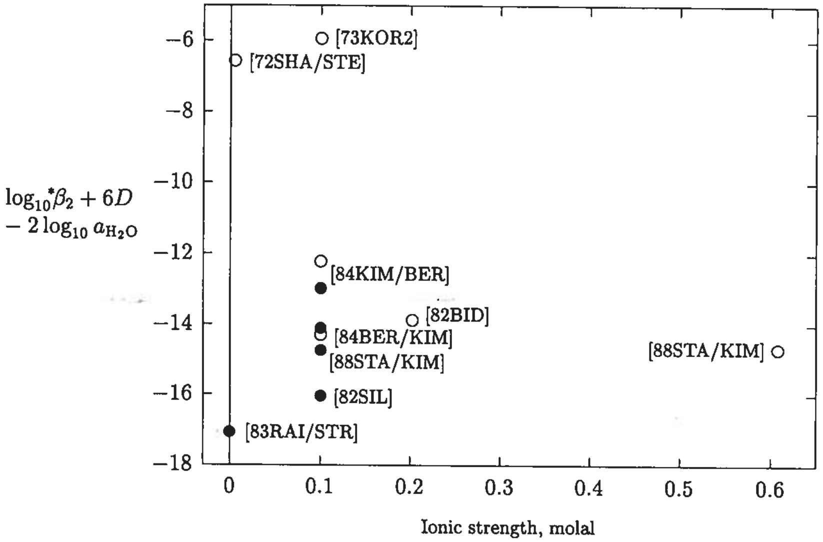


at 0.1 M and 1 M ionic strength (Table V.5) on behalf of Eq. (B.5) in Appendix B. However, the data are too sparse to allow an accurate least-square extrapolation to zero ionic strength. To this purpose, experimental measurements should be undertaken at other ionic strengths. Consequently, equilibrium constants in Table V.5 are separately extrapolated to infinite dilution. Since there are no interaction coefficient data for Am^{3+}, $AmOH^{2+}$ and $Am(OH)_2^+$, the correction has been made by taking the data for trivalent lanthanides, and for typical di- and monovalent ions, *cf.* Appendix B, Section B.1.4, together with the value for $\varepsilon_{(H^+,\ ClO_4^-)}$. This gives the following estimated values in sodium perchlorate media:

$$\begin{array}{lcl}
\Delta\varepsilon_1(\text{V.11}, n=1) & = & (0.04 \pm 0.05)\ \text{kg} \cdot \text{mol}^{-1} \\
\Delta\varepsilon_2(\text{V.11}, n=2) & = & -(0.04 \pm 0.07)\ \text{kg} \cdot \text{mol}^{-1} \\
\Delta\varepsilon_3(\text{V.11}, n=3) & = & -(0.07 \pm 0.07)\ \text{kg} \cdot \text{mol}^{-1}
\end{array}$$

A weighted average of the recalculated and then extrapolated values of ${}^*\beta_n^\circ$ gives $\log_{10}{}^*\beta_1^\circ = -(6.4 \pm 0.2)$ and $\log_{10}{}^*\beta_2^\circ = -(13.9 \pm 0.1)$. Although the calculated uncertainties are statistically correct, it is possible that the actual uncertainties are much

Figure V.3: Literature data (*cf.* Table V.4) for the equilibrium
$$Am^{3+} + 2\,H_2O(l) \rightleftharpoons Am(OH)_2^+ + 2\,H^+$$
plotted according to Eq. (B.5). Filled circles denote the original equilibrium constants in experimental studies that are re-evaluated in the present review as described in the text and in Appendix A. For the sake of clarity, the constant from [89PAZ/KOC] at 3.5 m $NaClO_4$ ($\log_{10}{}^*\beta_2 + 6D - 2\log_{10} a_{H_2O} = -11.66$) is not presented in this graph.



larger.

The value for the first hydrolysis constant implies a higher stability for $Am(OH)^{2+}$ than reported in previous reviews on americium and lanthanide hydrolysis. For example, values of $\log_{10}{}^*\beta_1^\circ = -(7.1 \pm 0.5)$, −7.5 and −6.6 have been selected, respectively, by Fuger [92FUG], Allard, Olofsson and Torstenfelt [84ALL/OLO] and Moulin *et al.* [88MOU/ROB]. Baes and Mesmer [76BAE/MES] assigned a value of $\log_{10}{}^*\beta_1^\circ = -8.0$ to Nd(III) (a chemical analogue of Am(III)), while Rard [85RAR3] selected a value of −8.25 for Eu(III). Moreover, $AmOH^{2+}$ was rejected on statistical grounds in the re-evaluation of the experimental data of Refs. [84BER/KIM, 84KIM/BER], suggesting that $AmOH^{2+}$ was not an important species in these experiments, *i.e.*, that $\log_{10}{}^*\beta_1 \leq \log_{10}{}^*K_2 = (\log_{10}{}^*\beta_2 - \log_{10}{}^*\beta_1)$. This result also favors a lower stability for $AmOH^{2+}$ and a value for $\log_{10}{}^*\beta_1^\circ$ near −7.0. The reason for the apparent discrepancy is unknown and may be due to unrecognised systematic errors in some of the experimental data. Furthermore, different procedures exist to calculate confidence intervals of predictor variables in non-linear regression analysis. Indeed, slightly different uncertainties have been obtained using different statistical computer packages. Therefore, it was felt that it would be more realistic to select the unweighted average of the values extrapolated to $I = 0$, *i.e.*, $\log_{10}{}^*\beta_1^\circ = -(6.4 \pm 0.7)$, where the uncertainty has been assigned to cover the maximum range of expectancy.

It is difficult to decide whether the values of $\log_{10}{}^*\beta_2^\circ$ belong to different parent distributions. A discrepancy may exist between the data in Ref. [82SIL] and [88STA/KIM], and the remaining values. A weighted average of $\log_{10}{}^*\beta_2^\circ = -(14.4 \pm 0.3)$ and $-(13.8 \pm 0.1)$ can be calculated, respectively, from the first and the second set of data. The unweighted average of the two values gives $\log_{10}{}^*\beta_2^\circ = -(14.1 \pm 0.6)$ where the uncertainty has been assigned to cover the maximum range of expectancy.

There are not many equilibrium data for $Am(OH)_3(aq)$. The value selected by this review is that recalculated from solubility data reported by Stadler and Kim [88STA/KIM] and extrapolated to infinite dilution. More accurate determinations of hydrolysis equilibria in the alkaline pH region are recommended.

This review selects the following standard equilibrium constants (*cf.* Table III.2):

$$\begin{aligned}
\log_{10}{}^*\beta_1^\circ\ (\mathrm{V.11}, n = 1, 298.15\,\mathrm{K}) &= -6.4 \pm 0.7\\
\log_{10}{}^*\beta_2^\circ\ (\mathrm{V.11}, n = 2, 298.15\,\mathrm{K}) &= -14.1 \pm 0.6\\
\log_{10}{}^*\beta_3^\circ\ (\mathrm{V.11}, n = 3, 298.15\,\mathrm{K}) &= -25.7 \pm 0.5
\end{aligned}$$

The standard Gibbs energies of formation have been calculated to be

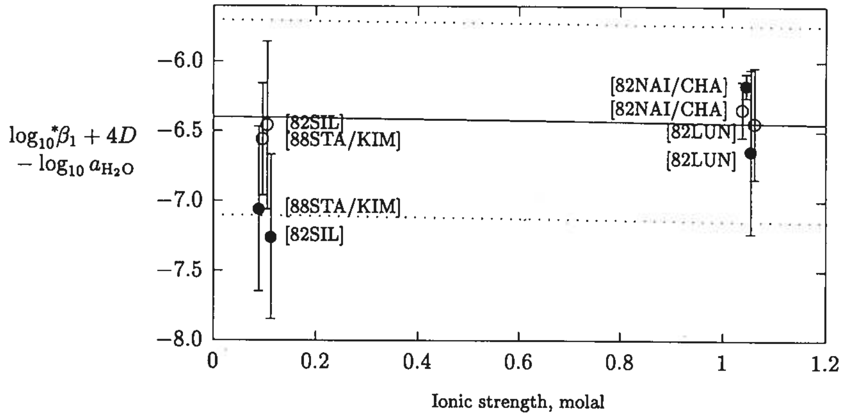
$$\begin{aligned}
\Delta_f G_m^\circ(\mathrm{AmOH^{2+}, aq, 298.15\,K}) &= -(799.3 \pm 6.2)\ \mathrm{kJ \cdot mol^{-1}}\\
\Delta_f G_m^\circ(\mathrm{Am(OH)_2^+, aq, 298.15\,K}) &= -(992.5 \pm 5.9)\ \mathrm{kJ \cdot mol^{-1}}\\
\Delta_f G_m^\circ(\mathrm{Am(OH)_3, aq, 298.15\,K}) &= -(1163.4 \pm 5.5)\ \mathrm{kJ \cdot mol^{-1}}
\end{aligned}$$

Figure V.4 shows the ionic strength dependence of the re-evaluated and original literature values of $\log_{10}{}^*\beta_1$ (*cf.* Tables V.5 and V.4) according to the specific ion interaction principles described in Appendix B, *cf.* Eq. (B.5). Although this Figure does not illustrate the selection procedure for the value of the equilibrium constant, ${}^*\beta_1^\circ$, at $I = 0$, it shows nevertheless that the recalculated values of ${}^*\beta_1$ given in Table V.5 do follow the ionic strength dependence predicted by the estimated specific interaction parameters in Section B.1.4. A linear fit of the original literature values (filled circles in Figure V.4) would instead require a value of $\varepsilon_{(\mathrm{AmOH^{2+},ClO_4^-})} \approx -0.4\ \mathrm{kg \cdot mol^{-1}}$, which would be inconsistent with the values of specific ion interaction coefficients for divalent ions, which are in the range $+0.09 \leq \varepsilon \leq +0.89$, *cf.* Table B.3 and Section B.1.4.

The distribution of dissolved species in the americium(III) hydroxide system in standard aqueous solutions (*i.e.*, at $I = 0$) at 298.15 K is illustrated in Figure V.5 for the range $6 \leq \mathrm{pH} \leq 12$. This diagram shows that $AmOH^{2+}$ is a relatively minor species predominating only in a pH range of about one unit, contrary to the other species in this system. Furthermore, increasing ionic strength reduces the acidity range in which $AmOH^{2+}$ predominates, as shown in Figure V.6. A distribution diagram for the hydrolysis of Am(III) in 0.1 M $NaClO_4$ solutions is presented in the lower part of Figure V.8.

The values for the second and third hydrolysis constants of americium(III) selected here fall in the range of values selected in other reviews for Am(III), and lanthanide(III) hydrolysis. For example, for $Am(OH)_2^+$ and $Am(OH)_3(aq)$ Fuger [92FUG] recommended $\log_{10}{}^*\beta_2^\circ = -(14.8 \pm 0.5)$ and suggested, by analogy with Nd(III), a value of $\log_{10}{}^*\beta_3^\circ = -26.5$ for Am(III). For the same equilibrium constants Allard, Olofsson and Torstenfelt [84ALL/OLO] selected -16.5 and -26.5 respectively, while Moulin *et al.* [88MOU/ROB] preferred -14.6 and -23.6. It must be pointed out, however, that these constants extend over a range of a few logarithmic units.

Figure V.4: Equilibrium constants for reaction: $Am^{3+} + H_2O(l) \rightleftharpoons AmOH^{2+} + H^+$ at 25°C in $NaClO_4$ solutions plotted according to Eq. (B.5). Open circles correspond to the values re-evaluated in this review and given in Table V.5, while filled circles correspond to the original values reported in the literature, *cf.* Table V.4 (with the uncertainties increased by a factor of 1.96 in order to approximate the 95% uncertainty level). For increased readability, the symbols are arbitrarily shifted ($\leq \pm 0.014$ mol/kg) along the X-axis. The solid line represents Eq. (B.5) with $\log_{10}{}^*\beta_1^\circ = -(6.4 \pm 0.2)$ and $\Delta\varepsilon = (0.04 \pm 0.05)\ \mathrm{kg \cdot mol^{-1}}$. The associated uncertainties are given by the dotted lines.



Hubbert *et al.* [76HUB/HUS] report $\Delta_r H_m(\mathrm{V.11}, n = 1, 298.15\,\mathrm{K}) = 65\ \mathrm{kJ \cdot mol^{-1}}$. However, due to the scarcity of the experimental data and the narrow pH range used (*cf.* Appendix A) this review does not consider the values reported by Hubbert *et al.* as reliable.

V.3.1.2. Aqueous Am(V) and Am(VI) hydroxide complexes

Cohen has described the instability of Am(VI) solutions [72COH]. The formation of $AmO_2OH(aq)$ was assumed by Kim *et al.* [85MAG/CAR, 86BUP/MAG, 88KIM/BUC, 88STA/KIM, 88STA/KIM2] in their interpretation of americium solubility measurements in aqueous solutions containing significant chloride concentrations. This is discussed in Section V.3.2.5. Tananaev proposed the existence

Figure V.5: Calculated distribution diagram of americium species at 25°C in standard aqueous solutions ($I = 0$) in the range $6 \leq \text{pH} \leq 12$. The precipitation of solid phases is not considered. The dotted curves represent the uncertainty range of each calculated fraction according to the rules of error propagation, *cf.* Eq. (C.18).

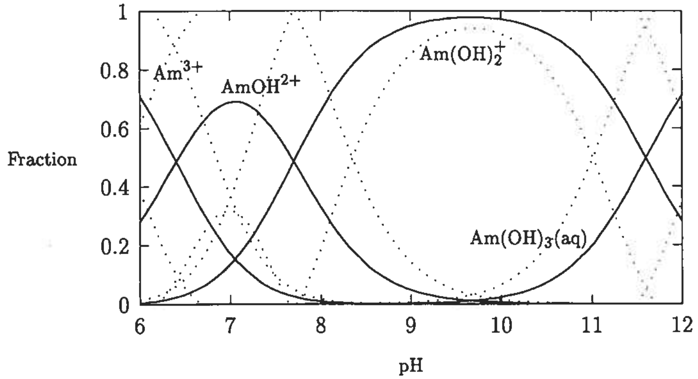
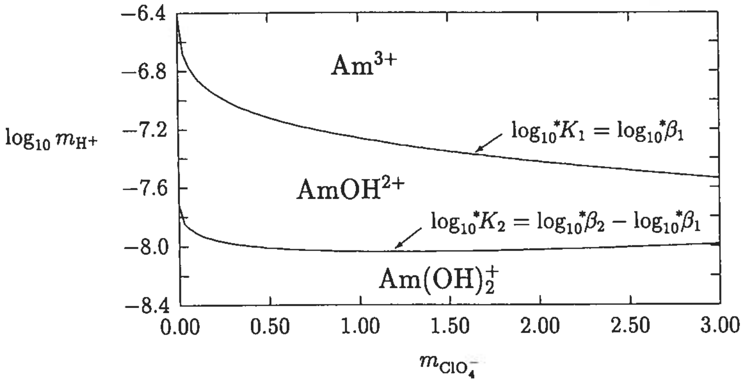


Figure V.6: Calculated ionic strength dependence of the distribution of Am^{3+}, $AmOH^{2+}$ and $Am(OH)_2^+$, at 25°C in $NaClO_4$ solutions. The precipitation of solid phases is suppressed. The curves represent the acidity at which two aqueous americium species have the same concentration, and are calculated with the specific ion interaction equations of Appendix B. For clarity, neither uncertainties nor the curve for $\log_{10}{}^*K_3$ are plotted in this diagram.



of $AmO_2(OH)_n^{(1-n)}$ with $n = 1 \ldots 4$ [90TAN2] and of $AmO_2(OH)_n^{(2-n)}$ also with $n = 1 \ldots 4$ [89TAN] based on spectrophotometric measurements in strongly alkaline solutions. No thermodynamic data can be recommended for any of these complexes.

V.3.2. *Solid americium oxides and hydroxides*†

V.3.2.1. *The americium-oxygen system*

It is still not possible to give a definite phase diagram for the Am–O system, since the principal studies are far from consistent. Chikalla and Eyring have investigated the system using room- and high-temperature X-ray techniques [68CHI/EYR] and have also measured the oxygen dissociation pressures and derived partial enthalpies and entropies for $1.8 < \text{O/Am} < 1.99$ from 1139 to 1445 K [67CHI/EYR], while Sari and Zamorani [70SAR/ZAM] have made DTA measurements for $1.67 < \text{O/Am} < 2.00$ and examined ceramographs for a wider range of compositions. However, since it is impossible to quench the hypostoichiometric fluorite phase, while the reactions involving oxides at lower O/Am are very sluggish, room-temperature X-ray patterns and ceramographs are difficult to interpret. In addition, the relatively short half-life of ^{241}Am, used in all these studies, means that any subtly ordered phases similar to those in the corresponding lanthanide oxide systems are unlikely to be observed due to the radiation self-damage (but see below). A possible phase diagram consistent with many of the observations of the major studies and with known behaviour of the Pu–O and Ln–O systems is shown in Figure V.7.

The major features are a broad fcc fluorite phase $AmO_{2-x}(cr)$ which certainly above 1300 K [70SAR/ZAM], and possibly above 1150 K [67CHI/EYR], extends from $\sim AmO_{1.65}(cr)$ to $AmO_2(cr)$. At lower temperatures, there is probably a bcc phase with a range of homogeneity around $AmO_{1.6}(cr)$, but the phase relationships in this region are very far from clear. The stoichiometric sesquioxide can exist in two and possibly three of the crystal structures adopted by the lanthanide oxides, see Section V.3.2.2.

Lyalyushkin *et al.* [86LYA/SUD] have shown that when heated in a closed capillary with finely-powdered $SiO_2(s)$, $AmO_2(cr)$ starts to decompose to lower oxides at temperatures appreciably lower than for pure $AmO_2(cr)$ under the same conditions. This was attributed to the formation of reducing gases such as $H_2(g)$ from radiolytic decomposition of vapours outgassed from the silica. The same authors also suggest that an intermediate phase formed under these conditions was a rhombohedral oxide $AmO_{1.71}(cr)$, based on splitting of the 220 reflections of the fundamental fcc structure, but this conclusion needs to be confirmed.

Akimoto [67AKI] claims to have prepared AmO(s) by heating "tens of micrograms" of americium metal in a sealed quartz capillary with the stoichiometric amount of (separately heated) $Ag_2O(s)$. Although it was intended to heat the Am(cr) to ~850°C, the actual reaction temperature was much higher, since the quartz capillary

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† Earlier versions of Sections V.3.2.1, V.3.2.2 and V.3.2.3 were published in the volume edited by Cordfunke and Konings [90COR/KON]. This, however, contained a number of misprints which have been corrected in the current version.

iments. Although HCO_3^- was the predominant ion of the carbonate system under the experimental conditions (p_{CO_2} = 0.1 and 1.0 atm), there was no evidence for $Am(HCO_3)_n^{(3-n)}$ complexes. The determined stability constants, converted to molal units, are extrapolated to zero ionic strength using the selected ion interaction coefficients (*cf.* Appendix B, Section B.1.4), to give $\log_{10}\beta_1^\circ = (8.00 \pm 0.10)$ and $\log_{10}\beta_2^\circ = (12.57 \pm 0.21)$. These values are used in the selection procedure described in Section V.7.1.2.1.

[82NAI/CHA]

Nair, G.M., Chander K., Joshi, J.K., Hydrolysis constants of plutonium(III) and americium(III), Radiochim. Acta, **30** (1982) 37–40.

The authors used a potentiometric method to measure the hydrolysis constants of Am(III), Pu(III), Sm(III) and Eu(III) in 1 M $NaClO_4$ at 25°C. The americium titration was carried out in the pH range from 4 to 7.2 until the precipitation of the hydroxide was observed. The authors estimated the value of the first hydrolysis constant, $\log_{10}{}^*\beta_1 = -(7.03 \pm 0.04)$, using a weighted least-square treatment of the experimental formation curve ($\bar{n}$ *vs.* pH). The weight of each point was iteratively calculated during the regression procedure rather than externally supplied as the inverse of the variance of individual measurements. This led to an underestimation of the uncertainty assigned to the ${}^*\beta_1$ value. For different $[Am]_{TOT}$ concentrations, the experimental points did not coincide into a single curve below pH = 6.5. Titrated concentrations were so low that scattering in the data may be ascribed to systematic errors in the measurement of small changes of ligand number ($\bar{n}$). A recalculation of the best fitting curve using a model including $Am(OH)_2^+$ as additional species provides a statistically significant decrease of the residual sum of squares. Although the hydrolysis constants derived from these calculations are of the correct order of magnitude, the choice of such a model is questionable, because the highest average ligand number achieved is only 0.6, and the addition of ${}^*\beta_2$ appears to be sensitive to only a few points of the formation curve. However, this does not seem to be a sufficient reason to discard the two-variable model. This review calculates $\log_{10}{}^*\beta_1 = -(7.2 \pm 0.2)$ and $\log_{10}{}^*\beta_2 = -(15.0 \pm 0.3)$. The associated uncertainties reflect the difficulties in selecting a model. Conversion to $I = 0$ using the specific ion interaction coefficients reported in Sections V.3.2.4 and B.1.4 yields $\log_{10}{}^*\beta_1^\circ = -(6.3 \pm 0.2)$ and $\log_{10}{}^*\beta_2^\circ = -(13.8 \pm 0.3)$.

[82RAI/STR]

Rai, D., Strickert, R.G., Solubilities of actinide solids under oxic conditions, Report PNL-SA-10368, Pacific Northwest Laboratory, Richland, Washington, 1982, 18p.

This reference includes the same solubility results for $Am(OH)_3(cr)$ as reference [83RAI/STR] but without giving any details.

[82SIL]

Silva, R.J., Thermodynamic properties of chemical species in nuclear waste. Topical report: The solubilities of crystalline neodymium and americium trihydroxides, LBL-15055, Lawrence Berkeley Laboratory, Berkeley, California, 1982, 57p.

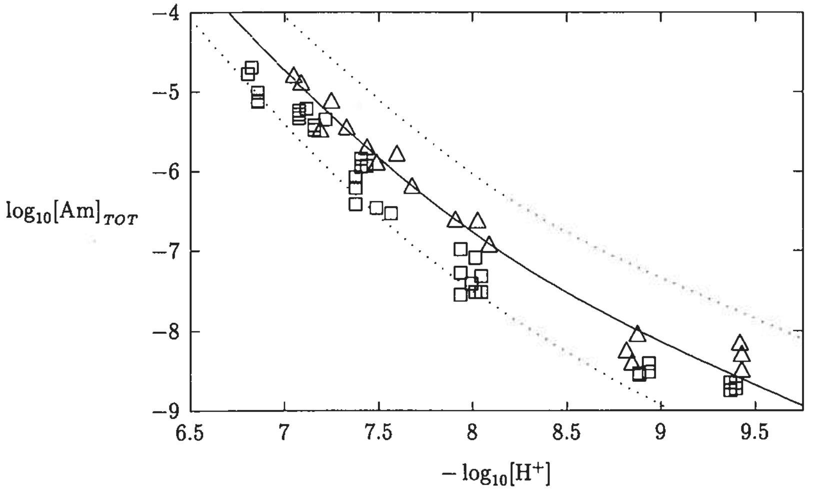
Solubility measurements of ${}^{243}Am(OH)_3(cr)$ and $Nd(OH)_3(cr)$ were made in 0.1 M $NaClO_4$ solutions at (25 ± 1)°C within the pH range 6 to 10.

This is the only solubility study with americium hydroxide using an X-ray characterised crystalline solid. The solid phase was prepared by rigorously controlled high-temperature transformation of $Am(OH)_3(am)$. Optical viewing by Scanning Electron Microscopy of $Nd(OH)_3(cr)$ samples at the end of the solubility experiments showed no changes in the crystals. By analogy, this was taken as a proof that no secondary solid phases were formed during the equilibration period of ${}^{243}Am(OH)_3(cr)$ (contact times of 17, 28 and 48 days). The α-radiation damage of the crystal structure observed by Haire *et al.* [77HAI/LLO] for ${}^{241}Am(OH)_3(cr)$ can reasonably be considered negligible in Silva's experiments, because of the much lower specific activity of ${}^{243}Am$ (6.8 MBq/mg) compared with ${}^{241}Am$ (120 MBq/mg).

Different techniques of solid/liquid separation were tested on the samples equilibrated for 48 days. Each measured americium concentration was then given equal weight and considered as an individual data point, instead of using average values. This improperly increased the degrees of freedom from $(18 - p)$ to $(30 - p)$, where the integer refers to the number of observations and p is the number of unknown regression coefficients in the model. Silva used a least-squares procedure keeping $\log_{10}{}^*\beta_1 = -(7.7 \pm 0.3)$ constant and solving simultaneously for ${}^*K_{s,0}$, ${}^*\beta_2$, ${}^*\beta_3$ and ${}^*\beta_4$. The $\log_{10}{}^*\beta_1$ value was taken from a previous work where the first hydrolysis constant of Cm(III) was measured by potentiometry [83EDE/BUC]. There is, however, a typing error in Table 9 of Ref. [82SIL]. The listed value of $\log_{10}{}^*\beta_1$ refers to an ionic strength of 0.1 M KCl. Silva reported thermodynamic constants after ionic strength corrections with the Davies equation. The same equation was used in this review to recalculate equilibrium constants at 0.1 M $NaClO_4$, obtaining $\log_{10}{}^*K_{s,0} = (16.6 \pm 0.4)$, $\log_{10}{}^*\beta_2 = -(16.7 \pm 0.7)$, $\log_{10}{}^*\beta_3 = -(25.0 \pm 0.3)$, and $\log_{10}{}^*\beta_4$ -34.9. Very similar values of hydrolysis constants for Nd(III) were derived from the $Nd(OH)_3(cr)$ solubility measurements.

This review performs a reinterpretation of the americium solubility data of Silva using only 18 experimental points. The lack of measurements in the pH range from 8 to 8.8, and the scarce data points in the plateau region make these data unsuitable for an interpretation using the full model. The results of the least-squares refinements indicate that the two-variable model including ${}^*K_{s,0}$ and ${}^*\beta_2$ yields the greatest initial decrease of the residual mean square (RMS). The stepwise additions of ${}^*\beta_1$ and ${}^*\beta_3$ further decrease the RMS, but the achieved reduction is not sufficient to justify the inclusion of ${}^*\beta_3$ in the regression equation. Figure A.3 shows that Silva's data compare well with those obtained by Stadler and Kim [88STA/KIM] who observed the solubility curve to level down at higher pH values, *cf.* Figure A.9. The statistical F-ratio tests indicate that adding ${}^*\beta_1$ to the model is significant at 5% but not at 1%. Examination of the residuals shows that the model does not perform satisfactorily below pH = 8 if ${}^*\beta_1$ is used, instead, as a fixed parameter. A statistically significant

Figure A.3: Solubility measurements of Am(III) hydroxide in 0.1 M $NaClO_4$ from Silva [82SIL] (△) and from Ref. [88STA/KIM] (□). The continuous curve represents the values calculated with the set of equilibrium constants re-estimated by this review from experimental data in Ref. [82SIL], and the dotted curves show the associated uncertainties.



description of the experimental data is then provided by

$$\begin{aligned}\log_{10}{}^*K_{s,0} &= 15.9 \pm 0.6\\ \log_{10}{}^*\beta_1 &= -6.9 \pm 0.6\\ \log_{10}{}^*\beta_2 &= -15.1 \pm 0.6\end{aligned}$$

Conversion to the molality scale and extrapolation to $I = 0$ with the selected specific ion interaction coefficients (*cf.* Section B.1.4) gives

$$\begin{aligned}\log_{10}{}^*K^\circ_{s,0} &= 15.2 \pm 0.6\\ \log_{10}{}^*\beta^\circ_1 &= -6.5 \pm 0.6\\ \log_{10}{}^*\beta^\circ_2 &= -14.4 \pm 0.6\end{aligned}$$

[83BOU/GUI]

Bourges, J.Y., Guillaume, B., Koehly, G., Hobart, D.E., Peterson, J.R., Coexistence of americium in four oxidation states in sodium carbonate - sodium bicarbonate medium, Inorg. Chem., 22 (1983) 1179–1184.

Bourges *et al.* combined spectrophotometry and cyclic voltammetry to study the speciation of americium in carbonate/bicarbonate media at 25°C. These results clearly demonstrate the coexistence of the four oxidation states of americium (III, IV,V,VI) in concentrated carbonate media. The authors measured the apparent normal potential of the Am(VI)/Am(V) and Am(IV)/Am(III) couples in $[\mathrm{HCO_3^-}] = 1.15$ M, $[\mathrm{CO_3^{2-}}] = 0.85$ M solutions, obtaining: $E^\circ(\mathrm{VI/V}) = 0.971$ V *vs.* SHE and $E^\circ(\mathrm{IV/III}) = 0.925$ V *vs.* SHE respectively. Bourges *et al.* also investigated the influence of the carbonate concentration on these formal potentials in aqueous solutions containing mixtures of $NaHCO_3$ and Na_2CO_3 ($[\mathrm{HCO_3^-}] + [\mathrm{CO_3^{2-}}] = 2$ M). The apparent normal potential of the Am(VI)/Am(V) couple was found to be practically independent of $[\mathrm{CO_3^{2-}}]$: $E^\circ(\mathrm{VI/V}) = (0.975 \pm 0.01)$ V *vs.* SHE. The value of $E^\circ(\mathrm{IV/III})$, instead decreased monotonically with increasing $[\mathrm{CO_3^{2-}}]$. Corrections for the liquid junction potential were apparently not performed by Bourges *et al.*, and estimations with the Henderson's equation [73BAT, *pp.*36–44] show that an additional uncertainty of ±0.015 V should be added to their measurements.

Several authors [83FER/GRE, 86GRE/ROB, 89ROB] have reinterpreted these experimental measurements, assuming the following equilibria:

$$\begin{aligned}\mathrm{AmO_2(CO_3)_3^{4-}} + \mathrm{e^-} &\rightleftharpoons \mathrm{AmO_2(CO_3)_3^{5-}} && \text{(A.4)}\\ \mathrm{Am(CO_3)_5^{6-}} + \mathrm{e^-} &\rightleftharpoons \mathrm{Am(CO_3)_3^{3-}} + 2\,\mathrm{CO_3^{2-}}. && \text{(A.5)}\end{aligned}$$

These reinterpretations indicate that $\mathrm{Am(CO_3)_5^{6-}}$, $\mathrm{AmO_2(CO_3)_3^{5-}}$ and $\mathrm{AmO_2(CO_3)_3^{4-}}$ are the limiting complexes for the IV,V and VI oxidation states (as expected by analogy with U(IV); Np(V) and U(VI)-Pu(VI), respectively). Furthermore, the measurements of Bourges *et al.* show that $\mathrm{Am(CO_3)_3^{3-}}$ is the Am(III) limiting complex, which is in agreement with the reinterpreted observations of Shiloh, Givon and Marcus (*cf.* the discussion of Ref. [69SHI/GIV] in this Appendix).

Following the reinterpretations in Refs. [83FER/GRE, 89ROB, 86GRE/ROB], this review assumes that the apparent normal potentials measured by Bourges *et al.* [83BOU/GUI], refer to reactions (A.4) and (A.5). From the formal redox potential of the Am(VI)/Am(V) couple it is possible to obtain $\log_{10} K(\mathrm{A.4}, [\mathrm{CO_3^{2-}}]_{TOT} = 2\ \mathrm{M}) = (16.48 \pm 0.42)$. The extrapolation of this equilibrium constant from $[\mathrm{NaHCO_3}] = 2$ M to standard conditions with the specific ion interaction equations of Appendix B is quite uncertain due to the uncertainty in the values of the ion interaction coefficients for the americium complexes. Nevertheless, assuming that $\Delta\varepsilon$ is similar to that of the same reaction involving uranium complexes in $NaClO_4$ medium but with increased uncertainty, $\Delta\varepsilon = (-0.61 \pm 0.3)\ \mathrm{kg \cdot mol^{-1}}$ [92GRE/FUG, *p.*322], and using $\Delta z^2 = 9$, we obtain $E^\circ(\mathrm{A.4}) = (0.775 \pm 0.038)$ V *vs.* SHE, *i.e.*, $\log_{10} K^\circ(\mathrm{A.4}) = (13.1 \pm 0.6)$.

The formal redox potential of the Am(IV)/Am(III) couple, which decreases with the ratio $[\mathrm{Na_2CO_3}]/[\mathrm{NaHCO_3}]$, *cf.* [83BOU/GUI, Figure 9], can be interpreted according to reaction (A.5):

$$E^{\circ\prime} = E^\circ(\mathrm{A.5}) + \frac{RT\ln(10)}{F}\log_{10}\left(\frac{\gamma_{\mathrm{Am(CO_3)_5^{6-}}}}{\gamma_{\mathrm{Am(CO_3)_3^{3-}}}[\mathrm{CO_3^{2-}}]^2\gamma^2_{\mathrm{CO_3^{2-}}}}\right)$$

where $E^{\circ\prime}$ stands for the formal redox potential of the Am(IV)/Am(III) couple. The specific ion interaction equations in Appendix B are used to calculate the activity coefficients with $\varepsilon_{(\mathrm{Am(CO_3)_5^{6-}},\mathrm{Na^+}))} \approx \varepsilon_{(\mathrm{U(CO_3)_5^{6-}},\mathrm{Na^+}))} = -(0.27 \pm 0.15)\ \mathrm{kg \cdot mol^{-1}}$, *cf.* Table B.4, obtaining $E^\circ(\mathrm{A.5}) = (1.19 \pm 0.05)$ V *vs.* SHE, *i.e.*, $\log_{10} K^\circ(\mathrm{A.5}) = (20.1 \pm 0.9)$.