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Uranium and Plutonium Equilibria in Aqueous Solutions to 200 °C

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Standard molal Gibbs energy of formation and entropy data for aqueous uranium and plutonium ions in all oxidation states and their complexes with OH^-, Cl^-, F^-, CO_3^{2-}, PO_4^{3-}, and SO_4^{2-} are critically reviewed. Selected values are used in a modified Criss–Cobble entropy extrapolation to derive self-consistent analytical expressions for the temperature dependence of the standard molal Gibbs energies of formation of 74 aqueous species and, hence, the Gibbs energy changes and equilibrium constants of their complexation and solubility reactions, from 25 to 200 °C.

Introduction

The thermodynamic properties of dissolved uranium species and uranium minerals near room temperature have been extensively evaluated by geochemists interested in the formation of uranium ore deposits (*1-7*), most recently by Langmuir (*8*). Some authors have considered hydrothermal ore body formation in terms of a few selected uranium solution species (*1*, *5-7*), but overall there has been only limited evaluation of the thermodynamic properties of uranium species at temperatures above 25 °C.

The need for reliable data at elevated temperatures has become much more crucial in recent years as attempts are now being made to analyze two new geological situations. These are the transfer of actinides by ground water from, first, the Oklo natural reactor in Gabon (*9*) and, second, from nuclear fuel or encapsulated high-level wastes in deep underground permanent disposal vaults (*10*). In both contexts, there is a need to understand the behavior of aqueous complexes of both uranium and higher actinides, in particular plutonium, at elevated temperatures. Rai and Serne (*11*) and Cleveland (*12*) have reported some information concerning the behavior of plutonium species at 25 °C, but they did not extend their work to higher temperatures.

In the present paper, we present a critical evaluation of the thermodynamic data at 25 °C available in the literature for uranium and plutonium oxide, hydroxide, phosphate, sulfate, carbonate, fluoride, and chloride equilibria. The results are then used in a modified Criss–Cobble extrapolation scheme (*13*, *14*), together with available high-temperature experimental data to estimate thermodynamic constants for these systems at temperatures up to 200 °C.

Thermochemical Data Assessment

Water and Potential Ligands. Gibbs free energies of formation and entropies for all the species not containing uranium or plutonium were taken from the CODATA (*15*) or NBS (*16*) tables except as noted below. Heat capacity functions for gases and for those solid phases not containing uranium or plutonium are from Kelley's compilation (*17*). Values for the ionic dissociation product of water K_w, and for the apparent molar free energy of water under its own vapor pressure were taken from Olofsson and Hepler (*18*) and from Helgeson and Kirkham (*19*), respectively. Temperature-dependent constants for the protonation reactions of HPO_4^{2-} in water are from Mesmer and Baes (*20*), and for SO_4^{2-}, F^-, and CO_3^{2-} from Marshall and Jones (*21*), Ellis (*22*), and Helgeson (*23*), respectively. Henry's law constants for CO_2 are also from Helgeson's tabulation (*23*).

Uranium. The thermochemical data base for the uranium system is detailed in Tables I and II. All of the data were critically evaluated. In cases where two values appeared equally plausible, we chose values consistent with Langmuir's comprehensive compilation (*8*). The source values for species considered here but not considered by Langmuir and for cases in which our choice of values for a species differed from Langmuir's are discussed below.

The free energy and entropy of $UO_2(s)$ were taken from Langmuir (*8*) as -1031.8 kJ mol^{-1} and 77.03 J mol^{-1} K^{-1}. The values for the free energy and entropy of γ-UO_3 and U_3O_8 were taken from the same source. The enthalpy of formation of U_4O_9 as recalculated by Fuger (*24*) from the enthalpy of solution data of Fitzgibbon et al. (*25*) is -4513.7 kJ mol. The entropy of U_4O_9 is 334.2 J mol^{-1} K^{-1} as determined by using the heat capacity data of Grønvold et al. (*26*). When combined with CODATA values for $S°(U)$ and $S°(O_2)$ a value of $\Delta G_f°(U_4O_9) = -4278._4$ kJ mol^{-1} is obtained (marginally lower than the value given by Langmuir (*8*)). However, U_4O_9 undergoes a λ transition near 75 °C with an associated transition enthalpy of 2.8 kJ mol^{-1} and transition entropy of 8.72 J mol^{-1} K^{-1} (*26*). As we are primarily interested in the behavior of the uranium species at and above 100 °C, the enthalpy and entropy change for the transition were added to the 25 °C $\Delta H_f°$ and $S°$ values to calculate the hypothetical $\Delta G_f° = -4278$ kJ mol^{-1} and $S° = 342.9$ J mol^{-1} K^{-1} for the high-temperature form of U_4O_9 at 25 °C. Cordfunke (*27*) has reported values for the enthalpies of solution of UO_3, $UO_2(OH)_2$, and $UO_3{\cdot}2H_2O$ in 6 M HNO_3. The value for $\Delta H_f°$ of γ-UO_3 is taken from Langmuir as $-1223._8$ kJ mol^{-1} and the partial molar enthalpy of transfer of water to 6 M $HNO_3(aq)$ is taken as -0.5_4 kJ mol^{-1} (*28*, *29*). Thus $\Delta H_f°(UO_3{\cdot}2H_2O)$ is $-1826._7$ kJ mol^{-1}. Langmuir has discussed the computation of a solubility product for $UO_2(OH)_2$ from the solubility data of Gayer and Leider (*30*). Naumov et al. (*6*, *31*) have noted that the solid phase in Gayer and Leider's experiments was probably $UO_3{\cdot}2H_2O$, not $UO_2(OH)_2$, as the dihydrate is the stable form at 25 °C (*32*). Thus we have assumed that the solubility product ($\log K_s^* = 5.6$) actually refers to $UO_3{\cdot}2H_2O + 2H^+ \rightleftarrows UO_2^{2+} + 3H_2O$ and calculated $\Delta G_f°(UO_3{\cdot}2H_2O) = -1632._2$ kJ mol^{-1} accordingly. We have also assumed that $\Delta G_R° = 0$ for $UO_3{\cdot}2H_2O \rightleftarrows UO_2(OH)_2 + H_2O$ at 60 °C (*6*) and used appropriate heat capacities and the Criss–Cobble principle (see below) to calculate $S°$ and $\Delta G_f°$ for β-$UO_3{\cdot}H_2O$.

Values for the Gibbs energies and entropies for the simple U^{3+}, U^{4+}, UO_2^+, and UO_2^{2+} ions were those of Fuger and Oetting (*29*) (as used by Langmuir). For the uranium(IV) aqueous hydrolysis species, the $\Delta G_f°$ values given by Langmuir were adopted. Langmuir (*8*) has discussed the difficulties of estimating entropies of actinide solution species. The several empirical approaches (*8*, *33-35*) for estimating $\bar{S}°$ for species of the type $M(OH)_x^{(4-x)+}$ yield very different results. For example, the treatment of Cobble (*34*) leads to $\bar{S}°(U(OH)_5^-) = 318$ J mol^{-1} K^{-1}, and a treatment based on modification of Baes' formula for the first hydrolysis constant (*35*) gives 485 J mol^{-1} K^{-1}. Langmuir estimates a value of 71 J mol^{-1} K^{-1} by assuming similar $\bar{S}°$ values for uranium complexes of the same charge, regardless of the oxidation state of the uranium. This last assumption is entirely arbitrary but is probably reasonable for

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complexes involving anions of a similar entropy per unit charge. Furthermore, the method is based on the behavior of uranium species rather than that of simple inorganic anions or of complexes of other metals. We, therefore, have adopted Langmuir's values for $\bar{S}°$ for the $U(OH)_x^{(4-x)+}$ species. As the series of hydrolysis products $U(OH)_x^{(4-x)+}$ was originally used by Baes and Mesmer (*35*) to circumvent considering ill-defined species such as $U_6(OH)_{15}^{9+}$, this last species was not considered in our analysis.

The $\Delta G_f°$ and $\bar{S}°$ values for $UO_2(OH)^+$, $(UO_2)_2(OH)_2^{2+}$, and $(UO_2)_3(OH)_5^+$ are those used by Langmuir (*8*), based on the work of Baes and Meyer (*36*). Sutton (*37*) has shown that an anionic hydrolysis species is formed in basic uranium(VI) solutions and has determined an equilibrium constant (log $K = -30.7$) for the reaction $3UO_2^{2+} + 7H_2O \rightleftarrows (UO_2)_3(OH_7)^- + 7H^+$ at an unspecified but low ionic strength, from potentiometric measurements. This leads to $\Delta G_f°((UO_2)_3(OH)_7^-) = -4343$ kJ mol^{-1}. Tsymbal's (*38*) much larger formation constant for $(UO_2)_3(OH)_7^-$ (log $K = -24.0$ at $I = 0.1$) is not consistent with solubility data for either β-$UO_2(OH)_2$ or $UO_3\cdot 2H_2O$ (*6*). Baes and Mesmer (*35*) have reported an empirical correlation of entropies of formation for polynuclear hydrolysis species. Using, in this formula, the value of the ratio of the charge to interatomic distance which correctly gives the experimental $\Delta S_R°$ for $(UO_2)_3(OH)_5^+$, it was calculated that $\Delta S_R°((UO_2)_3(OH)_7^-) = 101$ J mol^{-1} K^{-1} and hence $\bar{S}°((UO_2)_3(OH)_7^-) = 299$ J mol^{-1} K^{-1}. In interpreting the solubility of $UO_2(OH)_2(s)$ at high temperatures, Nikitin et al. (*6*) suggest that $UO_2(OH)_2(aq)$ is an important species. We accept Nikitin's value of 35 kJ mol^{-1} for the free energy of solution of $UO_2(OH)_2$ (assumed to be β-$UO_3\cdot H_2O$) and $16._3$ kJ mol^{-1} for the enthalpy of solution, both at 25 °C. These lead to $\Delta G_f°(UO_2(OH)_2(aq)) = -1359$ kJ mol^{-1} and $\bar{S}°(UO_2(OH)_2(aq)) = 59$ J mol^{-1} K^{-1}.

For $UF_4(s)$, more recent values than those used by Langmuir are available. Rand and Kubaschewski (*39*) estimated $\Delta H_f°(UF_4(s)) = -1882._8$ kJ mol^{-1}. A later value, due to Khanaev (*40*) has not been used as it depends on a value for $\Delta H_f°(UCl_4)$, a quantity which itself is the subject of debate (*41, 42*). $S°(UF_4(s))$ is taken as 151.7 J mol^{-1} K^{-1} from the work of Burns et al. (*43*), giving $\Delta G_f°(UF_4(s)) = -1792$ kJ mol^{-1}. The $\Delta G_f°$ of $UF_4\cdot 2.5H_2O$ was taken from Langmuir (*8*). The enthalpy of hydration of $UF_4(s)$ to $UF_4\cdot 2.5H_2O$ was found to be -34 kJ mol^{-1} by Popov et al. (*44*), who used a well-characterized UF_4 sample. This gives $\Delta H_f°(UF_4\cdot 2.5H_2O) = -263._2$ kJ mol^{-1} and hence $S° = 289$ J mol^{-1} K^{-1}. The Gibbs energies and entropies of the U^{4+} and UO_2^{2+} fluoride complexes at 25 °C are taken from Langmuir.

Langmuir (*8*) has taken the values of Day et al. (45) (log $\beta_1^* = 2.52$, log $\beta_2^* = 3.87$) for the complexation reactions $U^{4+} + nHSO_4^- \rightleftarrows U(SO_4)_n^{(4-2n)+} + nH^+$ ($n = 1, 2$) at $I = 2$. The values for the complexation constants with sulfate ions (rather than with hydrogen sulfate ions) at $I = 0$ were found by applying the same corrections used by Wagman et al. (*46*) for the corresponding thorium complexes. This gave log $\beta_1 = 5.47$, log $\beta_2 = 9.72$, and $\Delta G_f°(USO_4^{2+}) = -1307$ kJ mol^{-1}, $\Delta G_f°(U(SO_4)_2(aq)) = -2076$ kJ mol^{-1}. To obtain $\bar{S}°$ for the thorium complexes, Wagman (*46*) used -122 J mol^{-1} K^{-1} for the entropy of deprotonation of the monohydrogen sulfate ion at $I = 2$. By use of this value, the CODATA value of $\bar{S}°(SO_4^{2-})$ and $\Delta S_R° = 3$ J mol^{-1} K^{-1} for ($U^{4+} + HSO_4^- \rightleftarrows USO_4^{2+} + H^+$) (*45*) gives $\bar{S}°(USO_4^{2+}) = -272$ J mol^{-1} K^{-1}. Similarly, Day's value (*45*), $\Delta S_R° = 42$ J mol^{-1} K^{-1} for the reaction of HSO_4^- with USO_4^{2+} gives $\bar{S}°(U(SO_4)_2(aq)) = -110$ J mol^{-1} K^{-1}. For $UO_2(SO_4)(aq)$, Langmuir uses $\Delta G_f°$ and $\bar{S}°$ based on the solubility study of Leitzke and Stoughton (*47*). A recent potentiometric study by Nikolaeva (*48, 49*), done at lower ionic strength and over the temperature range 25–150 °C, is in basic agreement with the solubility study to about 100 °C. Above this temperature, Nikolaeva finds a markedly lower complexation constant for the UO_2^{2+}/SO_4^{2-} system, possibly because of inadequate consideration of the UO_2^{2+} hydrolysis equilibria in the earlier study (*49*). We have taken log $\beta_1 = 2.93$ for the complexation reaction from the work of Nikolaeva and obtain $\Delta G_f°(UO_2SO_4(aq)) = -1714$ kJ mol^{-1}. A least-squares fit of Nikolaeva's data yielded the function $RT \ln \beta_1 = 16350 - 6.8(T - 298.15) + 137T \ln (T/298.15)$. This corresponds to a value for $\Delta S_R°$ of 130.2 J mol^{-1} K^{-1} and, hence, $\bar{S}°(UO_2SO_4(aq)) = 52$ J mol^{-1} K^{-1}. Only the monosulfate complex of uranyl ion was considered in this analysis, since further association to form anionic complexes is expected to be small (*49*) at low sulfate ion concentrations (<0.1 mol dm^{-3}).

Langmuir recalculated the solubility data of Sergeeva et al. (*7*) for 25 °C to obtain $\Delta G_f°(UO_2CO_3(s)) = -1563$ kJ mol^{-1}, and used Sergeeva's sparse high-temperature to obtain $S°$. Nikolaeva (*50*) has also recently determined the solubility product of UO_2CO_3 at 25 °C and obtained the value log $K_s = -14.15$ for $UO_2CO_3(s) \rightleftarrows UO_2^{2+} + CO_3^{2-}$. This leads to a similar value of -1561 kJ mol^{-1}. Nikolaeva obtained more experimental solubility product data in the range of 75–125 °C, a region which is of primary importance for our present purposes. We therefore chose to fit Nikolaeva's temperature-dependent solubility data to a least-squares function using a value of $\Delta C_{p,R}°$ based on the heat capacity values in Tables I–III. The fitted expression yielded a value for $\Delta S_R°$ at 25 °C and, from it, $S°(UO_2CO_3(s)) = 194$ J mol^{-1} K^{-1}. For similar reasons the potentiometric study of Piroshkov and Nikolaeva (*51*) was preferred to that of Sergeeva et al. for calculation of $\Delta G_f°$ and $\bar{S}°$ of $UO_2CO_3(aq)$. It is worth noting that again $\Delta G_f°$ is in good agreement with the value chosen by Langmuir from Sergeeva's data, while the difference in $\bar{S}°$ (0 J mol^{-1} K^{-1} vs. 51 J mol^{-1} K^{-1} from Sergeeva's data) is quite marked. For $UO_2(CO_3)_2^{2-}$, Langmuir's values for $\Delta G_f°$ and $\bar{S}°$ have been used as has his value for $\Delta G_f°(UO_2(CO_3)_3^{4-})$. These values for $\Delta G_f°$, based on measurements by Tsymbal (*38*), are unaffected by his choice for the formation constant for $(UO_2)_3(OH)_7^-$. Langmuir's value for $\bar{S}°(UO_2(CO_3)_3^{4-})$ was based on a single estimated value for β_3 at 150 °C and we have used, instead, $\Delta G_f° = 2659._5$ kJ mol^{-1} for $UO_2(CO_3)_3^{4-}$, with the value of Devina et al. (*52*), $\Delta H_R° = -40.3$ kJ mol^{-1}, for $UO_2^{2+} + 3CO_3^{2-} \rightleftarrows UO_2(CO_3)_3^{4-}$ at 25 °C, obtaining $\Delta S_R° = 274$ J mol^{-1} K^{-1} for this reaction and hence $\bar{S}°(UO_2(CO_3)_3^{4-}) = 6._7$ J mol^{-1} K^{-1}.

Values for $\Delta G_f°$ and $\bar{S}°$ for UO_2Cl^+ and UCl^{3+} were calculated from the extrapolation of the data of Nikolaeva (*53, 54*) for the high-temperature complexation constant. It should be noted that the 25 °C complexation constants, log $\beta_1 = 1.61$ for UO_2Cl^+ and log $\beta_1 = 2.60$, are markedly larger than those used by Langmuir. Our use of these larger values represents a conservative approach when possible solubilization of uranium species by complex formation is being considered in mass transport calculations. It should also be noted that the complexation constant for UO_2Cl^+ used by Langmuir is based on the spectrophotometric work of Davies and Monk (*55*). Recalculation of their data using an ionic strength calculated from the concentration data in their paper gives log $\beta_1 \geq 1$ ($\neq 0.21$), in better agreement with the value used here.

While the entropies and free energies for the uranium phosphate species used in the present work are those chosen by Langmuir, it should be noted that the free energies listed for the monohydrogen phosphate complexes are probably too low. The stability constants for these complexes were determined by Moskvin and co-workers (*56*). In their calculations, the occurrence of more highly protonated phosphate complexes in acid solution appears to have been neglected, although the formation of dihydrogen phosphate complexes of the uranyl ion in such solutions is well established (*57, 58*).

The heat capacity of UO_2 as a function of temperatures was obtained by fitting the equally weighted experimental data (0–275

°C only) of Huntzicker and Westrum (*59*) and of Grønvold and co-workers (*26*). The heat capacity for α-U_3O_8 was similarly determined from the data ($T < 175$ °C) of Girdhar and Westrum (*60*). As previously mentioned, U_4O_9 has a λ transition at 75 °C. The heat capacity of U_4O_9 can be calculated from literature data for temperatures both above and below T_λ (*26*, *61*, *62*). Since changes in ΔG_f° and S° at T_λ are small (3 kJ mol^{-1} and 9 J mol^{-1} K^{-1}, respectively) (*26*), the high temperature $C_p^\circ(T)$ was used at all temperatures, even below the transition temperature. $C_p^\circ(\gamma\text{-}UO_3)$ was taken from the compilation of Rand and Kubaschewski (*39*). The heat capacity for β-$UO_2(OH)_2$ was estimated by using the sums and differences of the known heat capacities of UO_2SO_4 (*63*), $Ba(OH)_2$, and $BaSO_4$. The value of $C_p^\circ(UO_3{\cdot}2H_2O)$ was estimated as the sum of $C_p^\circ(UO_3{\cdot}H_2O)$ plus $C_p^\circ(H_2O)$, but, as $UO_3{\cdot}2H_2O$ is stable with respect to dehydration only below 60 °C, the choice for $C_p^\circ(UO_3{\cdot}2H_2O)$ is not critical.

For $UO_2CO_3(s)$, C_p° was calculated as $C_p^\circ(UO_2SO_4) - C_p^\circ(BaSO_4) + C_p^\circ(BaCO_3)$. The heat capacity of UF_4 was taken from Rand and Kubaschewski (*39*) and for $UF_4{\cdot}2.5H_2O$, C_p° was estimated as $C_p^\circ(UF_4)$ plus $2.5C_p^\circ(H_2O)$. Values of C_p° for the solids $(UO_2)_3(PO_4)_2$, $(UO_2)_2(HPO_4)_2$, and $U(HPO_4)_2{\cdot}4H_2O$ were estimated by Kopp's law as outlined by Sturtevant (*64*) with the heat capacity of water of hydration estimated as noted previously.

Plutonium. The enthalpy of formation of PuO_2 has been determined by Johnson et al. (*65*) (−1056 kJ mol^{-1}). The entropy of PuO_2 was reported by Flotow and co-workers (*66*) as 66.13 J mol^{-1} K^{-1}. Combining this value with $S^\circ(\alpha\text{-}Pu)$ (*29*) and $S^\circ(O_2)$ (*15*) gives $\Delta G_f^\circ(PuO_2) = -998.0$ kJ mol^{-1}.

The values for ΔG_f° and S° for hexagonal Pu_2O_3 were calculated from the high-temperature calorimetric data of Chereau et al. (*67*) for the reaction $2Pu_2O_3 + O_2 \rightleftarrows 4PuO_2$ at 1100 °C, $\Delta H_R^\circ = -879$ kJ mol^{-1}, and $\Delta S_R^\circ = 217._1$ J mol^{-1} K^{-1}. We adopted the IAEA committee's suggestion (*68*) to estimate $C_p^\circ(Pu_2O_3)$, from the expression $C_p(Pu_2O_3) = [2C_p^\circ(PuO_2) - 8.8]$ J mol^{-1} K^{-1}, and hence, derived the value $\Delta H_R^\circ = -861$ kJ mol^{-1} for the reaction at 25 °C. This gives $\Delta H_f^\circ(Pu_2O_3) = -1681$ kJ mol^{-1}, slightly less negative than Chereau's value of −1710 kJ mol^{-1}, which was based on the IAEA constants for PuO_2 (*68*). The same estimated differences in heat capacity give $\Delta S_R^\circ = 194.1$ J mol^{-1} K^{-1} and, hence, $S^\circ(Pu_2O_3) = 127$ J mol^{-1} K^{-1} and $\Delta G_f^\circ(Pu_2O_3) = -159_4$ kJ mol^{-1}, again based on $S^\circ(PuO_2) = 66.13$ J mol^{-1} K^{-1} and the CODATA value for $S^\circ(O_2)$. We note that the value for $S^\circ(Pu_2O_3)$ is markedly lower than earlier estimates (*68*), primarily because of the use of the more recent value for $S^\circ(PuO_2)$. Several mixed Pu(III)/Pu(IV) oxides are known to exist (*68*). One of these, cubic $PuO_{1.52}$ (or "α-Pu_2O_3") is thought to be stable relative to Pu_2O_3 below 300 °C but no reliable thermodynamic constants have been reported for its formation.

The value for $\Delta G_f^\circ(Pu(OH)_3(s))$ was calculated from log $K_s^* = -19.6$ given by Busey and Cowan (*69*) for the reaction $Pu(OH)_3 + 3H^+ \rightleftarrows Pu^{3+} + 3H_2O$. $S^\circ(Pu(OH)_3(s))$ was calculated by adding the difference in entropy between PuO_2 and UO_2 (−10.9 J mol^{-1} K^{-1}) to a value of 105 J mol^{-1} K^{-1} estimated for $U(OH)_3$ by the method of Latimer (*70*). The solubility product of $Pu(OH)_4$ is somewhat in doubt. Recent work on the solubility of $^{239}PuO_2$ suggests that much of the ^{239}Pu in solution above the $^{239}Pu(IV)$ solid phase may exist in higher oxidation states (possible as a result of reaction of water radiolysis products with the solid). Thus the "true" solubility product of $Pu(OH)_4$ may also be considerably smaller than many results noted in the literature (*35*). As we are concerned here with equilibrium conditions, the low value of Kasha of log $K_s^* = 0.85$ for $Pu(OH)_4 + 4H^+ \rightleftarrows Pu^{4+} + 4H_2O$ has been used to calculate $\Delta G_f^\circ(Pu(OH)_4(s))$. In the absence of any better method, a value for $S^\circ(Pu(OH)_4(s))$ was estimated as $(S^\circ(Pu(OH)_3) + \phi)$ where ϕ, the contribution to the entropy for addition of the fourth OH group, was arbitrarily taken as $12._6$ J mol^{-1} K^{-1} (equal to the value given in Latimer (*70*) for an OH group attached to a central atom of charge three). This yields the results $S^\circ(Pu(OH)_4(s)) = 107$ J mol^{-1} K^{-1}. The value −1056 kJ mol^{-1} for $\Delta G_f^\circ(PuO_2(OH)(am))$ was calculated from the solubility product log $K_s^* = 5.4$ given by Kraus and Nelson (*72*) for the reaction $PuO_2(OH)(am) + H^+ \rightleftarrows PuO_2^+ + H_2O$. S° was estimated as the sum of $S^\circ(PuO_2)$ and of Latimer's suggested entropy contribution ($20._9$ J mol^{-1} K^{-1}) for an OH group attached to a singly charged central ion. For $PuO_2(OH)_2(s)$, $\Delta G_f^\circ = -1211$ kJ mol^{-1} was similarly calculated from log $K_s = 3.5$ for $PuO_2(OH)_2(s) + 2H^+ \rightleftarrows PuO_2^{2+} + 2H_2O$ (*12*) and S° was estimated as for $PuO_2(OH)(am)$ but using a contribution of $18._8$ J mol^{-1} K^{-1}/OH group, appropriate for a central ion of charge two (*70*).

Values of ΔG_f° and $\bar{S}^\circ$ for the simple plutonium ions are those of Fuger and Oetting (*29*). It should be noted that the ΔG_f° and $\bar{S}^\circ$ values for all of the aqueous plutonium species are based on an extrapolated activity coefficient for $SmCl_3$ which was used to estimate the activity coefficient for $PuCl_3$ in a saturated aqueous solution of $PuCl_3$. This approximation could lead to a systematic error of 1–3 kJ mol^{-1} in ΔG_f° and of several J mol^{-1} K^{-1} in $\bar{S}^\circ$ for the aqueous plutonium species.

Hydrolysis constants from Baes and Mesmer (*35*) were used to calculate ΔG_f° for $Pu(OH)^{2+}$, $Pu(OH)^{3+}$, $Pu(OH)_2^{2+}$, $Pu(OH)_3^+$, $Pu(OH)_4(aq)$, $Pu(OH)_5^-$, $PuO_2OH(aq)$, $PuO_2(OH)^+$, $(PuO_2)_2(OH)_2^{2+}$, and $(PuO_2)_3(OH)_5^+$. Entropies for the plutonyl species were calculated by assuming values of ΔS_R° for the hydrolysis reaction equal to those for the similar uranyl ion hydrolysis (*36*). $\bar{S}^\circ$ values for the Pu(IV) hydrolysis species were similarly estimated from the $\bar{S}^\circ$ values chosen for the U(IV) species. The $\bar{S}^\circ$ value for $Pu(OH)^{2+}$ was calculated by using an estimated value for the entropy change of the first step in mononuclear cation hydrolysis. On the assumption that the general hydrolysis behavior of Pu^{3+} is similar to that for lanthanide ions and the ratio of the charge to Pu(III)–O distance is 1.25 (*73*), the formula of Baes and Mesmer (*35*) gives $\Delta S_R^\circ = 26.9$ J mol^{-1} K^{-1} for the first hydrolysis step and hence $\bar{S}^\circ(PuOH^{2+}) = -88$ J mol^{-1} K^{-1}. For $PuO_2OH(aq)$, $\bar{S}^\circ$ was calculated by assuming ΔS_R° is the same as for the first hydrolysis step of UO_2^{2+}.

Osborne's values of $S^\circ(PuF_3) = 126.1$ J mol^{-1} K^{-1} and $S^\circ(PuF_4) = 147.3$ J mol^{-1} K^{-1} from heat capacity measurements (*74*, *75*) were used. The ΔG_f° values were calculated for the solid fluorides by using these entropies and Rand's estimates (*76*) for $\Delta H_f^\circ(PuF_3) = -1552$ kJ mol^{-1} and $\Delta H_f^\circ(PuF_4) = -1778$ kJ mol^{-1}.

The $\Delta G_f^\circ(PuF^{3+})$ was calculated from the value of log $\beta_1 = 7.94$ ($I = 0$) (*77*, *78*) for this complex. The values of log $\beta_1 = 5.06$, log $\beta_2 = 10.05$, log $\beta_3 = 14.93$, and log $\beta_4 = 18.10$ are reported by Ahrland et al. (*79*) for the plutonyl fluoride complexes at $I = 1$. These values were obtained by using the data from the ion-exchange study of Krylov et al. (*80*) and a value for the association contant of log $K = 2.95$ for the reaction $H^+ + F^- \rightleftarrows HF(aq)$. We have corrected the values of the complexation constants to $I = 0$ by using the corrections determined by Langmuir (*8*) for the equivalent uranyl complexes and obtain log $\beta_n = 5.63$, 11.02, 15.86, and 18.82 for $n = 1$–4, respectively. These give $\Delta G_f^\circ(PuO_2F^+) = -1071$ kJ mol^{-1}, $\Delta G_f^\circ(PuO_2F_2(aq)) = -1383$ kJ mol^{-1}, $\Delta G_f^\circ(PuO_2F_3^-) = -1693$ kJ mol^{-1} and $\Delta G_f^\circ(PuO_2F_2^{2-}) = -1991$ kJ mol^{-1}. $\bar{S}^\circ$ for the plutonium fluoride complexes were calculated by assuming the entropies of complexation to be the same for the corresponding uranium and plutonium species.

Patil and Ramakrishna (*81*) have studied the complexation of Pu^{4+} with hydrogen sulfate by ion-exchange methods at 10, 25, and 40 °C. At 25 °C and $I = 2$, log $\beta_1^* = 2.76$, log $\beta_2^* = 4.37$. Wagman's corrections to $I = 0$ for the corresponding thorium complexes (*46*) were applied giving log $\beta_1 = 5.71$ and log $\beta_2 = 10.22$ for the sulfate complexation reactions and

$\Delta G_f^\circ(\mathrm{PuSO_4^{2+}}) = -1259$ kJ mol^{-1}, $\Delta G_f^\circ(\mathrm{Pu(SO_4)_2(aq)}) = -2029$ kJ mol^{-1}. Patil and Ramakrishna's value (*81*) of $\Delta S_R^\circ = 30._5$ J mol^{-1} K^{-1} for the reaction ($\mathrm{Pu^{4+} + HSO_4^- \rightleftarrows PuSO_4^{2+} + H^+}$) was used. Their values of β_2/β_1 at 10, 25, and 40 °C were used to estimate an approximate $\Delta S_R^\circ = (64 \pm 20)$ J mol^{-1} K^{-1} for the reaction $\mathrm{PuSO_4^{2+} + HSO_4^- \rightleftarrows Pu(SO_4)_2(aq) + H^+}$. As pointed out by Patil, this type of calculation is open to criticism because of the errors inherent in the calculation of β_2/β_1. Use of Wagman's value (46) for the entropy of deprotonation of $\mathrm{HSO_4^-}$ at $I = 2$, as discussed for the corresponding uranium complexes, give $\bar{S}^\circ(\mathrm{PuSO_4^{2+}}) = -218$ J mol^{-1} K^{-1} and $\bar{S}^\circ(\mathrm{Pu(SO_4)_2(aq)}) = -17$ J mol^{-1} K^{-1}.

While literature values are available for the complexation constant of $\mathrm{PuSO_4^+}$, such values have been obtained only at high ionic strength, $I = 1-2$ (*82*). However, complexation constants for tripositive lanthanide ions with sulfate have been determined at very low ionic strengths (*83*). The lanthanide values are similar to those for $\mathrm{Pu^{3+}}$ at high ionic strengths (*84*). Rather than attempt to correct the literature complexation constant to zero ionic strength for $\mathrm{PuSO_4^+}$, a value of $\log \beta_1 = -3.5 \pm 0.5$ (typical for $\mathrm{Ln^{3+}/SO_4^{2-}}$ interactions) was chosen. This gives ΔG°(complexation) = (-20 ± 3) kJ mol^{-1} and $\Delta G_f^\circ(\mathrm{PuSO_4^+}) = (-1343 \pm 5)$ kJ mol^{-1}. For $\mathrm{PuO_2SO_4(aq)}$ a value of $\log \beta_1 = 2.23$ has been reported (*85*) from an ion-exchange study ($I = 2$). As part of this study the same workers obtained $\log \beta_1 = 1.96$ for $\mathrm{UO_2SO_4(aq)}$ also at $I = 2$. As previously noted, at low ionic strength the complexation constant for sulfate with uranyl ion may be expressed as $\log \beta_1 = 2.93$ at 25°C. The change in both complexation equilibria with ionic strength was assumed to be the same, giving a value of $\log \beta_1(\mathrm{PuO_2SO_4(aq)}) = 3.20$ ($I \rightarrow 0$). Therefore, ΔG°(complexation) = -18.3 kJ mol^{-1} and $\Delta G_f^\circ(\mathrm{PuO_2SO_4(aq)}) = -1520$ kJ mol^{-1}.

The entropy of the $\mathrm{M^{3+}/SO_4^{2-}}$ complexation reaction has been found (*86*) to be 112–120 J mol^{-1} K^{-1} at $I = 0$ for a large number of tripositive lanthanide ions. Values at high ionic strengths for the tripositive actinides and lanthanides have been shown to be similar in magnitude (*84*). Therefore, we have taken $\Delta S_R^\circ = (116 \pm 20)$ J mol^{-1} K^{-1} for the first $\mathrm{Pu^{3+}/SO_4^{2-}}$ complexation step. This gave $\bar{S}^\circ(\mathrm{PuSO_4^+}) = -50 \pm 30$ J mol^{-1} K^{-1}. For $\mathrm{PuO_2SO_4(aq)}$, ΔS_R° of complex formation was taken as -130 J mol^{-1} K^{-1} as for the corresponding uranium reaction. This gave $\bar{S}^\circ(\mathrm{PuO_2SO_4(aq)}) = 61 \pm 20$ J mol^{-1} K^{-1}.

Literature values for complexation constants of plutonium cations with carbonate ions are few, and what data do exist have been strongly criticized (*12*). Reevaluation of the data of Moskvin and Gel'man (*87*) using Kasha's value for the solubility product of $\mathrm{Pu(OH)_4}$ (*88*) corrected to 20 °C gives $\log \beta_1 = 41.3$ for the association constant of $\mathrm{PuCO_3^{2+}}$. Therefore $\Delta G_f^\circ(\mathrm{PuCO_3^{2+}})$ is -1245 kJ mol^{-1} at 20 °C based on $\mathrm{Pu(OH)_4}$ as the poorly defined solid phase in Moskvin and Gel'man's experiments. No suitable method is available to allow for the fact that the $\mathrm{PuCO_3^{2+}}$ association constant was obtained from experiments carried out at extremely high ionic strength ($I \geq 7$). A value of -293 J mol^{-1} K^{-1} was estimated for $\bar{S}^\circ(\mathrm{PuCO_3^{2+}})$ by assuming an entropy of complexation equal to 153 J mol^{-1} K^{-1} as for the reaction $\mathrm{Pu^{4+} + SO_4^{2-} \rightleftarrows PuSO_4^{2+}}$ for which the charge types are similar. This was then used to correct the value of ΔG_f° to -1242 kJ mol^{-1} at 25 °C.

The hydroxycarbonate complexes of $\mathrm{PuO_2^{2+}}$ were not considered, because the calculations in the best quantitative reference concerning these complexes (*89*) appear to be internally inconsistent, and insufficient data were presented to permit reevaluation. Further, the solubility product for $\mathrm{PuO_2CO_3}$ noted in the same work appears doubtful because the equilibrium solid phase apparently is not this compound. However, it does appear that an anionic complex, plutonyl carbonate, exists (*90*, *91*), and the value (*87*) of $\log \beta_2 = 15$ for the formation constant of $\mathrm{PuO_2(CO_3)_2^{2-}}$ is not unreasonable, being similar to that for the corresponding uranyl complex. Therefore, in the absence of other data, this value was used to obtain $\Delta G_f^\circ(\mathrm{PuO_2(CO_3)_2^{2-}})$. A value for $\bar{S}^\circ(\mathrm{PuO_2(CO_3)_2^{2-}})$ was then estimated as $\bar{S}^\circ(\mathrm{UO_2(CO_3)_2^{2-}}) + \bar{S}^\circ(\mathrm{PuO_2^{2+}}) - \bar{S}^\circ(\mathrm{UO_2^{2+}})$. A value for the formation constant of $\mathrm{PuO_2(CO_3)_3^{4-}}$ is not available, although there is good evidence for the existence of this complex in basic carbonate solutions (*91*).

Complexation constants for $\mathrm{PuO_2Cl^+}$ ($\log \beta_1 = 0.097$) and for $\mathrm{PuCl^{3+}}$ ($\log \beta_1 = 0.15$) have been reported (*92*, *93*) at $I = 2$ mol kg^{-1}. These have been corrected to $I = 0$ assuming the same activity behavior for the chloro complexes as for the corresponding hydrolysis products (*8*, *35*). This gives $\log \beta_1 = 0.94$, $\Delta G_f^\circ = -618$ kJ mol^{-1} for $\mathrm{PuCl^{3+}}$ and $\log \beta_1 = -0.30$, $\Delta G_f^\circ = -887$ kJ mol^{-1} for $\mathrm{PuO_2Cl^+}$. $\bar{S}^\circ$ values for these complexes were estimated from ΔS of complexation of the corresponding uranium species.

The solubility products of $\mathrm{PuO_2(HPO_4)}$ and $\mathrm{Pu(HPO_4)_2}$ have been reported by Denotkina et al. (*94*–*96*). While the value of $[\mathrm{Pu^{4+}}][\mathrm{HPO_4^{2-}}]^2 = 2.0 \times 10^{-28}$ at $I = 2$ (*97*) appears to be reasonable, the value (*95*) of $[\mathrm{PuO_2^{2+}}][\mathrm{HPO_4^{2-}}] = 3.1 \times 10^{-13}$ appears to be only a rough approximation (at some unstated ionic strength). The free energies of formation of the solids were estimated from these solubility products without any attempt to first correct them to zero ionic strength. S° was estimated from the expression $S^\circ(\mathrm{PuO_2HPO_4}) \approx S^\circ(\mathrm{UO_2HPO_4}) - S^\circ(\mathrm{UO_2}) + S^\circ(\mathrm{PuO_2})$ and $S^\circ(\mathrm{Pu(HPO_4)_2(s)})$ was similarly derived from $S^\circ(\mathrm{U(HPO_4)_2{\cdot}4H_2O(s)})$ using 38 J mol^{-1} K^{-1} for S° for each water of hydration (*70*). We recognize that such estimates of entropies contain many inherent uncertainties, particularly the estimate of the entropy of hydrated water and the estimates of differences in entropies for M(VI) compounds based on the relative entropies of M(IV) compounds; however, these are small compared to the uncertainties in the estimated $\bar{S}^\circ$ values for many of the aqueous species.

The free energy of $\mathrm{PuO_2(H_2PO_4)^+}$ was calculated from the solubility and electrophoresis work of Denotkina and Shevchenko (*95*) who give $\log \beta_1 = 3.93$ ($\beta_1 = [\mathrm{PuO_2^{2+}}][\mathrm{H_2PO_4^-}]/[\mathrm{PuO_2(H_2PO_4)^+}]$). For the plutonium(IV) complexes with monohydrogen phosphate, the complexation constants reported by Denotkina et al. (*96*) were used ($\log \beta_n = 12.9, 23.7, 33.4, 43.2$; $n = 1-4$). In neither case are the data unambiguous, but no other values are available. The experimental determinations (*95*, *96*) of the plutonium–phophate complex stability "constants" were done at variable ionic strength, but the average concentration "constants" reported have been used without further correction. For these phosphate complexes, $\bar{S}^\circ$ was again based on equality of ΔS_R° of complexation for the corresponding uranium and plutonium species. The formation constant $\log \beta_1 = 2.51$ has been reported (*98*) for $\mathrm{AmH_2PO_4^{2+}}$ as a value corrected to $I = 0$. Moskvin (*99*) has shown that β_1 values for the $\mathrm{Pu^{3+}}$ and $\mathrm{Am^{3+}}$ dihydrogenphosphate complexes are similar at higher ionic strength. Therefore, $\log \beta_1 = 2.51$ was taken as the formation constant for $\mathrm{PuH_2PO_4^{2+}}$ at $I = 0$ and used to calculate $\Delta G_f^\circ = -1723$ kJ mol^{-1} for the plutonium complex. $\bar{S}^\circ$ for $\mathrm{Pu(H_2PO_4)^{2+}}$ was estimated to be 63 J mol^{-1} K^{-1} using a method suggested by Cobble (*34*, *100*) and 0.100 nm as the radius of $\mathrm{Pu^{3+}}$ (*73*). The function for the temperature dependence of the heat capacity of $\mathrm{PuO_2}$ was obtained by applying a least-squares program to the raw data of Flotow (*66*) for temperatures above 0 °C. The heat capacity of $\mathrm{Pu_2O_3}$ was estimated as $(2C_p^\circ(\mathrm{PuO_2}) - 8.8)$ J mol^{-1} K^{-1} based on the differences in heat capacities for the corresponding cerium oxides (*68*). Values of C_p° for $\mathrm{Pu(OH)_3}$, $\mathrm{Pu(OH)_4}$, $\mathrm{PuO_2OH}$, $\mathrm{PuO_2(OH)_2}$, $\mathrm{PuO_2HPO_4}$, and $\mathrm{Pu(HPO_4)_2}$ were estimated by Kopp's law (*64*). The heat capacity for $\mathrm{PuF_4}$ is that reported by Osborne (*74*) for the temperature range 250–350 K. The heat capacity of $\mathrm{PuF_3}$ was taken from a least-squares fit of data (*75*) covering the same temperature range.

Table I. Thermodynamic Parameters for Water, Gases, and Solid Uranium and Plutonium Compounds[a]

			$C_p°$/J mol^{-1} K^{-1} = $A + 10^{-3} BT + 10^{+5}C/T^2$		
	$\Delta G_f°$/kJ mol^{-1}	$S°$/J mol^{-1} K^{-1}	A	B/K	C/K^{-2}
H_2O(l)	−237.18	69.95	75.291[b]	0	0
H^+(aq)	0	0	0	0	0
OH^-(aq)	−157.29	−10.84	2236.3	−4426	−954
O_2(g)	0	205.03	29.957	4.18	−1.67
CO_2(g)	−394.38	213.68	44.22	8.79	−8.62
UO_2(s)	−1031.8 ± 1.0	77.03 ± 0.21	68.90	22.62	−10.4
β-$UO_2(OH)_2$(s)	−1394 ± 4	123 ± 13	41.8	200	35.3
$UO_3 \cdot 2H_2O$(s)	−1632 ± 2	171 ± 4	94.8	248	28.0
γ-UO_3(s)	−1146 ± 2	96.1 ± 0.4	92.5	11.05	−11.1
α-U_3O_8(s)	−3370 ± 3	282.6 ± 0.5	332.9	−62.93	−68.1
UO_2CO_3(s)	−1561 ± 2	194 ± 25	61.1	155	18.9
UF_4(s)	−1792 ± 21	151.7 ± 0.4	108	29	−0.25
$UF_4 \cdot 2.5H_2O$(s)	−2408 ± 13	289 ± 25	240	149	−18.4
U_4O_9(s)	−4278 ± 6	342.9 ± 0.5	253.1	141.5	5.146
$(UO_2)_3(PO_4)_2$(s)	−5176 ± 17	406 ± 21	357	0	0
$(UO_2)_2(HPO_4)_2$(s)	−4218 ± 13	331 ± 17	298	0	0
$U(HPO_4)_2 \cdot 4H_2O$(s)	−3811 ± 3	356 ± 17	436	190	−29.0
Hx-Pu_2O_3(s)	−1594 ± 21	127 ± 8	89.87	161	−12.56
PuO_2(s)	−998.0 ± 0.8	66.13 ± 0.25	49.32	80.47	−6.281
$Pu(OH)_3$(s)	−1162 ± 7	*92 ± 8*	105	0	0
$Pu(OH)_4$(s)	−1426 ± 29	*107 ± 21*	131	0	0
$PuO_2(OH)$(am)	−1056 ± 8	*87 ± 8*	86	0	0
$PuO_2(OH)_2$(s)	−1211 ± 8	*104 ± 13*	112	0	0
PuF_3(s)	−1482 ± 13	126.1 ± 0.4	92.17	26.67	−6.69
PuF_4(s)	−1684 ± 33	147.3 ± 0.4	127.6	3.11	−10.91
PuO_2HPO_4(s)	−1918 ± 13	154 ± 8	159	0	0
$Pu(HPO_4)_2$(s)	−2818 ± 8	187 ± 17	224	0	0

[a] Numbers in italics represent estimated values. [b] Helgeson and Kirkham's values (*19*) for $C_p°(H_2O)$ increase with temperature so that, at 200 °C, $C_p°(H_2O)$ is 7% higher than the 25 °C value, assumed in this work to be a constant. This assumption (*109*) introduces errors of <4 J mol^{-1} in $\Delta G_f°(H_2O,T)$ and greatly simplifies $\Delta C_{p,R}°$ calculations from data in Tables II–IV.

Extrapolation to Elevated Temperatures

The temperature dependence of the Gibbs energy and entropy of a system are described by its heat capacity function, $C_p°(T)$ (*101*). Although $C_p°(T)$ data are known for the uranium and plutonium solids, and several of their complexation reactions, no values have been reported for any of the aqueous species. Several methods for estimating such data have been proposed (*13*, *102–105*). The most widely used method which can be applied to polyatomic species is the Criss–Cobble entropy correspondence principle (*13*, *14*). Below 200 °C, the correspondence principle is sufficiently accurate for our purposes and was adopted in the modified form discussed below.

Criss and Cobble derived the correspondence principle by correlating entropy data from a large number of aquo ions, the bulk of which have no electronic degeneracy (Russell–Saunders total angular momentum quantum number, $J = 0$ (*106*)). To be consistent with the entropy data for the trivalent actinide aquo ions (*29*, *107*), we subtracted the contribution of electronic degeneracy, $\bar{S}_e°$, from the room-temperature entropy and treated it separately from the residual or "adjusted" entropy $\bar{S}°_{adj}$. Assuming spin–orbit coupling effects are large compared to ligand field effects and that the ligand field effects are of the order of kT or smaller, $\bar{S}_e°$ is equal to that of the free metal ion in the gas phase (*107*)

$$\bar{S}_e° \approx R \ln (2J + 1) \qquad (1)$$

Values of J for the free ions were the ground-state values reported by Figgis (*106*) (M^{4+}), Hinchey and Cobble (*107*) (M^{3+}), and McGlynn and Smith (*108*) (MO_2^{2+}). The adjusted partial molal entropy, $\bar{S}_{adj}°(T) = \bar{S}°(T) - \bar{S}_e°$, was estimated at 60, 100, 150, and 200 °C from the Criss–Cobble principle in the usual way (*109*). These values were then put in a convenient analytical form by a least-squares curve fit to the expression

$$\bar{S}°(T) = \bar{S}° + \bar{C}_p°|_{25}^{200} \ln (T/298.15) \qquad (2)$$

where $\bar{S}°$ is the partial molal entropy at 25 °C and $\bar{C}_p°|_{25}^{200}$, the curve-fitted constant, is defined to be mean partial molal heat capacity over the range 25–200 °C. More complex expressions for the heat capacity function (*13*, *14*) are unjustified in view of the large uncertainties in the room-temperature entropy data used here. The assumption that $\bar{C}_p°$ is a constant between 25 and 200 °C introduces an error of less than 17 J mol^{-1} K^{-1} in the Criss–Cobble values of $\bar{S}°(T)$, generally much less than the precision of the extrapolation. We note that the values for $\bar{S}°$ and $\bar{C}_p°|_{25}^{200}$ listed here are conventional standard properties which should not be confused with the so-called "absolute" parameters referred to in Criss and Cobble's papers (*13*, *14*).

The validity of the Criss–Cobble method is most firmly established for simple anions and cations. We therefore based our data tables on Criss–Cobble entropies for the species U^{3+}, U^{4+}, UO_2^+, UO_2^{2+}, Pu^{3+}, Pu^{4+}, PuO_2^+, PuO_2^{2+}, F^-, HPO_4^{2-}, and SO_4^{2-}, for which no experimental $\bar{C}_p°$ data above 100 °C have been measured, and for Cl^-, since the estimated and experimental entropies are virtually identical (*13*, *33*). The mean heat capacity for CO_3^{2-}, $\bar{C}_p°|_{25}^{200}$ (CO_3^{2-}), was calculated by combining data for gaseous CO_2 with Henry's law data and dissociation constants for H_2CO_3 tabulated by Helgeson (*23*).

Values for the other ligand species of importance were determined by combining these data with experimental constants for the appropriate reactions, wherever possible. Mean heat capacities for the species $H_2PO_4^-$, H_3PO_4, HCO_3^-, H_2CO_3, HF, and HSO_4^- were calculated from the data in ref 20–23. For UO_2CO_3(aq) and UO_2SO_4(aq), the high-temperature $\Delta G_f°$ values were determined from the temperature dependence of the UO_2^{2+}/CO_3^{2-} and UO_2^{2-}/SO_4^{2-} complexation reactions (*34*, *51*), respectively. The high-temperature $\Delta G_f°$ values for $UO_2(CO_3)_2^{2-}$ were similarly calculated by using the expression for association as a function of temperature which was given by Langmuir (*8*) as previously discussed. For both UO_2Cl^+ and UCl^{3+}, the Gibbs energies at elevated temperatures have been based on temperature-dependent complexation constant data from the potentiometric studies of Nikolaeva (*53*, *54*). For PuO_2SO_4(aq), $PuO_2(CO_3)_2^{2-}$ PuO_2Cl^+, and $PuCl^{3+}$, the Gibbs energies at tem-

Table II. Aqueous Ligand Species[a]

	ΔG_f°/kJ mol^{-1}	$\bar{S}^\circ$/J mol^{-1} K^{-1}	$\bar{C}_p^\circ\|_{25}^{200}$/J mol^{-1} K^{-1}
H^+ [b]	0	0	0
Cl^-	−131.29	56.73	*−125*
F^-	−281.75	−13.18	*−122*
HF(aq)	−299.93	94.98	*39*[c]
HF_2^-	−584.80	104.8	*−66*[c]
CO_3^{2-}	−527.90	−56.90	−267
HCO_3^-	−586.85	91.21	10
H_2CO_3(aq)	−623.12	187.4	269
SO_4^{2-}	−744.46	18.83	*−177*
HSO_4^-	−756.09	86.48	*163*[c]
HPO_4^{2-}	−1089.3	−33.47	*−297*
$H_2PO_4^-$	−1130.5	93.76	*−102*[c]
H_3PO_4(aq)	−1142.9	161.1	*38*[c]

[a] Numbers in italics represent values estimated from Criss–Cobble entropies. [b] Values for OH^-, which are defined by K_w (*18*), are listed with those for H_2O in Table I. [c] Calculated from data for the species above using experimental data for the appropriate protonation reaction.

Table III. Aqueous Uranium Species[a]

	ΔG_f°/kJ mol^{-1}	$\bar{S}^\circ$/J mol^{-1} K^{-1}	$\bar{C}_p^\circ\|_{25}^{200}$/J mol^{-1} K^{-1}
U^{3+}	−480.7 ± 4.6	−174.9 ± 8	*−64*
U^{4+}	−530.9 ± 2.1	−414 ± 20	*−48*
$U(OH)^{3+}$	−764 ± 8	−192 ± 40	*−54*
$U(OH)_2^{2+}$	*−992 ± 20*	*−69 ± 40*	*−1*
$U(OH)_3^+$	*−1214 ± 20*	*19 ± 40*	*74*
$U(OH)_4$(aq)	*−1431 ± 20*	*50 ± 40*	
$U(OH)_5^-$	−1642 ± 8	*71 ± 40*	*−169*
UO_2^+	−968.6 ± 5.1	−25 ± 8	*98*
UO_2^{2+}	−952.7 ± 2.1	−97 ± 4	*5*
$UO_2(OH)^+$	−1157 ± 3	16 ± 25	*64*
$(UO_2)_2(OH)_2^{2+}$	−2348 ± 5	−19 ± 17	*−42*
$(UO_2)_3(OH)_5^+$	−3955 ± 7	111 ± 17	*7*
$(UO_2)_3(OH)_7^-$	−4343 ± 20	*299 ± 80*	*840*
$UO_2(OH)_2$(aq)	−1359 ± 5	59 ± 17	
UO_2CO_3(aq)	−1538 ± 3	0 ± 60	*496*
$UO_2(CO_3)_2^{2-}$	−2106 ± 2	166 ± 80	*−387*[b]
$UO_2(CO_3)_3^{4-}$	−2659 ± 2	7 ± 8	*294*
UCl^{3+}	−677 ± 8	−283 ± 80	*285*[b]
UF^{3+}	−862 ± 8	*−192 ± 80*	*−54*
UF_2^{2+}	−1177 ± 8	*−63 ± 200*	*−4.4*
UF_3^+	−1485 ± 13	*13 ± 200*	*78*
UF_4(aq)	−1793 ± 13	*50 ± 200*	
UF_5^-	−2084 ± 17	*71 ± 200*	*−125*
UF_6^{2-}	−2379 ± 17	*84 ± 200*	*14*
UO_2F^+	−1264 ± 3	−19 ± 20	*85*
UO_2F_2(aq)	−1567 ± 3	35 ± 20	
$UO_2F_3^-$	−1863 ± 3	69 ± 20	*−255*
$UO_2F_4^{2-}$	−2151 ± 3	76 ± 20	*−56*
UO_2Cl^+	−1094 ± 8	−6 ± 80	*427*[b]
UO_2HPO_4(aq)	−2090 ± 42[c]	*50 ± 200*	
$UO_2(HPO_4)_2^{2-}$	−3237 ± 42[c]	*126 ± 200*	*354*
$UO_2(H_2PO_4)^+$	−2100 ± 3	*63 ± 200*	*36*
$UO_2(H_2PO_4)_2$(aq)	−3245 ± 4	*84 ± 200*	
$UO_2(H_2PO_4)_3^-$	−4385 ± 4	*105 ± 200*	*43*
$UHPO_4^{2+}$	−1689 ± 21	*−63 ± 200*	*−4*
$U(HPO_4)_2$(aq)	−2835 ± 21	*63 ± 200*	
$U(HPO_4)_3^{2-}$	−3974 ± 21	*105 ± 200*	*194*
$U(HPO_4)_4^{4-}$	−5109 ± 21	*21 ± 200*	*302*
$U(SO_4)^{2+}$	−1307 ± 8	−272 ± 30	*121*
$U(SO_4)_2$(aq)	−2076 ± 17	−110 ± 50	
UO_2SO_4(aq)	−1714 ± 4	52 ± 60	*354*[b]

[a] Numbers in italics represent estimated values. [b] Heat capacities estimated from the temperature dependence of ΔG_f° of the species—see text. [c] This value of ΔG_f° is a lower limit which may overestimate the solubility of the species.

peratures above 25 °C were calculated by assuming that the equilibrium constants for the plutonium complexation reactions have the same temperature dependence as the constants for the corresponding uranium reactions (*8*, *48*, *53*, *54*).

Table IV. Aqueous Plutonium Species[a]

	ΔG_f°/kJ mol^{-1}	$\bar{S}^\circ$/J mol^{-1} K^{-1}	$\bar{C}_p^\circ\|_{25}^{200}$/J mol^{-1} K^{-1}
Pu^{3+}	−578.6 ± 3.3	−185 ± 8	*−61*
$Pu(OH)^{2+}$	−770.3 ± 4.2	−88 ± 40	*9*
Pu^{4+}	−481.6 ± 3.3	−389 ± 20	*−63*
$Pu(OH)^{3+}$	*−715.9 ± 20*	*−167 ± 40*	*−69*
$Pu(OH)_2^{2+}$	*−942.7 ± 20*	*−44 ± 80*	*−16*
$Pu(OH)_3^+$	*−1163 ± 20*	*44 ± 110*	*59*
$Pu(OH)_4$(aq)	*−1376 ± 20*	*75 ± 130*	
$Pu(OH)_5^-$	*−1582 ± 20*	*96 ± 170*	*−66*
PuO_2^+	850 ± 8	−21 ± 8	*98*
PuO_2^{2+}	−756.9 ± 7	−88 ± 8	*11*
$PuO_2(OH)^+$	−961.9 ± 8	*26 ± 80*	*70*
$(PuO_2)_2(OH)_2^{2+}$	−1941 ± 13	*0 ± 80*	*−53*
$(PuO_2)_3(OH)_5^+$	−3333 ± 21	*140 ± 80*	*2*
PuO_2OH(aq)	−1032 ± 13	*96 ± 200*	
$PuCO_3^{2+}$	−1242 ± 21[c]	*−293 ± 200*	*134*
$PuO_2(CO_3)_2^{2-}$	−1898 ± 13	*175 ± 130*	*−379*[b]
PuF^{3+}	−808.8 ± 8	*−167 ± 130*	*−69*
PuO_2F^+	−1071 ± 8	*−10 ± 80*	*91*
PuO_2F_2(aq)	−1383 ± 8	*44 ± 80*	
$PuO_2F_3^-$	−1693 ± 8	*79 ± 80*	*−273*
$PuO_2F_4^{2-}$	−1991 ± 8	*85 ± 80*	*−75*
$PuCl^{3+}$	−618 ± 4	*−257 ± 130*	*266*[b]
PuO_2Cl^+	−887 ± 8	*3.8 ± 130*	*436*[b]
$PuO_2(H_2PO_4)^+$	−1910 ± 13	*71 ± 200*	*42*
$Pu(HPO_4)^{2+}$	−1645 ± 8	*−38 ± 200*	*−19*
$Pu(HPO_4)_2$(aq)	−2796 ± 8	*88 ± 200*	
$Pu(HPO_4)_3^{2-}$	−3940 ± 8	*130 ± 200*	*297*
$Pu(HPO_4)_4^{4-}$	−5085 ± 8	*46 ± 200*	*405*
$Pu(H_2PO_4)^{2+}$	−1723 ± 4	*63 ± 200*	*−82*
$Pu(SO_4)^+$	*−1343 ± 5*	*−50 ± 30*	*113*
$Pu(SO_4)^{2+}$	−1259 ± 8	−218 ± 30	*88*
$Pu(SO_4)_2$(aq)	−2029 ± 17	−17 ± 50	
PuO_2SO_4(aq)	−1520 ± 9	*61 ± 100*	*360*[b]

[a] Numbers in italics represent estimated values. [b] Heat capacities estimated from the temperature dependence of ΔG_f° of the species (based on data for the corresponding uranium species)—see text. [c] This value of ΔG_f° is a lower limit which may overestimate the stability of the species.

Because there are no high-temperature data, we calculated $\bar{C}_p^\circ|_{25}^{200}$ values for the hydrolyzed species, the fluoride and phosphate complexes, USO_4^{2+}, $UO_2(CO_3)_3^{4-}$, $PuSO_4^+$, $PuSO_4^{2+}$, and $PuCO_3^{2+}$, directly from the Criss–Cobble method using coefficients for the simple cations, anions, oxyanions, and acid oxyanions. The assumption that the coefficients for a simple species can be applied to metal complexes is widely used (*109–111*) but we note that it is clearly an oversimplification.

Results and Discussion

Thermochemical data for H_2O, relevant gases, and the solid U and Pu compounds are listed in Table I. Gibbs energies and entropies at 25 °C and the values for $\bar{C}_p^\circ|_{25}^{200}$ derived from the Criss–Cobble calculations are tabulated in Tables II–IV for the aqueous ligands, U species, and Pu species, respectively. Gibbs energies of reaction, $\Delta G_R^\circ(T)$, and equilibrium constants, $K(T)$, for reactions involving these species can be calculated from the data in Tables I–IV using the expressions (*101*, *104*)

$$\Delta G_R^\circ(T) = \Delta G_R^\circ(298.15) + [\Delta C_{p,R}^\circ - \Delta S_R^\circ](T - 298.15) - T\Delta C_{p,R}^\circ \ln (T/298.15)$$

$$\log K(T) = -\Delta G_R^\circ(T)/(2.3026RT)$$

Equilibrium constants for a selection of key reactions at 25, 60, 100, 150, and 200 °C are tabulated in Tables V and VI. For most of the neutral aqueous species considered no high-temperature Gibbs energy data were available, nor is there a good general method, comparable to the Criss–Cobble treatment for

Table V. Equilibrium Constants for Uranium

		log *K*				
no.	reaction	25 °C	60 °C	100 °C	150 °C	200 °C
	A. Solid Transformations					
1	$2UO_2 + O_2 + 2H_2O = 2\beta\text{-}UO_2(OH)_2$	44 ± 1	38 ± 1	32 ± 1	27 ± 1	23 ± 1
2	$2UO_2 + O_2 = 2\gamma\text{-}UO_3$	40.0 ± 0.8	34.9 ± 0.7	30.2 ± 0.6	25.6 ± 0.6	22.0 ± 0.5
3	$2UO_2 + O_2 + 4H_2O = 2UO_3{\cdot}2H_2O$	44.2 ± 0.8	37.9 ± 0.7	32.1 ± 0.6	26.4 ± 0.6	21.8 ± 0.5
4	$3UO_2 + O_2 = U_3O_8$	48.1 ± 0.7	42.2 ± 0.7	36.8 ± 0.6	31.6 ± 0.5	27.4 ± 0.5
5	$8UO_2 + O_2 = 2U_4O_9$	53 ± 3	47 ± 2	41 ± 2	35 ± 2	31 ± 2
6	$2UO_2 + O_2 + 2CO_2 = 2UO_2CO_3$	47.4 ± 0.8	40.3 ± 0.8	33.7 ± 0.8	27 ± 1	22 ± 1
	B. Redox Reactions					
7	$4UO_2^{2+} + 2H_2O = 4UO_2^{+} + 4H^+ + O_2$	−72 ± 4	−62 ± 3	−53 ± 3	−45 ± 3	−37 ± 3
8	$2UO_2^{2+} + 4H^+ = 2U^{4+} + 2H_2O + O_2$	−64.7 ± 0.4	−59.4 ± 0.4	−54.6 ± 0.4	−49.8 ± 0.5	−46.0 ± 0.5
9	$4UO_2^{2+} + 4H^+ = 4U^{3+} + 2H_2O + 3O_2$	−248 ± 2	−219 ± 2	−193 ± 2	−168 ± 2	−148 ± 3
	C. Oxide Dissolution Reactions					
10	$\gamma\text{-}UO_3 + 2H^+ = UO_2^{2+} + H_2O$	7.7 ± 0.5	6.2 ± 0.5	4.8 ± 0.4	3.5 ± 0.4	2.4 ± 0.3
11	$\beta\text{-}UO_2(OH)_2 + 2H^+ = UO_2^{2+} + 2H_2O$	5.7 ± 0.8	4.7 ± 0.7	3.7 ± 0.7	2.8 ± 0.6	2.1 ± 0.6
12	$UO_3{\cdot}2H_2O + 2H^+ = UO_2^{2+} + 3H_2O$	5.6 ± 0.5	4.7 ± 0.5	3.9 ± 0.4	3.1 ± 0.4	2.5 ± 0.4
13	$2U_3O_8 + 12H^+ + O_2 = 6UO_2^{2+} + 6H_2O$	70 ± 2	58 ± 2	46 ± 2	35 ± 2	26 ± 2
14	$2U_4O_9 + 16H^+ + 3O_2 = 8UO_2^{2+} + 8H_2O$	169 ± 4	143 ± 3	119 ± 3	95 ± 3	77 ± 2
15	$UO_2 + 4H^+ = U^{4+} + 2H_2O$	−4.6 ± 0.4	−6 ± 1	−7 ± 1	−9 ± 1	−10 ± 1
16	$2UO_2 + 4H^+ + O_2 = 2UO_2^{2+} + 2H_2O$	55.4 ± 0.8	47.3 ± 0.7	39.9 ± 0.7	32.6 ± 0.6	26.9 ± 0.5
17	$4UO_2 + 4H^+ + O_2 = 4UO_2^{+} + 2H_2O$	39 ± 4	32 ± 3	26 ± 3	21 ± 3	16 ± 3
18	$4UO_2 + 12H^+ = 4U^{3+} + 6H_2O + O_2$	−137 ± 3	−125 ± 3	−113 ± 3	−102 ± 2	−94 ± 2
	D. Dissolution of Uranium Compounds					
19	$UO_2CO_3(s) = UO_2^{2+} + CO_3^{2-}$	−14.2 ± 0.2	−14.7 ± 0.6	−15 ± 1	−17 ± 2	−18 ± 2
20	$UF_4(s) = U^{4+} + 4F^-$	−24 ± 4	−25 ± 3	−26 ± 3	−28 ± 3	−30 ± 2
21	$2UF_4{\cdot}2.5H_2O = 2U^{4+} + 8F^- + 5H_2O$	−55 ± 4	−56 ± 4	−58 ± 4	−60 ± 3	−63 ± 3
22	$(UO_2)_3(PO_4)_2(s) + 3H^+ = 3UO_2^{2+} + 2HPO_4^{2-}$	−24 ± 3	−26 ± 3	−29 ± 2	−32 ± 2	−35 ± 2
23	$(UO_2)_2(HPO_4)_2(s) = 2UO_2^{2+} + 2HPO_4^{2-}$	−23 ± 2	−24 ± 2	−26 ± 2	−28 ± 2	−30 ± 1
24	$U(HPO_4)_2{\cdot}4H_2O = U^{4+} + 2HPO_4^{-} + 4H_2O$	−26.8 ± 0.4	−27.3 ± 0.4	−28.3 ± 0.5	−29.8 ± 0.6	−31.6 ± 0.6
	E. Hydrolysis Reactions					
25	$UO_2^{2+} + H_2O = UO_2(OH)^+ + H^+$	−5.8 ± 0.4	−4.9 ± 0.4	−4.2 ± 0.4	−3.4 ± 0.5	−2.9 ± 0.5
26	$2UO_2^{2+} + 2H_2O = (UO_2)_2(OH)_2^{2+} + 2H^+$	−5.6 ± 0.4	−4.9 ± 0.3	−4.4 ± 0.3	−4.0 ± 0.4	−3.8 ± 0.4
27	$3UO_2^{2+} + 5H_2O = (UO_2)_3(OH)_5^{+} + 5H^+$	−15.6 ± 0.4	−13.8 ± 0.3	−12.4 ± 0.3	−11.3 ± 0.3	−10.7 ± 0.3
28	$3UO_2^{2+} + 7H_2O = (UO_2)_3(OH)_7^{-} + 7H^+$	−31 ± 4	−27 ± 3	−23 ± 3	−19 ± 3	−16 ± 3
29	$UO_2^{2+} + 2H_2O = UO_2(OH)_2(aq) + 2H^+$	−12 ± 1	−11 ± 1	−10 ± 1	−9 ± 1	−8 ± 1
30	$U^{4+} + H_2O = U(OH)^{+3} + H^+$	−1 ± 1	0 ± 1	1 ± 1	2 ± 1	2 ± 1
31	$U^{4+} + 2H_2O = U(OH)_2^{2+} + 2H^+$	−2 ± 4	−1 ± 3	0 ± 3	1 ± 3	2 ± 2
32	$U^{4+} + 3H_2O = U(OH)_3^{+} + 3H^+$	−5 ± 4	−3 ± 3	−2 ± 3	0 ± 3	1 ± 2
33	$U^{4+} + 4H_2O = U(OH)_4(aq) + 4H^+$	−9 ± 4	−7 ± 3	−5 ± 3	−4 ± 3	−3 ± 2
34	$U^{4+} + 5H_2O = U(OH)_5^{-} + 5H^+$	−13 ± 1	−11 ± 1	−10 ± 1	−9 ± 1	−8 ± 1
	F. Complexation Reactions					
35	$UO_2^{2+} + SO_4^{2-} = UO_2SO_4(aq)$	2.9 ± 0.5	3.5 ± 0.6	4.4 ± 0.8	6 ± 1	7 ± 1
36	$U^{4+} + SO_4^{2-} = USO_4^{2+}$	5 ± 1	6 ± 1	6 ± 1	7 ± 1	8 ± 1
37	$U^{4+} + 2SO_4^{2-} = U(SO_4)_2(aq)$	10 ± 3	10 ± 3	11 ± 2	12 ± 2	13 ± 2
38	$UO_2^{2+} + CO_3^{2-} = UO_2CO_3(aq)$	10.1 ± 0.4	10.2 ± 0.5	10.6 ± 0.7	12 ± 1	13 ± 1
39	$UO_2^{2+} + 2CO_3^{2-} = UO_2(CO_3)_2^{2-}$	17.1 ± 0.4	17.4 ± 0.6	18 ± 1	18 ± 1	19 ± 2
40	$UO_2^{2+} + 3CO_3^{2-} = UO_2(CO_3)_3^{4-}$	21.4 ± 0.4	21.0 ± 0.3	21.3 ± 0.3	22.4 ± 0.3	24.0 ± 0.3
41	$UO_2^{2+} + Cl^- = UO_2Cl^+$	2 ± 1	2 ± 1	2 ± 1	3 ± 2	4 ± 2
42	$U^{4+} + Cl^- = UCl^{3+}$	3 ± 1	3 ± 1	3 ± 1	4 ± 2	5 ± 2
43	$UO_2^{2+} + F^- = UO_2F^+$	5.1 ± 0.3	5.1 ± 0.3	5.3 ± 0.3	5.6 ± 0.4	6.0 ± 0.4
44	$UO_2^{2+} + 2F^- = UO_2F_2(aq)$	9.0 ± 0.4	9.0 ± 0.4	9.1 ± 0.4	9.4 ± 0.4	9.8 ± 0.5
45	$UO_2^{2+} + 3F^- = UO_2F_3^{-}$	11.3 ± 0.4	11.3 ± 0.4	11.4 ± 0.4	11.5 ± 0.4	11.6 ± 0.5
46	$UO_2^{2+} + 4F^- = UO_2F_4^{2-}$	12.6 ± 0.4	12.6 ± 0.4	12.9 ± 0.4	13.6 ± 0.5	14.3 ± 0.5
47	$U^{4+} + F^- = UF^{3+}$	9 ± 1	9 ± 1	9 ± 1	10 ± 2	11 ± 2
48	$U^{4+} + 2F^- = UF_2^{2+}$	14 ± 1	15 ± 2	16 ± 2	17 ± 3	18 ± 3
49	$U^{4+} + 3F^- = UF_3^{+}$	19 ± 2	20 ± 2	21 ± 2	22 ± 3	23 ± 4
50	$U^{4+} + 4F^- = UF_4(aq)$	24 ± 2	24 ± 2	25 ± 2	26 ± 3	27 ± 4
51	$U^{4+} + 5F^- = UF_5^{-}$	25 ± 3	26 ± 3	27 ± 3	28 ± 3	29 ± 4
52	$U^{4+} + 6F^- = UF_6^{2-}$	28 ± 3	28 ± 3	29 ± 3	31 ± 3	32 ± 4
53	$UO_2^{2+} + HPO_4^{2-} + H^+ = UO_2H_2PO_4^{+}$	10.2 ± 0.5	10 ± 1	11 ± 2	11 ± 3	12 ± 3
54	$UO_2^{2+} + 2HPO_4^{2-} + 2H^+ = UO_2(H_2PO_4)_2(aq)$	19.9 ± 0.7	19 ± 1	19 ± 2	20 ± 3	20 ± 3
55	$UO_2^{2+} + 3HPO_4^{2-} + 3H^+ = UO_2(H_2PO_4)_3^{-}$	28.8 ± 0.7	28 ± 1	27 ± 2	28 ± 3	28 ± 3
56	$UO_2^{2+} + HPO_4^{2-} = UO_2HPO_4(aq)$	<8	<9	<9	<10	<10
57	$UO_2^{2+} + 2HPO_4^{2-} = UO_2(HPO_4)_2^{2-}$	<19	<18	<19	<20	<22
58	$U^{4+} + HPO_4^{2-} = UHPO_4^{2+}$	12 ± 4	13 ± 3	14 ± 3	15 ± 4	17 ± 4
59	$U^{4+} + 2HPO_4^{2-} = U(HPO_4)_2(aq)$	22 ± 4	23 ± 3	24 ± 3	26 ± 4	27 ± 4
60	$U^{4+} + 3HPO_4^{2-} = U(HPO_4)_3^{2-}$	31 ± 4	31 ± 3	32 ± 3	34 ± 4	37 ± 4
61	$U^{4+} + 4HPO_4^{2-} = U(HPO_4)_4^{4-}$	39 ± 4	38 ± 3	39 ± 3	40 ± 4	43 ± 4

ions, available for calculating such data. In such cases we arbitrarily set $\bar{C}_p{}^\circ|_{25}^{200}$ equal to zero for the equilibrium constant calculations.

Error limits for the Gibbs energies, entropies, and equilibrium constants in the tables are our best estimate of the 90% confidence limits or, where available, the author's stated

Table VI. Equilibrium Constants for Plutonium

no.	reaction	log K				
		25 °C	60 °C	100 °C	150 °C	200 °C
	A. Solid Transformations					
1	$2PuO_2 + O_2 + 2H_2O = 2PuO_2(OH)_2$	−8 ± 3	−9 ± 3	−10 ± 2	−10 ± 2	−11 ± 2
2	$4PuO_2 + O_2 + 2H_2O = 4PuO_2(OH)$	−42 ± 6	−39 ± 5	−37 ± 5	−34 ± 4	−32 ± 4
3	$4PuO_2 = 2Pu_2O_3 + O_2$	−141 ± 7	−125 ± 7	−110 ± 6	−96 ± 5	−85 ± 5
4	$PuO_2 + 2H_2O = Pu(OH)_4$	−8 ± 5	−8 ± 5	−8 ± 4	−8 ± 4	−7 ± 3
5	$4PuO_2 + 6H_2O = 4Pu(OH)_3 + O_2$	−134 ± 4	−121 ± 4	−109 ± 4	−97 ± 3	−88 ± 3
	B. Redox Reactions					
6	$4PuO_2^{2+} + 2H_2O = 4PuO_2^{+} + 4H^+ + O_2$	−18 ± 4	−14 ± 3	−11 ± 3	−7 ± 3	−4 ± 2
7	$2PuO_2^{2+} + 4H^+ = 2Pu^{4+} + 2H_2O + O_2$	−13 ± 2	−13 ± 2	−13 ± 2	−13 ± 2	−13 ± 2
8	$4PuO_2^{2+} + 4H^+ = 4Pu^{3+} + 2H_2O + 3O_2$	−42 ± 5	−35 ± 5	−30 ± 4	−24 ± 4	−19 ± 4
	C. Oxide Dissolution Reactions					
9	$PuO_2(OH)_2 + 2H^+ = PuO_2^{2+} + 2H_2O$	3 ± 1	3 ± 1	2 ± 1	2 ± 1	1 ± 1
10	$PuO_2(OH) + H^+ = PuO_2^{+} + H_2O$	5 ± 1	5 ± 1	4 ± 1	3 ± 1	3 ± 1
11	$PuO_2 + 4H^+ = Pu^{4+} + 2H_2O$	−7 ± 1	−8 ± 1	−9 ± 1	−10 ± 1	−11 ± 1
12	$Pu(OH)_4 + 4H^+ = Pu^{4+} + 4H_2O$	1 ± 4	0 ± 3	−2 ± 3	−2 ± 3	−3 ± 2
13	$Pu_2O_3 + 6H^+ = 2Pu^{3+} + 3H_2O$	48 ± 4	41 ± 3	35 ± 3	29 ± 3	25 ± 2
14	$Pu(OH)_3 + 3H^+ = Pu^{3+} + 3H_2O$	22 ± 1	20 ± 1	17 ± 1	15 ± 1	13 ± 1
15	$2PuO_2 + 4H^+ + O_2 = 2PuO_2^{2+} + 2H_2O$	−1 ± 2	−3 ± 2	−5 ± 2	−7 ± 2	−8 ± 1
16	$4PuO_2 + 4H^+ + O_2 = 4PuO_2^{+} + 2H_2O$	−21 ± 5	−21 ± 5	−21 ± 4	−20 ± 4	−20 ± 3
17	$4PuO_2 + 12H^+ = 4Pu^{3+} + 6H_2O + O_2$	−44 ± 2	−42 ± 2	−40 ± 2	−37 ± 2	−36 ± 2
	D. Dissolution of Plutonium Compounds					
18	$PuF_4(s) = Pu^{4+} + 4F^-$	−13 ± 6	−15 ± 5	−18 ± 5	−20 ± 4	−23 ± 4
19	$PuF_3(s) = Pu^{3+} + 3F^-$	−10 ± 2	−11 ± 2	−12 ± 2	−14 ± 2	−16 ± 1
20	$PuO_2HPO_4(s) = PuO_2^{2+} + HPO_4^{2-}$	−13 ± 1	−13 ± 1	−13 ± 1	−14 ± 1	−15 ± 1
21	$Pu(HPO_4)_2(s) = Pu^{4+} + 2HPO_4^{2-}$	−28 ± 1	−29 ± 2	−30 ± 2	−32 ± 2	−34 ± 1
	E. Hydrolysis Reactions					
22	$PuO_2^{2+} + H_2O = PuO_2(OH)^+ + H^+$	−5.6 ± 0.4	−4.8 ± 0.6	−4 ± 1	−3 ± 1	−3 ± 2
23	$2PuO_2^{2+} + 2H_2O = (PuO_2)_2(OH)_2^{2+} + 2H^+$	−8.3 ± 0.4	−7.3 ± 0.6	−7 ± 1	−6 ± 1	−6 ± 2
24	$3PuO_2^{2+} + 5H_2O = (PuO_2)_3(OH)_5^{+} + 5H^+$	−21.6 ± 0.4	−19.2 ± 0.6	−17 ± 1	−16 ± 1	−15 ± 2
25	$PuO_2^{+} + H_2O = PuO_2OH(aq) + H^+$	−10 ± 2	−8 ± 2	−7 ± 2	−7 ± 3	−6 ± 4
26	$Pu^{4+} + H_2O = PuOH^{3+} + H^+$	−1 ± 4	0 ± 3	1 ± 3	2 ± 3	2 ± 2
27	$Pu^{4+} + 2H_2O = Pu(OH)_2^{2+} + 2H^+$	−2 ± 4	−1 ± 3	0 ± 3	1 ± 3	2 ± 3
28	$Pu^{4+} + 3H_2O = Pu(OH)_3^{+} + 3H^+$	−5 ± 4	−4 ± 3	−2 ± 3	−1 ± 3	0 ± 3
29	$Pu^{4+} + 4H_2O = Pu(OH)_4(aq) + 4H^+$	−9 ± 4	−8 ± 3	−6 ± 3	−5 ± 4	−4 ± 4
30	$Pu^{4+} + 5H_2O = Pu(OH)_5^{-} + 5H^+$	−15 ± 4	−13 ± 3	−11 ± 3	−10 ± 4	−9 ± 4
31	$Pu^{3+} + H_2O = PuOH^{2+} + H^+$	−8.0 ± 0.4	−7.0 ± 0.4	−6.1 ± 0.5	−5.2 ± 0 7	−4.5 ± 0.8
	F. Complexation Reactions					
32	$PuO_2^{2+} + SO_4^{2-} = PuO_2SO_4(aq)$	3 ± 1	4 ± 1	5 ± 1	6 ± 2	7 ± 2
33	$Pu^{4+} + SO_4^{2-} = PuSO_4^{2-}$	6 ± 1	6 ± 1	7 ± 1	7 ± 1	8 ± 1
34	$Pu^{4+} + 2SO_4^{2-} = Pu(SO_4)_2(aq)$	10 ± 3	11 ± 3	12 ± 2	14 ± 2	15 ± 2
35	$Pu^{3+} + SO_4^{2-} = PuSO_4^{+}$	3.5 ± 0.6	3.9 ± 0.5	4.4 ± 0.5	5.3 ± 0.5	6.1 ± 0.5
36	$PuO_2^{2+} + 2CO_3^{2-} = PuO_2(CO_3)_2^{2-}$	15 ± 2	16 ± 2	16 ± 2	17 ± 2	17 ± 3
37	$Pu^{4+} + CO_3^{2-} = PuCO_3^{2+}$	⩽41	⩽37	⩽35	⩽32	⩽31
38	$PuO_2^{2+} + Cl^- = PuO_2Cl^+$	−0.3 ± 0.7	0 ± 1	1 ± 1	2 ± 2	3 ± 2
39	$Pu^{4+} + Cl^- = PuCl_3^{+}$	0.9 ± 0.7	1 ± 1	2 ± 1	3 ± 2	4 ± 2
40	$PuO_2^{2+} + F^- = PuO_2F^+$	5.6 ± 0.7	5.6 ± 0.8	6 ± 1	6 ± 1	6 ± 2
41	$PuO_2^{2+} + 2F^- = PuO_2F_2(aq)$	11.0 ± 0.7	10.8 ± 0.8	11 ± 1	11 ± 1	11 ± 2
42	$PuO_2^{2+} \pm 3F^- = PuO_2F_3^{-}$	15.9 ± 0.7	15.4 ± 0.8	15 ± 1	15 ± 1	14 ± 2
43	$PuO_2^{2+} + 4F^- = PuO_2F_4^{2-}$	18.8 ± 0.7	18.2 ± 0.8	18 ± 1	18 ± 1	18 ± 2
44	$Pu^{4+} + F^- = PuF^{3+}$	8 ± 1	8 ± 1	9 ± 2	10 ± 2	10 ± 3
45	$PuO_2^{2+} + HPO_4^{2-} + H^+ = PuO_2H_2PO_4^{+}$	11 ± 2	11 ± 2	11 ± 2	12 ± 3	12 ± 4
46	$Pu^{4+} + HPO_4^{2-} = PuHPO_4^{2+}$	13 ± 1	14 ± 2	15 ± 2	16 ± 3	17 ± 3
47	$Pu^{4+} + 2HPO_4^{2-} = Pu(HPO_4)_2(aq)$	24 ± 1	24 ± 2	25 ± 2	27 ± 3	29 ± 3
48	$Pu^{4+} + 3HPO_4^{2-} = Pu(HPO_4)_3^{2-}$	33 ± 1	34 ± 2	35 ± 2	37 ± 3	39 ± 3
49	$Pu^{4+} + 4HPO_4^{2-} = Pu(HPO_4)_4^{4-}$	43 ± 1	42 ± 2	43 ± 2	44 ± 3	46 ± 3
50	$Pu^{3+} + HPO_4^{2-} + H^+ = PuH_2PO_4^{2+}$	9.7 ± 0.4	10 ± 1	11 ± 2	12 ± 2	13 ± 3

"uncertainty". The effect of uncertainties in the room-temperature data on the equilibrium constants in Tables V and VI was estimated from the expression

$$\sigma(\log K, T) = \frac{1}{2.303RT}\{\sigma(\Delta G_R°,298)^2 + [T - 298.15]^2\sigma(\Delta S_R°,298)^2\}^{1/2}$$

The room-temperature error limit for values derived from data obtained at high ionic strength was generally assumed to include a term of the order of magnitude of the correction used to obtain the standard state ($I = 0$) value. Where markedly discordant experimental results exist for a particular value, each having a relatively small experimental deviation, e.g. $\bar{S}°(UO_2CO_3(aq))$, the error limit in the tables generally represents an attempt to reflect the overall uncertainty in the value, rather than the precision in individual measurements. In cases where a method similar to that of Latimer (*70*) was used to estimate $S°$ for solid materials, the error in $S°$ was taken to be about 5%. The estimated size of the error was increased where only limited comparison data were available for particular M^{n+}/anion combinations (e.g., Pu^{4+}/OH^-). Large error limits were chosen for the Gibbs energies of the uranium monohydrogen phosphate complexes, because these are merely approximate minimum values. Errors in the free energies for those uranium(IV) hydrolysis products not directly established by experiment were estimated as ±20 kJ mol^{-1}. The error in the free energy of $U(OH)^-_5$ may be as large as ±8 kJ mol^{-1} because neither the solid phase nor aqueous species was well established in Gayer and Leider's experiment (*112*).

Although Langmuir's estimated entropies for uranium complexes and hydrolyzed species are consistent with data for other similarly charged species, we judged that his stated accuracies of ±20–40 J mol^{-1} K^{-1} are overly optimistic, particularly for the U^{4+} complexes where little experimental information is available. The values in Table III are our more conservative estimates. Somewhat larger, admittedly arbitrary, error limits were estimated for the $\bar{S}°$ values for the Pu complexes derived from these data.

The solubility products calculated for UF_4 and PuF_4 (reactions 20 and 18 in Tables V and VI, respectively) differ by many orders of magnitude. This difference is unlikely to be real and suggests a significant error in the literature data base—probably in the enthalpies of formation of the solid tetrafluoride compounds.

Obvious sources of indeterminate systematic errors are the uncertainty in the value for $\Delta G_f°(PuCl_3)$ on which much of the Pu data are based, unresolved inconsistencies in $\Delta H_f°(UCl_4)$ which affect many of the U^{4+} data (*29*), and inaccuracies in the Criss–Cobble extrapolation procedure.

This last point has been examined in some detail (*101*–*104*). The entropy correspondence principle is based on the ionic entropy data available in 1963 (*13*). Comparison of limited new results with the predictions indicates that the Criss–Cobble treatment predicts the temperature dependence of the Gibbs energies of simple anions and cations to within a few kilojoules per mole below 150 °C. Large inaccuracies have been observed at 200 °C and above, where the Criss–Cobble coefficients were themselves an extrapolation (*14*). We note that, up to 150 °C, the values for $\bar{S}°(T)$ calculated for Cl^-, F^-, SO_4^{2-}, CO_3^{2-}, and HPO_4^{2-} agree with experimental values from which the correspondence principle was derived to within 22 J mol^{-1} K^{-1} in $\bar{S}°(T)$. Thus, the effect of such errors in the contribution of any ion to $[\Delta G_R(T) - \Delta G_R°(298.15)]$ is no more than ~1.5 kJ mol^{-1}. Also, the recently determined value (*113*) for $\bar{C}_p°(Th^{4+})$ agrees with the Criss–Cobble prediction to within 27 J mol^{-1} K^{-1}. Errors of this magnitude in the extrapolation method are far outweighed by the uncertainties in $\bar{S}°$ for the species considered here.

The assumption that the solvated or complexed ions of a particular actinide in a particular oxidation state have the same electronic ground-state degeneracy as the free ions is undoubtedly an oversimplification, primarily because ligand field effects may be sufficient to remove or alter the ground-state degeneracy but also because the Russell–Saunders coupling scheme may not give a proper description of the energy levels for actinide ions (*106*, *107*). Uncertainties in the extrapolated values of $\bar{S}°(T)$ due to this assumption are of the order of 5 J mol^{-1} K^{-1} for most species but as much as 36 J mol^{-1} K^{-1} at 200 °C for those species ($J \neq 0$) which were treated as oxyanions and oxyacid anions by the Criss–Cobble method. In all cases these differences are still within the limits of accuracy of the $\bar{S}°$ data.

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Glossary

$C_p°$, $\bar{C}_p°$	standard molar and partial molar heat capacities, at 25 °C unless the temperature is noted ($\bar{C}_p°(H^+,T) \equiv 0$)
$\bar{C}_p°\|_{25}^{200}$	effective constant partial molal heat capacity over the range 25–200 °C ($\bar{C}_p°\|_{25}^{200}(H^+) \equiv 0$), calculated by a least-squares fit to eq 2 using values for $\bar{S}°(T)$ at 25, 60, 100, 150, and 200 °C
$\Delta C_{p,R}°$	heat capacity change for reaction
$\Delta G_f°$	standard molal Gibbs energy of formation, at 25 °C unless the temperature is noted
$\Delta G_R°$	standard Gibbs energy of reaction
$\Delta H_f°$	standard molal enthalpy of formation, at 25 °C unless the temperature is noted
$\Delta H_R°$	standard enthalpy of reaction
I	ionic strength (in general, ionic strength concentrations in the literature were expressed in mol dm^{-3}, but the few which were reported in mol kg^{-1} are not distinguished)
k	Boltzmann constant
K_w	ionic dissociation product of water
K	equilibrium constant for the aqueous solution reaction as written
$K_s^\bullet$	the solubility product defined for the reaction $MO_p(OH)_g + qH^+ + 2(p-r)H^+ \rightleftarrows MO_r^{(2p+q-2r)+} + (q+p-r)H_2O$ $K_s^* = [MO_r^{(2(p-r)+q)+}]/[H^+]^{q+2(p-r)}$ for oxides and hydroxides (M = metal ion)
K_s	the solubility product for salts (ligand L charge q) $ML_n \rightleftarrows M^{nq+} + nL^{q-}$, $K_s = [M^{nq+}][L^{q-}]^n$
$S°$,$\bar{S}°$	standard and partial molal entropies, at 25 °C unless the temperature is noted ($\bar{S}°(H^+,T) \equiv 0$)
$\Delta S_R°$	standard molal entropy of reaction at T
$\Delta S_f°$	standard molal entropy of formation
$\bar{S}_e°$	the contribution to the partial molal entropy from the ground-state electronic degeneracy of the aqueous species
$\bar{S}°_{adj}$	the temperature-dependent portion of the partial molal entropy
T	absolute temperature in Kelvin
β_n	the cumulative stoichiometric formation constant for the reaction $M^{p+} + nL^{q-} \rightleftarrows ML_n^{(p-nq)}$, $\beta_n = [ML_n^{(p-nq)}]/[M][L]^n$. If the ionic strength is not stated, then the β_n is the value at infinite dilution
$\beta_n^\bullet$	formation constants similar to β_n but involving complexation of protonated ligands with loss of protons $M^{p+} + nHL^{q-} \rightleftarrows ML_n^{(p-nq)} + nH^+$, $\beta_n^* = [ML_n^{(p-nq)}][H^+]^n/[M^{p+}][HL^{q-}]^n$

Literature Cited

(1) L. J. Miller, *Econ. Geol.*, **53**, 521 (1958).
(2) P. B. Hostetler and R. M. Garrels, *Econ. Geol.*, **57**, 137 (1962).
(3) A. K. Lisitsin, *Geochemistry* (*USSR*), 876 (1962).
(4) A. K. Lisitsin, *Int. Geol. Rev.*, **13**, 744 (1971).
(5) R. A. Rich, H. D. Holland, and U. Peterson, "Developments in Economic Geology", Vol. 6, Elsevier, Amsterdam, 1977.
(6) A. A. Nikitin, E. I. Sergeeva, I. L. Khodakovsky, and G. B. Naumov, *Geokhimiya*, 297 (1972).
(7) E. I. Sergeeva, A. A. Nikitin, I. L. Khodakovsky, and G. B. Naumov, *Geochem. Int.*, **9**, 900 (1972).
(8) D. Langmuir, *Geochim. Cosmochim. Acta*, **42**, 547 (1978).
(9) D. G. Brookins, *Chem. Geol.*, **23**, 309 (1978).
(10) See, for example: G. de Marsily, E. Ledoux, A. Barbreau, and J. Margat, *Science* (*Washington, D.C.*), **197**, 519 (1977); B. L. Cohen, *Sci. Am.*, **236** (6), 21 (1977).
(11) D. Rai and R. J. Serne, *J. Environ. Qual.*, **6**, 89 (1977).
(12) J. M. Cleveland, "The Chemistry of Plutonium", Gordon and Breach, New York, 1970.
(13) C. M. Criss and J. W. Cobble, *J. Am. Chem. Soc.*, **86**, 5385 (1964).
(14) C. M. Criss and J. W. Cobble, *J. Am. Chem. Soc.*, **86**, 5390 (1964).
(15) CODATA "Recommended Key Values for Thermodynamics", *J. Chem. Thermodynam.*, **10**, 903 (1978).
(16) D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, *NBS Tech. Note* (*U.S.*), **No. 270-3** (1968) and **No. 270-4** (1969).
(17) K. K. Kelley, *Bull.-U.S., Bur. Mines*, **No. 584** (1960).
(18) G. Olofsson and L. G. Hepler, *J. Solution Chem.*, **4**, 127 (1975).
(19) H. C. Helgeson and D. H. Kirkham, *Am. J. Sci.*, **274**, 1089 (1974).
(20) R. E. Mesmer and C. F. Baes, Jr., *J. Solution Chem.*, **3**, 307 (1974).
(21) W. L. Marshall and E. V. Jones, *J. Phys. Chem.*, **70**, 4028 (1966).
(22) A. J. Ellis, *J. Chem. Soc.*, 4300 (1963).
(23) H. C. Helgeson, *J. Phys. Chem.*, **71**, 3121 (1967).
(24) J. Fuger, *MTP Int. Rev. Sci.: Inorg. Chem., Ser. One*, **7**, Chapter 5 (1972).

(25) G. C. Fitzgibbon, D. Pavone, and C. E. Holley, Jr., *J. Chem. Eng. Data*, **12**, 122 (1967).
(26) F. Grønvold, N. J. Kveseth, A. Sveen, and J. Tichý, *J. Chem. Thermodyn.*, **2**, 665 (1970).
(27) E. H. P. Cordfunke, *J. Phys. Chem.*, **68**, 3353 (1964).
(28) V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes", *Natl. Stand. Ref. Data Ser.* (U.S., *Natl. Bur. Stand.*), **NSRDS-NBS 2** (1965).
(29) F. L. Oetting, M. H. Rand, and R. J. Ackermann, "The Chemical Thermodynamics of Actinide Elements and Compounds-Part 1-The Actinide Elements", IAEA, Vienna, 1976; J. Fuger and F. L. Oetting, "The Chemical Thermodynamics of Actinide Elements and Compounds-Part 2-The Actinide Aqueous Ions", IAEA, Vienna, 1976.
(30) K. H. Gayer and H. Leider, *J. Am. Chem. Soc.*, **77**, 1448 (1955).
(31) G. B. Naumov, B. N. Ryzhenko, and I. L. Khodakovsky, "Handbook of Thermodynamic Data", Atomizdat, Moscow, 1971, English Translation by G. J. Soleimani, NTIS PB-226 722 (1974).
(32) R. G. Robins, *J. Inorg. Nucl. Chem.*, **28**, 119 (1966).
(33) P. R. Tremaine, IAEA Symposium on Thermodynamics of Nuclear Materials, Jülich, 1979, in press.
(34) J. W. Cobble, *J. Chem. Phys.*, **21**, 1446 (1953).
(35) C. F. Baes, Jr., and R. E. Mesmer, "The Hydrolysis of Cations", Wiley-Interscience, New York, 1976.
(36) C. F. Baes, Jr., and N. J. Meyer, *Inorg. Chem.*, **1**, 780 (1962).
(37) J. Sutton, *J. Chem. Soc.*, S275 (1949). We have used $K_2 = 5 \times 10^{-8}$ as indicated in Figure 6 of this reference, not 5×10^{-9} as written on p 282.
(38) C. Tsymbal, *Comm. Energie At. Fr. Rapp.*, CEA-R-3476 (1969).
(39) M. H. Rand and O. Kubaschewski, "The Thermochemical Properties of Uranium Compounds", Oliver and Boyd, Edinburgh, 1963.
(40) E. I. Khanaev, *Sib. Chem. J.* (*Engl. Transl.*), 449 (1968).
(41) I. G. Suglobova and D. E. Chirkst, *Sov. Radiochem.* (*Engl. Transl.*), **20**, 175 (1978).
(42) E. H. P. Cordfunke, W. Ouweltjes, and G. Prins, *J. Chem. Thermodyn.*, **8**, 241 (1976).
(43) J. H. Burns, D. W. Osborne, and E. F. Westrum, Jr., *J. Chem. Phys.*, **33**, 387 (1960).
(44) M. M. Popov, F. A. Kostylev, and T. F. Karpova, *J. Inorg. Chem.* (*USSR*) **2** (1), 9 (1957).
(45) R. A. Day, Jr., R. N. Wilhite, and F. D. Hamilton, *J. Am. Chem. Soc.*, **77**, 3180 (1955).
(46) D. D. Wagman, R. H. Schumm, and V. B. Parker, "A Computer Assisted Evaluation of the Thermochemical Data of the Compounds of Thorium", *Natl. Bur. Stand.*, [Tech. Rep.]NBSIR (U.S.), **NBSIR-77-1300** (PB 273 171) (1977).
(47) M. H. Lietzke and R. W. Stoughton, *J. Phys. Chem.*, **64**, 816 (1960).
(48) N. M. Nikolaeva, *Izv. Sib. Otd. Akad. Nauk SSSR*, *Ser. Khim. Nauk*, (3) 61 (1971).
(49) N. M. Nikolaeva in "High Temperature High Pressure Electrochemistry in Aqueous Solutions", National Association of Corrosion Engineers, Houston, 1978, p 146.
(50) N. M. Nikolaeva, *Izv. Sib. Otd. Akad. Nauk SSSR*, *Ser. Khim. Nauk*, (6) 30 (1976).
(51) A. V. Piroshkov and N. M. Nikolaeva, *Izv. Sib. Otd. Akad. Nauk SSSR*, *Ser. Khim. Nauk*, (5) 55 (1976).
(52) O. A. Devina, I. L. Khodakovsky, M. E. Efimov, and V. A. Medvedev, 7th All Union Conference on Calorimetry, 231 (1977); J. Fuger, I. L. Khodakovsky, V. A. Medvedev, and J. D. Navratil, IAEA Symposium on Thermodynamics of Nuclear Materials, Jüllich, 1979, in press.
(53) N. M. Nikolaeva, *Izv. Sib. Otd. Akad. Nauk SSSR*, *Ser. Khim. Nauk*, (1) 56 (1977).
(54) N. M. Nikolaeva, *Izv. Sib. Otd. Akad. Nauk SSSR*, *Ser. Khim. Nauk*, (3) 114 (1977).
(55) E. W. Davies and C. B. Monk, *Trans. Faraday Soc.*, **53**, 442 (1957).
(56) A. I. Moskvin, A. M. Shelyakina, and P. S. Perminov, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), **12**, 1756 (1967); A. I. Moskvin, L. N. Essen, and T. N. Bukhtiyarova, *ibid.*, **12**, 1794 (1967).
(57) B. J. Thamer, *J. Am. Chem. Soc.*, **79**, 4298 (1957).
(58) Y. Marcus, *Proc. Int. Conf. Peaceful Uses At. Energy*, *2nd*, **3**, 465 (1958).
(59) J. J. Huntzicker and E. F. Westrum, Jr., *J. Chem. Thermodyn.*, **3**, 61 (1971).
(60) H. L. Girdhar and E. F. Westrum, Jr., *J. Chem. Eng. Data*, **13**, 531 (1968).
(61) E. F. Westrum, Jr., Y. Takahashi, and F. Grønvold, *J. Phys. Chem.*, **69**, 3192 (1965).
(62) D. W. Osborne, E. F. Westrum, Jr., and H. R. Lohr, *J. Am. Chem. Soc.*, **79**, 529 (1957).
(63) B. B. Owens and S. W. Mayer, *J. Inorg. Nucl. Chem.*, **26**, 501 (1964).
(64) J. M. Sturtevant, "Technique of Organic Chemistry, Physical Methods," Vol. I, Part I, 3rd ed., A. Weissberger, Ed., Interscience, New York, 1959, p 557.
(65) G. K. Johnson, E. H. van Deventer, O. L. Kruger, and W. N. Hubbard, *J. Chem. Thermodynam.*, 1, 89 (1969).
(66) H. E. Flotow, D. W. Osborne, S. M. Fried, and J. G. Malm, *J. Chem. Phys.*, **65**, 1124 (1976).
(67) P. Chereau, G. Dêan, M. de Franco, and P. Gerdanian, *J. Chem. Thermodynam.*, **9**, 211 (1977).
(68) IAEA Panel on Thermodynamics of Plutonium Oxides, *Tech. Rep. Ser.-I.A.E.A.*, **No. 79** (1967).
(69) H. M. Busey and H. D. Cowan, LAMS-1105 Los Alamos Scientific Laboratory, University of California, Los Alamos, CA, 1950.
(70) W. M. Latimer, "Oxidation Potentials", 2nd ed., Prentice-Hall, Englewood Cliffs, N.J., 1952.
(71) S. I Auerbach, D. E. Reichle and E. G. Struxness, ORNL 5257, Oak Ridge National Laboratory, Oak Ridge, TN, 1977, p 138.
(72) K. A. Kraus and F. Nelson, AECD-1864 Clinton National Laboratory, 1948. (Available from the U.S. Dept. of Energy, Box 62, Oak Ridge, TN.)
(73) R. D. Shannon and C. T. Prewitt, *Acta Crystallogr.*, *Sect. B*, **25**, 925 (1969).
(74) D. W. Osborne, H. E. Flotow, S. M. Fried, and J. G. Malm, *J. Chem. Phys.*, **63**, 4613 (1975).
(75) D. W. Osborne, H. E. Flotow, S. M. Fried, and J. G. Malm, *J. Chem. Phys.* **61**, 1463 (1974).
(76) M. H. Rand, *At. Energy Rev.*, **4**, Spec. Issue **No.** 1, 7 (1966).
(77) C. K. McLane in "Transuranium Elements", Part I, G. T. Seaborg, J. J. Katz, and W. M. Manning, Eds., National Nuclear Energy Series IV, Vol. 14B, McGraw-Hill, New York, 1949, pp 414–422.
(78) A. D. Paul, *Rep. ORO* (*U.S. Dep. Energy*), **UCRL-2926** (1955).
(79) S. Ahrland, J. O. Liljenzin, and J. Rydberg in "Comprehensive Inorganic Chemistry", Vol. 5, J. C. Bailar, Jr., H. J. Emeléus, R. S. Nyholm, and A. F. Trotman-Dickenson, Eds., Pergamon Press, Oxford, 1973, p 465ff.
(80) V. N. Krylov, E. V. Komarov, and M. F. Pushlenkov, *Sov. Radiochem.* (*Engl. Transl.*), **10**, 705 (1968).
(81) S. K. Patil and V. V. Ramakrishna, *Radiochim. Acta*, **19**, 27 (1973).
(82) P. R. V. Rao, S. V. Bagawde, V. V. Ramakrishna, and S. K. Patil, *J. Inorg. Nucl. Chem.*, **40**, 123 (1978).
(83) L. G. Sillén and A. E. Martell, *Chem. Soc.*, *Spec. Publ.*, **No. 17** (1964); **No. 25** (1971).
(84) R. G. de Carvalho and G. R. Choppin, *J. Inorg. Nucl. Chem.*, **29**, 737 (1967).
(85) S. K. Patil and V. V. Ramakrishna, *J. Inorg. Nucl. Chem.*, **38**, 1075 (1976).
(86) R. M. Izatt, D. Eatough, J. J. Christensen, and C. H. Bartholomew, *J. Chem. Soc. A*, 47 (1969).
(87) A. I. Moskvin and A. D. Gel'man, *Russ. J. Inorg. Chem.* (*USSR*), **3** (4), 198 (1958).
(88) M. Kasha in "Transuranium Elements", Part I, G. T. Seaborg, J. J. Katz, and W. M. Manning, Eds., National Nuclear Energy Series, Div. IV, Vol. 14B, 1949, p 295.
(89) A. D. Gel'man, A. I. Moskvin, and V. P. Zaitseva, *Sov. Radiochem.* (*Engl. Transl.*) **4**, 138 (1962).
(90) L. J. Wittenberg and R. H. Steinmeyer, *J. Inorg. Nucl. Chem.*, **24**, 1015 (1962).
(91) M. Woods, M. L. Mitchell, and J. C. Sullivan, *Inorg. Nucl. Chem. Lett.*, **14**, 465 (1978).
(92) T. W. Newton and F. B. Baker, *J. Phys. Chem.*, **61**, 934 (1957).
(93) S. V. Bagawde, V. V. Ramakrishna, and S. K. Patil, *J. Inorg. Nucl. Chem.*, **38**, 1339 (1976).
(94) R. G. Denotkina and V. B. Shevchenko, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), **12**, 42 (1967).
(95) R. G. Denotkina and V. B. Shevchenko, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), **12**, 1237 (1967).
(96) R. G. Denotkina, A. I. Moskvin, and V. B. Shevchenko, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), **5**, 731 (1960).
(97) R. G. Denotkina, A. I. Moskvin, and V. B. Shevchenko, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), **5**, 387 (1960).
(98) M. S. Bousov, A. A. Elesin, I. A. Lebedev, V. T. Filimonov, and G. N. Yakovlev, *Sov. Radiochem.* (*Engl. Transl.*), **8**, 40 (1966).
(99) A. I. Moskvin, *Sov. Radiochem.* (*Engl. Transl.*), **13**, 688 (1971).
(100) J. W. Cobble, *J. Chem. Phys.*, **21**, 1443 (1953).
(101) H. C. Helgeson, *Am. J. Sci.*, **267**, 729 (1969).
(102) J. W. Cobble and R. C. Murray, Jr., *Faraday Discuss. Chem. Soc.*, **64**, 144 (1978).
(103) I. L. Khodakovsky, B. N. Ryzhenko, and G. B. Naumov, *Geokhimiya*, 1486 (1988).
(104) P. R. Tremaine and S. Goldman, *J. Phys. Chem.*, **62**, 2317 (1978).
(105) H. C. Helgeson and D. H. Kirkham, *Am. J. Sci.*, **276**, 97 (1976).
(106) B. N. Figgis, "Introduction to Ligand Fields", Interscience, New York, 1966.
(107) R. J. Hinchey and J. W. Cobble, *Inorg. Chem.*, **9**, 922 (1970).
(108) S. P. McGlynn and J. K. Smith, *J. Mol. Spectrosc.*, **6**, 188 (1961).
(109) D. D. Macdonald and P. Butler, *Corros. Sci.*, **13**, 259 (1973).
(110) D. D. Macdonald, *Mod. Aspects Electrochem.*, **11**, 141 (1975).
(111) R. J. Biernat and R. G. Robins, *Electrochim. Acta*, **17**, 1261 (1972).
(112) K. H. Gayer and H. Leider, *Can. J. Chem.*, **35**, 5 (1957).
(113) L. R. Morss and M. C. McCue, *J. Chem. Eng. Data*, **21**, 337 (1976).

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