TECHNICAL REPORT

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Plutonium solubilities

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PLUTONIUM SOLUBILITIES

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ABSTRACT

Thermochemical data has been selected for plutonium oxide, hydroxide, carbonate and phosphate equilibria. Equilibrium constants have been evaluated in the temperature range 0 to 300°C at a pressure of 1 bar for $T \leq 100°C$ and at the steam saturated pressure at higher temperatures.

Measured solubilities of plutonium that are reported in the literature for laboratory experiments have been collected. Solubility data on oxides, hydroxides, carbonates and phosphates have been selected. No solubility data were found at temperatures higher than 60°C.

The literature solubility data have been compared with plutonium solubilities calculated with the EQ3/6 geochemical modelling programs, using the selected thermodynamic data for plutonium.

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1 INTRODUCTION

This document reports a comparison between experimental plutonium solubilities found in the literature, and the results of calculations obtained with a combination of a geochemical computer program (EQ3/6) and the thermodynamic data base given in the Appendices.

The calculation of equilibrium radionuclide solubilities is of importance for nuclear waste disposal programs (see for example section 6 in Hodgkinson, 1987, and Puigdomenech and Bruno, 1988). Particularly, to define the source term in the near-field as a function of the different physicochemical conditions (T, P, pH, Eh, etc).

Agreement between model solubilities and experimental results is necessary in order to have any confidence in the long time predictions of the chemical behaviour of radionuclides in geological environments. Therefore some comparison between model calculations and laboratory data have already been reported (e.g., Schweingruber, 1983; Pryke and Rees, 1986). The development of workable thermodynamic data bases for safety assessment within the Swedish nuclear waste management program has created a need for similar validation exercises, and the work reported here is a continuation of the uranium data base verification-validation (Puigdomenech and Bruno, 1988).

The solubilities of plutonium presented in this report are useful for the evaluation of radiological consequences from nuclear waste disposal. The potential health hazard of a natural water containing plutonium will depend on the isotope composition, as indicated in Table 1 for some plutonium nuclides.

Table 1. Emission and dosimetric data for some Pu-radionuclides.

	Pu-238	Pu-239	Pu-241
Half life /y	87.74	24065.	14.4
Bq/mol	$1.5 \cdot 10^{14}$	$5.5 \cdot 10^{11}$	$9.2 \cdot 10^{14}$
Average Energy per transformation MeV/Bq (ICRP, 1983)	5.59	5.23	0.0054
Dose Eqv. µSv/Bq Adults (ICRP, 1989)	0.88	0.97	0.019

Thus, ingestion by an adult individual of 1 litre of a well groundwater containing 10^{-8} mol-Pu/l (2.4 ppb) will cause a 70-year dose commitment of 1320, 5.3 or 175 mSv, if the plutonium in the water is Pu-238, Pu-239 or Pu-241 respectively. This can be compared with the recommended maximum life-long dose rate of 1 mSv/y for members of the public (ICRP, 1977), and gives some perspective to the solubility levels discussed later in this report.

2 METHODS OF CALCULATION

The EQ3/6 code package (versions: EQ3NR: 3245R110, EQ6: 3245R100) has been used to calculate plutonium solubilities in aqueous solutions. The MCRT program (our PC-version of 3245R111) has been used to calculate the equilibrium constants (given in Appendix B) from the thermodynamic data for plutonium (given in Appendix A). The EQ3/6 code package is described in: Wolery (1979 and 1983), Wolery et al. (1984 and 1990), Delany and Wolery (1984), Bourcier (1985), Delany et al. (1986), Jackson (1988), Jackson et al. (1988) and Wolery et al. (1990).

For the calculation of chemical equilibrium in aqueous systems, the EQ3NR code is based both on the charge balance equation, and on the mass balance equations for all elements except hydrogen and oxygen, while the EQ6 code is based on mass balance equations for all elements (including oxygen and hydrogen). For the specific case of solubility calculations with the EQ3NR program, the alternative constraint of phase equilibrium with a mineral substitutes the mass balance equation for plutonium. For calculations with a fixed partial pressure of $CO_2(g)$, this constrain will substitute the mass balance equation for inorganic carbon in the EQ3NR calculations. The redox constraint used was either a given redox potential, or oxygen or hydrogen fixed gas fugacity.

For EQ3/6, the principal unit of concentration on which thermodynamic activities, mass balances, equilibrium constants and activity coefficients are based, is molality (mols/1000 g H_2O).

Single ion activity coefficients (y_i, based on the molality scale) are normally expressed in the EQ3/6 package as a function of the ionic strength, I. The default function is the $B^{\bullet}$ equation (Helgeson, 1969, Eqn. 43),

$$\log y_i = \frac{-A\, z_i^2\, I^{\frac{1}{2}}}{1 + å_i\, B\, I^{\frac{1}{2}}} + B^{\bullet}\, I \qquad (2.1)$$

where A and B are Debye-Hückel parameters (which at 25°C are equal to 0.5092 and 0.3283), $å_i$ and z_i are the "distance of closest approach" (in Å) and the electrical charge respectively, and $B^{\bullet}$ is a temperature dependent constant (equal to 0.041 at 25°C). Among other alternatives, the Davies equation may be selected by the EQ3/6 user,

$$\log y_i = -A\, z_i^2 \left(\frac{I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} - 0.2\, I \right) \qquad (2.2)$$

In order to follow the NBS pH-standard, the single ion activity coefficients are, by default, scaled in the EQ3/6 package to set the following activity coefficient for the chloride ion

$$\log \gamma_{Cl^-} = \frac{-A I^{1/2}}{1 + 1.5 I^{1/2}}$$

In this work, the $B^{\bullet}$ equation has been used for all EQ3/6 runs, except those to calculate Pu-solubilities in aqueous solutions containing phosphate, for which the Davies equation was used. In many calculations, the ionic strength exceeded the range of applicability for both the $B^{\bullet}$ and Davies equations. For ionic strengths above 0.5 m, substantial errors in the calculated solubilities should be expected if any of these two equations are used.

All EQ3NR and EQ6 calculations were performed for aqueous solutions electrically neutral, achieved by adjusting the concentration of either Na^+ or Cl^- in the modelled solutions. This is needed to make realistic calculations of the activity coefficients for the aqueous species. In the case of solubility calculations in aqueous solutions containing a supporting electrolyte, the individual concentrations of the ions in the ionic media were not adjusted, and therefore, in these cases the electrical charge balance sometimes was in error by a few percent, although this does not have much influence on the value of the calculated activity coefficients in such concentrated solutions.

Calculated solubilities (in mols per 1000 g H_2O) as a function of pH (= $-\log a_{H+}$, activity in molal scale) have been compared in this work with experimental values, which are not always given as molalities. The densities required for the EQ3/6 calculations were estimated from linear interpolations among the values tabulated in the Landolt-Börnstein compilation (D'Ans et al., 1977).

The difference between molar (M = mols/l) and molal (m = mols/1000 g H_2O) concentration units, is not important for dilute solutions at 25°C, where plutonium solubilities are low and pH is within the range 2-12. For example,

- the solubility of $Pu(OH)_4(am)$ in I=1 mol/l of Lierse (1985) can be converted from molar to molal scale using the following densities,

  1.075 g/cm^3 for 1 M $NaClO_4$
  1.051 g/cm^3 for 1 M $NaHCO_3$
  1.033 g/cm^3 for 0.333 M Na_2CO_3

  (in the EQ3NR calculations, a linear dependence between density and concentrations was assumed for mixtures of these salts). In Figure 5.8, the experimental Pu-solubilities of Lierse (1985) could be corrected to molal units, for 1 M $NaClO_4$:

  $$[Pu]_{tot}/m = 1000*([Pu]_{tot}/M) \div (1075 - 122.44)$$
  $$= 1.05*([Pu]_{tot}/M)$$

  on a logarithmic scale, this correction would be negligible

In all instances, the conversion factor is well within the expected uncertainty (due both to experimental errors, and activity coefficient corrections in the ionic media involved) and to apply a correction to the solubilities for the mismatch concentration units is unnecessary. Nevertheless, in Figure 4.9 (solubility of $PuO_2(CO_3)(s)$ in 3 M $NaClO_4$) the Pu-solubilities calculated with EQ3NR were converted from molal to molar units.

Equilibrium diagrams in section 3 have been drawn with a modified version (Puigdomenech, 1983) of the SOLGASWATER program (Eriksson, 1979), using the equilibrium constants for 25°C listed in Appendix B, and Davies equation for the calculation of single-ion activity coefficients.

3 THE THERMODYNAMIC DATA BASE

The final goal of the Swedish program for disposal of spent nuclear fuel is to adopt the recommendations arisen from the NEA-TDB data selection groups (Wanner, 1988). In the meantime, there is a need for workable databases, hence, a selection of a thermodynamic data base has to be made for the chemical elements of radiological interest in the Swedish nuclear waste program.

Among existing data bases, the EQ3/6 data base has been selected and has been updated for uranium (Puigdomenech and Bruno, 1988). The data base consists of two files: one with thermodynamic quantities (MDAS-file, with standard Gibbs free energies of formation, standard enthalpies of formation, standard entropies, heat capacities, etc), and another file (DATA0-file) with equilibrium constants as a function of temperature (log $K_{eq}(T)$ for T=0 to 300°C, and p=1 bar (≅1 atm) up to 100°C and steam/$H_2O(l)$ equilibrium pressure at T>100°C). The structure of the files that make up the data base includes the possibility to contain literature references, comments, quality description, etc.

The EQ3/6 package also contains the computer program MCRT (Jackson et al., 1988) to calculate equilibrium constants of reaction as a function of temperature using thermodynamic quantities. This program uses as input a direct access copy, MDAR, of the MDAS-file. The MDAR-file is created and updated with the help of another computer program: MDAP. The MCRT program, and its companion MDAP, have been adapted within this work to run on personal computers using the DOS operative system, and may be requested from the authors of this report.

Note however, that at the Earth Sciences Department in Livermore (where the EQ3/6 package has been developed), the MCRT program is no longer used, and codes accessing a relational data base are used instead (DB Management System INGRES Vers. 5.0).

3.1 DATA BASE DESCRIPTION

The plutonium thermodynamic data base consists of:

1 - the complete plutonium set included in the original EQ3/6 thermodynamic data base (with species not listed in the appendices, such as: Cl^-, F^- & NO_3^- complexes, etc), where: a) the entropy of Pu element is set to 56.15 J/(mol K) (Lemire and Garisto, 1989), b) the species $Pu(OH)_5^-$ has been withdrawn, c) for duplicated mineral data blocks ($Pu(OH)_3$, PuO_3, $Pu(OH)_4$ and $PuO_2(OH)_2$), only one of the blocks has been left in the DATA0 file, and d) some of the species have been renamed ($PuHPO_4^{2+}$ to $Pu(HPO_4)^{2+}$, etc, see Appendix A).

2 - the data listed in the Appendices. These data were replaced or added to the MDAS and DATA0 files of the EQ3/6 package

The plutonium data base, which is validated in this report and listed in the Appendices, is essentially that of Lemire and Tremaine (1980), with the changes introduced by Lemire and Garisto (1989) and the modifications listed below. Table 2 summarises the differences between the data base used here, the original EQ3/6 DATA0 (version 3235r54) and the data base used by Lemire and Garisto (1989). The following changes and additions have been included to the data base used by Lemire and Garisto (1989):

- $PuCO_3^+$: in analogy with the americium complex (Kerrisk and Silva, 1986) the formation of this complex is estimated as

  $$Pu^{3+} + CO_3^{2-} = PuCO_3^+ \qquad \log K = 9 \pm 1$$

  and the entropy change for this reaction is estimated

Table 2. Summary of differences between the data base used here and both the original EQ3/6 DATA0 (version 3235r54) and the data base used by Lemire and Garisto (1989, Table B-4).

Species	Not present in[a] A	B	Comments[a,b]
Pu(III):			
$PuCO_3{}^+$	x	x	Estimated.
$Pu(OH)CO_3(s)$	x	x	Estimated.
Pu(IV):			
Pu^{4+}			Data in **A** originates from Rai (1984).
$Pu(OH)_5{}^-$			Present in **A**. Not included in this work.
$PuCO_3{}^{2+}$	x		S° taken from **B**, new β selected (similar to β in **A**).
$Pu(CO_3)_5{}^{6-}$	x		Estimated data from **B**.
Pu(V):			
$PuO_2CO_3{}^-$	x		S° taken from **B**, new β selected.
$PuO_2(CO_3)_2{}^{3-}$	x		Estimated data from **B**.
Pu(VI):			
$PuO_2(OH)_2{}^\circ$	x	x	Selected β and S° estimated.
$PuO_2(OH)_3{}^-$	x	x	Selected β and S° estimated.
$PuO_2CO_3{}^\circ$	x	x	Selected β and S° estimated.
$PuO_2(CO_3)_2{}^{2-}$			New selected data.
$PuO_2(CO_3)_3{}^{4-}$	x	x	New selected data.
$PuO_2(OH)_2HCO_3{}^-$		x	New selected data.
$PuO_2(OH)_2(cr)$			New selected β.
$PuO_2CO_3(s)$	x	x	Selected β, estimated S° and C°_p.

a: **A** refers to the original EQ3/6 data base DATA0.3235r54. **B** stands for the data base listed in Lemire and Garisto (1989).

b: β is used here to represent the equilibrium constant of formation at infinite dilution

to be equal to 147±40 J/(mol K) from:

- a comparison of reaction entropies between several ligands and both Ca^{2+} and trivalent metal ions
- the entropy change for the Ca^{2+}-$CO_3{}^{2-}$ reaction (106±18 J/(mol K), calculated from equilibrium constants reported by Plummer and Busenberg, 1982)

- $PuCO_3^{2+}$: the maximum value for the equilibrium constant of formation of this complex, as given by Silva and Nitsche (1985) is adopted here.
- $PuO_2CO_3^-$: the equilibrium constant reported by Bennett et al. (1990) is adopted here.
- $PuO_2(OH)_x^{(2-x)}$: For $PuO_2(OH)^+$, the data is taken from Lemire and Garisto (1989), i.e., log K_{eq} is that of Baes and Mesmer (1976, Table 9.9), and S° is calculated from the entropy of reaction for the uranyl complex. For $PuO_2(OH)_2(aq)$ and $PuO_2(OH)_3^-$: the equilibrium constants selected are an average of literature ß values extrapolated to I=0 with the Specific Interaction equations (Grenthe and Wanner, 1989; and estimated interaction coefficients: $\epsilon(PuO_2(OH)_2,NaClO_4)=0.05$, $\epsilon(PuO_2(OH)_3^-,Na^+)=-0.05$). The following literature reports have been considered: Kraus and Dam (1949), Musante and Porthault (1973), Schedin (1975) and Kim et al. (1984). The data of Kraus and Dam (1949) has been re-evaluated by Schedin (1975), but the change in log K_{eq} for $PuO_2(OH)_2(aq)$ is negligible. An inspection of the results of Ahrland and Kullberg (1971) for the UO_2^{2+}/F^- system suggest the following relationship: $\Delta S_{n+1} = \Delta S_n - 6$ cal/(mol K), for the reactions,
$$UO_2F_n^{(2-n)} + F^- = UO_2F_{(n+1)}^{(1-n)}$$
Here the following assumptions are made: 1) the same relationship is also valid for the uranyl hydroxide complexes, and 2) the reaction entropies for the formation of plutonyl and uranyl hydroxide complexes are the same. Therefore, for the $PuO_2(OH)^+$ reaction:
$$PuO_2^{2+} + OH^- = PuO_2(OH)^+ \qquad \Delta S_1=+30 \text{ cal/(mol K)}$$
(the uranyl value reported in Baes and Mesmer, 1976), which gives,
$$PuO_2^{2+} + 2OH^- = PuO_2(OH)_2(aq) \qquad \Delta S_2=+54 \text{ cal/(mol K)}$$
$$PuO_2^{2+} + 3OH^- = PuO_2(OH)_3^- \qquad \Delta S_3=+72 \text{ cal/(mol K)}$$
The ionic entropies for $PuO_2(OH)_2(aq)$ and $PuO_2(OH)_3^-$ are calculated from these estimated reaction entropies.

- $PuO_2CO_3(aq)$: the equilibrium constant of Robouch and Vitorge (1987) is used. The ΔS_r for
  $$PuO_2^{2+} + CO_3^{2-} = PuO_2CO_3(aq)$$
  is set equal to the value for the uranyl reaction (60 ± 5 cal/(mol K), Puigdomenech and Bruno, 1988).
- $PuO_2(CO_3)_2^{2-}$: the equilibrium constant of Robouch and Vitorge (1987) is used. The entropy is calculated from the ΔS_r reported by Sullivan et al. (1982).
- $PuO_2(CO_3)_3^{4-}$: the equilibrium constant of Robouch and Vitorge (1987) is used. The entropy is calculated from the ΔH_r reported by Ullman and Schreiner (1988).
- $PuO_2(OH)_2HCO_3^-$: the equilibrium constant of Sullivan et al. (1982) is used (see also p. 396 and Table 2 in Newton and Sullivan, 1985). The same authors give $\Delta S_r=-151\pm50$ J/(mol K) for
  $$PuO_2(CO_3)_2^{2-} + 2\ H_2O = PuO_2(OH)_2HCO_3^- + HCO_3^-$$
  which is combined with the entropy of $PuO_2(CO_3)_2^{2-}$ to get the entropy of the hydroxide-bicarbonate mixed complex.
- $PuO_2(OH)_2(c)$: the equilibrium constant for reaction
  $$PuO_2(OH)_2(c) = PuO_2^{2+} + 2\ OH^-$$
  of Kim et al. (1984) is extrapolated to zero ionic strength with the specific interaction equations of Grenthe and Wanner (1989), log $K^\circ_{sp}=-23.60$. The value used by Lemire and Tremaine (1980) originates from the data of Krevinskaya et al. (1959), recalculated by Gelman et al. (1962b, p.27), and reported by Cleveland (1979, p.312). The solubility product reported by Kim et al. (1984) is dependent on the aqueous model used in their calculation (hydrolysis species and their equilibrium constants), which does not coincide with the aqueous model used in this work. Nevertheless, their equilibrium constant is used here, because a) it will produce calculated solubilities which are higher than those obtained from the solubility product used by Lemire and Tremaine (1980), and b) the experimental data of Krevinskaya et al. (1959) seems less reliable.

- $Pu(OH)CO_3(s)$: in analogy with americium (Kerrisk and Silva, 1986) the equilibrium constant for
  $Pu^{3+} + CO_3^{2-} + OH^- = Pu(OH)CO_3(s)$
  is estimated to: log K = 22 ± 2. As the existence of this plutonium solid species has not been proved, entropy and heat capacity were not estimated.
- $PuO_2CO_3(s)$: the equilibrium constant of Robouch and Vitorge (1987) is used. The ΔS_r for
  $PuO_2^{2+} + CO_3^{2-} = PuO_2CO_3(s)$
  is set equal to the value for the uranyl reaction (83 cal/(mol K), Lemire, 1988). C_p° is estimated from Kopp's law (according to Sturtevant, 1959)

The source of thermochemical data for the other species is discussed in Lemire and Tremaine (1980) and Lemire and Garisto (1989), and may be summarised as follows.

The hydrolysis constants of Baes and Mesmer (1976) are the source for the standard Gibbs free energies of formation of aqueous hydrolysis species. The ionic entropies for these species are estimated (mainly from corresponding uranium reactions, c.f. Lemire and Tremaine, 1980).

Data for the carbonate complexes of PuO_2^+ are estimated from the Np(V) reactions (Lemire and Garisto, 1989).

Standard Gibbs free energies of formation for the phosphate species have their origin (Lemire and Tremaine, 1980) in corresponding equilibrium constants (Pu(III): Moskvin, 1971; Pu(IV): Denotkina et al., 1960a & 1960b; Pu(VI): Denotkina and Shevchenko, 1977b).

Standard entropies for the phosphate species where estimated (mainly from corresponding uranium reactions, c.f. Lemire and Tremaine, 1980).

Heat capacities for all solid species listed in Lemire and Tremaine (1980) were estimated, mainly with Kopp's law, as described by Sturtevant (1959), except for PuO_2(cr), for which there is experimental data in the literature.

For ionic species, the heat capacity has been estimated in the present work with the method of Criss and Cobble, which is programmed in the MCRT code (Jackson et al., 1988). For neutral aqueous species, the "DQUANT" equation (Eqn. 16 in Helgeson, 1969) has been used to estimate the temperature variation of the heat capacity.

3.2 AQUEOUS EQUILIBRIUM CHEMISTRY OF PLUTONIUM

The solution chemistry of plutonium differs from that of more stable actinides (i.e., thorium and uranium) in many aspects:

a) plutonium is stable in four oxidation states (III, IV, V and VI) in aqueous solutions, and all four of these can exist simultaneously in equilibrium (c.f. Figure 3.1)

b) under certain conditions, Pu(IV) hydrolysis proceeds rapidly and irreversibly to form large colloidal aggregates which are kinetically stable, and adsorb on glass, silica surfaces, etc.

c) due to radioactive decay of the dissolved plutonium, alpha radiolysis of water will generate H_2O_2, H·, HO_2· causing the reduction of Pu(VI) solutions to Pu(V), Pu(IV) and Pu(III) (Cleveland, 1979).

d) alpha-radiation damage of solid Pu(IV) oxide and hydroxide increase their solubility and induces the formation of micro-colloids (<10Å) (Rai and Ryan, 1982; Kim et al., 1985). As a consequence, measured solubilities in the literature are often upper limits, as colloidal Pu(IV) might have been included in the analysed total plutonium in solution, thus increasing the apparent solubility.

Plutonium(IV) is stable over a large range of acidity and redox potential. This is reflected in its very low thermodynamic solubility (Figure 3.2). $PuO_2(s)$ solubility might be a limiting factor for the dissolution and release of plutonium from the near field of a nuclear waste repository. However, a more probable scenario description is the congruent release of plutonium as the UO_2-matrix dissolves, and a later precipitation along the groundwater flow path as $Pu(OH)_4(am)$, which is then slowly aged into $PuO_2(c)$.

Amorphous Pu(IV) hydroxide will be the limiting constrain for precipitation of oversaturated plutonium solutions in

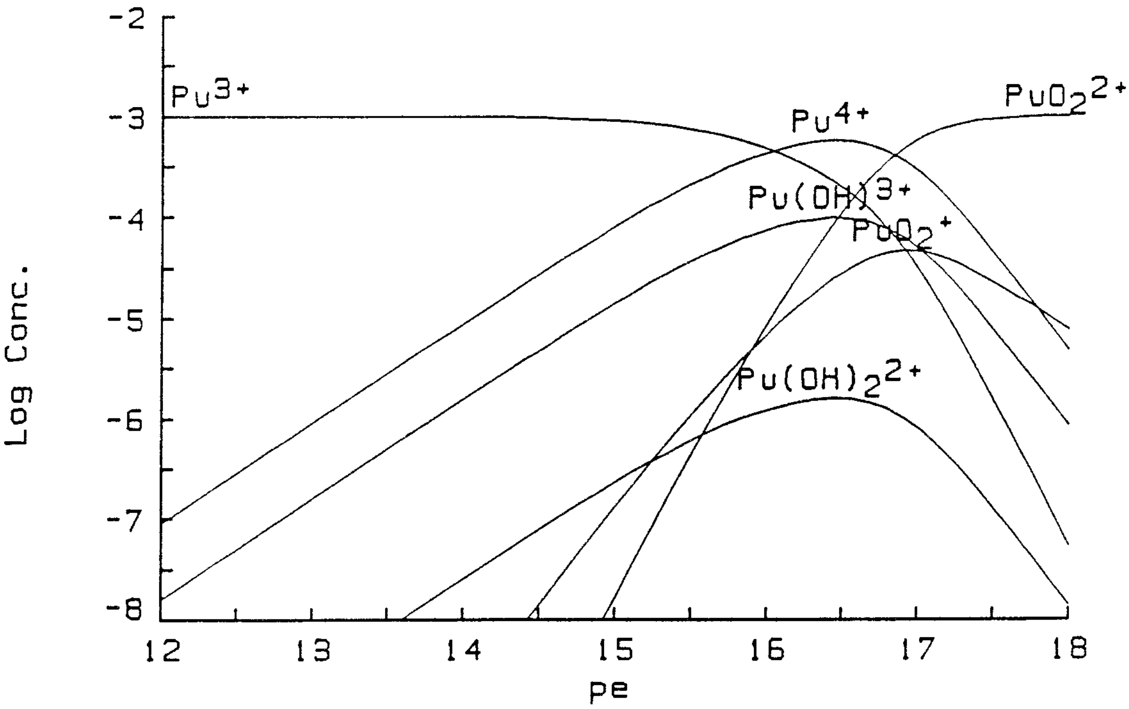

Figure 3.1 Calculated Pu(III), Pu(IV), Pu(V) and Pu(VI) concentrations as a function of pe (=Eh·F/RTln(10)) at pH=0.7, $[Pu]_{Tot}$=1mM, I=0.5 mol/l, and 25°C.

the geosphere and biosphere. The solubility of $Pu(OH)_4$(am) is higher than that of PuO_2(s) (compare Figure 3.3 with 3.2). The solubility of PuO_2(cr) increases as a function of time due to the loss of crystallinity accomplished by alpha radiation. On the other hand, the solubility of $Pu(OH)_4$(am) decreases with time due to increase in crystallinity and dehydration. Because of this phenomena, the steady state solubilities

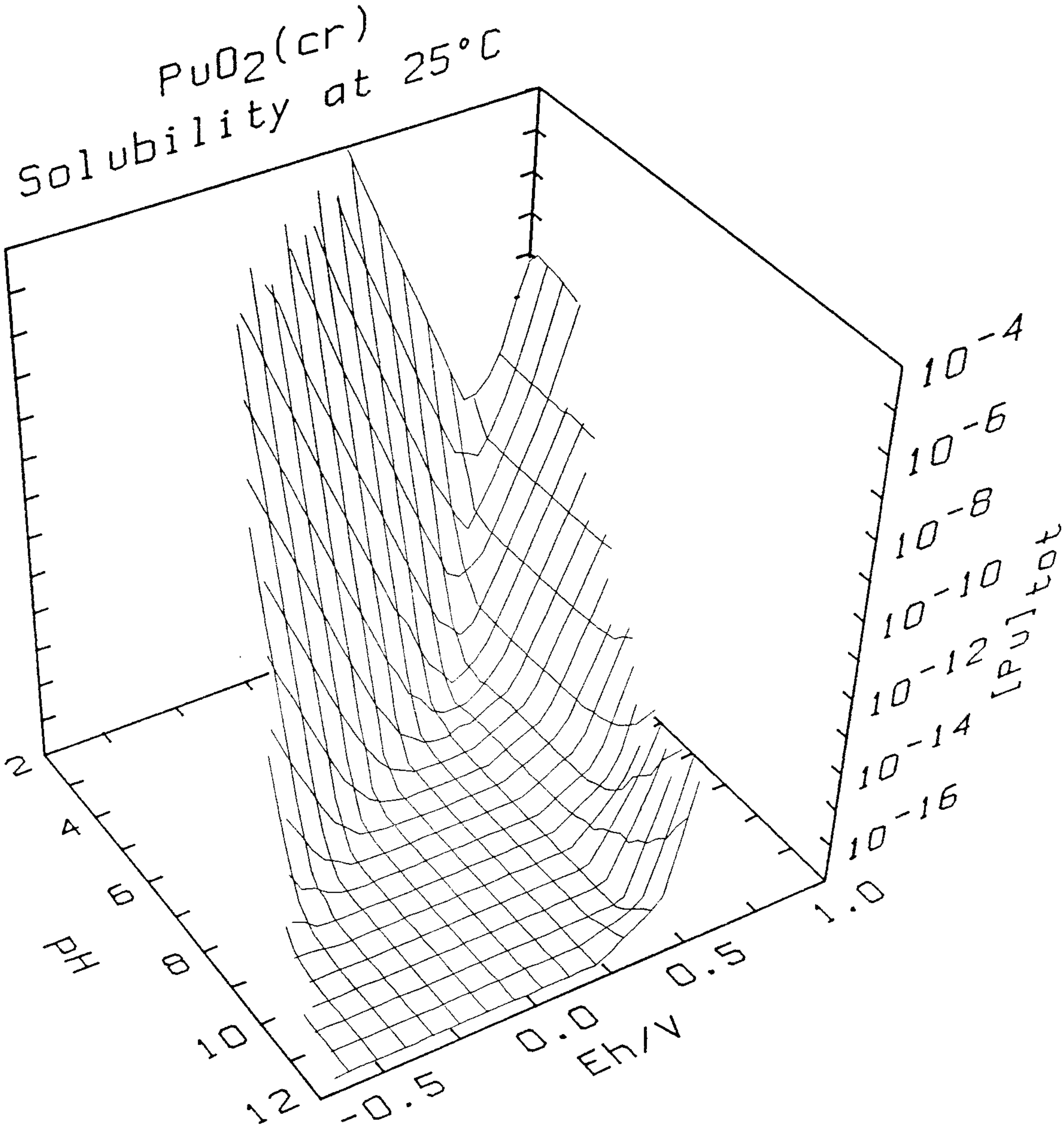

Figure 3.2 The solubility of PuO_2(s) calculated with EQ3NR as a function of pH and pe at 25°C.

of PuO_2(cr), $Pu(OH)_4$(am) and Pu(IV) polymer are similar (Rai and Ryan, 1982; Rai and Swanson, 1981).

The range of stability for $Pu(OH)_4$(am) is given in Figure 3.4. Figure 3.3 also shows which aqueous species are responsible for the calculated solubility, and a comparison between Figures 3.3 and 3.4 shows that the range of predominance of $Pu(OH)_4$(am) spans over Pu(III), Pu(IV) and Pu(V) solutions.

Figure 3.5 shows the relative importance of phosphate complex formation in the data base used in this work. The concentration of carbonate (2 mM) and phosphate (0.01 mM) in Figure 3.5 correspond to probable concentrations

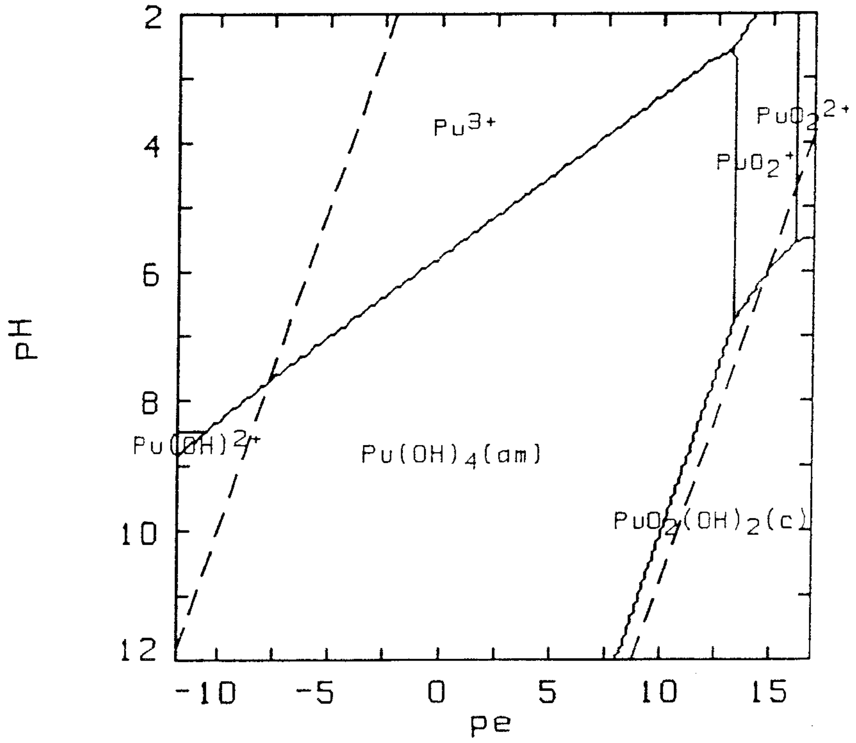

Figure 3.3 Predominance area (pH/pe) diagram for 0.1 M NaCl calculated for 10^{-6} M total plutonium, and 25°C. PuO_2(s) has been excluded from the diagram to show the predominance of $Pu(OH)_4$(am). The limits of stability for water are indicated (partial pressure of oxygen and hydrogen >1 atm to the right and left respectively, of the dashed lines).

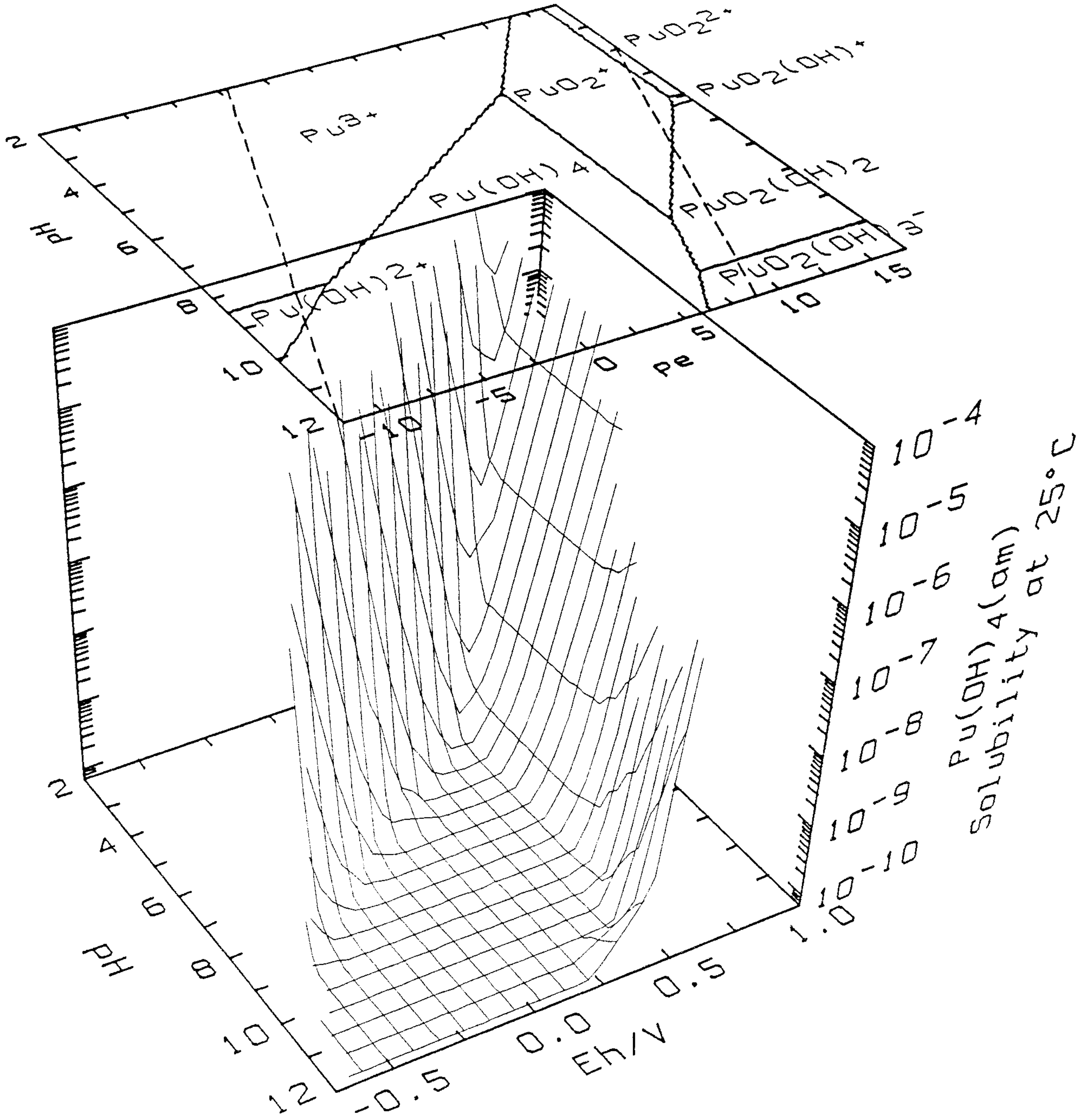

Figure 3.4 The solubility of $Pu(OH)_4$(am) calculated with EQ3NR as a function of pH and pe at 25°C. The predominating aqueous species are shown in the upper diagram, where the limits of stability for water are indicated (partial pressure of oxygen and hydrogen >1 atm to the right and left respectively, of the dashed lines).

in granitic groundwaters (Allard et al., 1981; Wikberg, 1988).

Figures 3.6 and 3.7 show "cross-sections" of Figure 3.5 at pH=7 and pe=5. No carbonate complexes of Pu(IV) appear in the calculations, due to the predominance of $Pu(HPO_4)_4^{4-}$. The equilibrium constants of formation of Pu(IV) carbonate complexes are not well established. The formation of $Pu(CO_3)_5^{6-}$ is given in the data base by analogy with the uranium(IV) complex, and it might be formed in alkaline carbonate solutions, as shown in Figure 3.8.

Other plutonium solid phases that might precipitate in granitic groundwaters are shown in Figure 3.5.

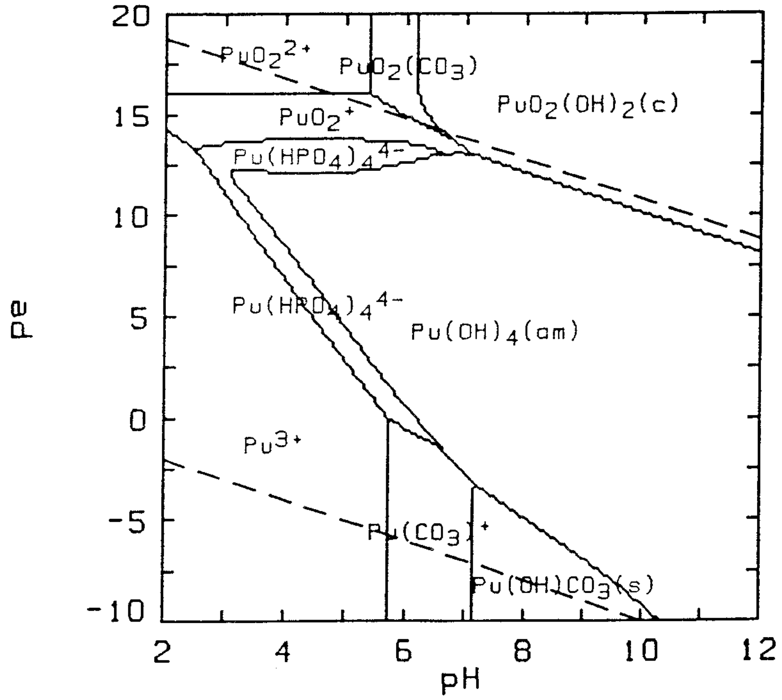

Figure 3.5 Predominance area diagram for 0.1 M NaCl containing 2 mM $[CO_3^{2-}]_{tot}$ and 0.01 mM $[PO_4^{3-}]_{tot}$, calculated for 10^{-6} M total plutonium, and 25°C. $PuO_2(s)$ has been excluded from the diagram to show the predominance of $Pu(OH)_4(am)$. Partial pressures are >1 atm above ($O_2(g)$) and below ($H_2(g)$) the dashed lines.

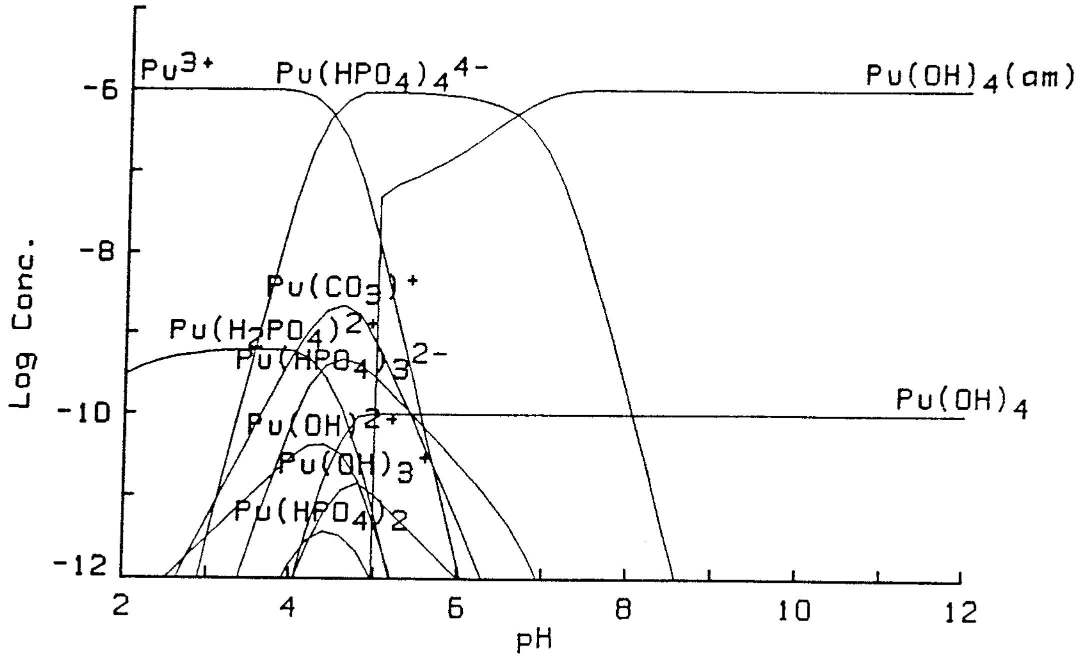

Figure 3.6 Concentrations of Pu-species as a function of pH in 0.1 M NaCl solutions containing 2 mM $[CO_3^{2-}]_{tot}$ and 0.01 mM $[PO_4^{3-}]_{tot}$, calculated for 10^{-6} M total plutonium, pe=5 (Eh = +0.296 V), and 25°C.

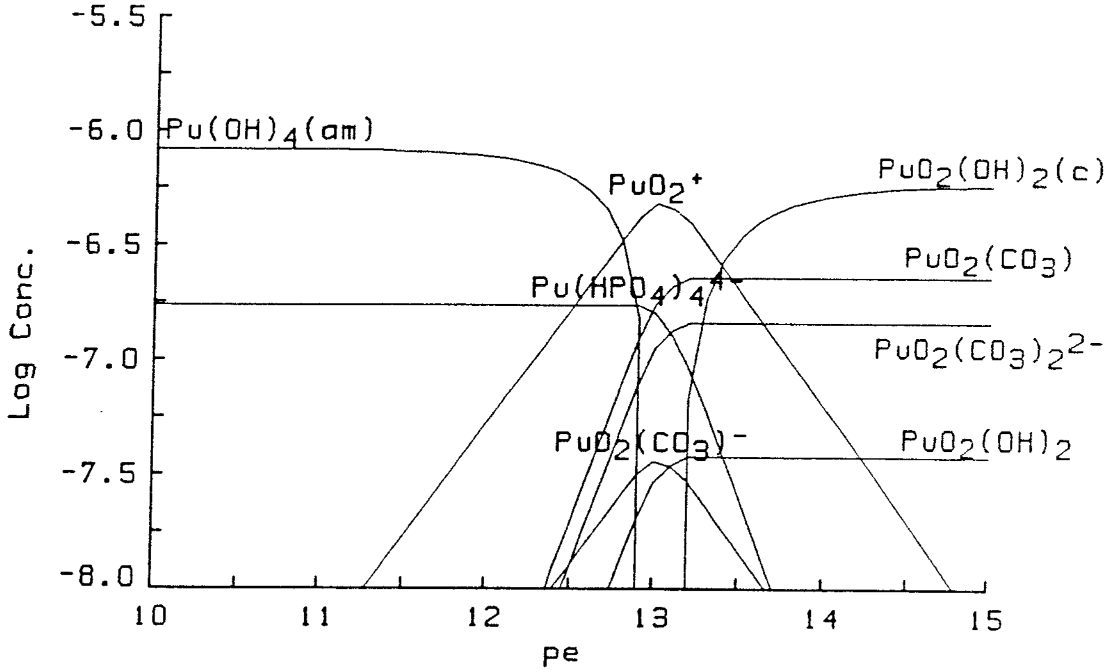

Figure 3.7 Concentrations of Pu-species as a function of redox potential in 0.1 M NaCl solutions containing 2 mM $[CO_3^{2-}]_{tot}$ and 0.01 mM $[PO_4^{3-}]_{tot}$, calculated for 10^{-6} M total plutonium, pH=7, and 25°C.

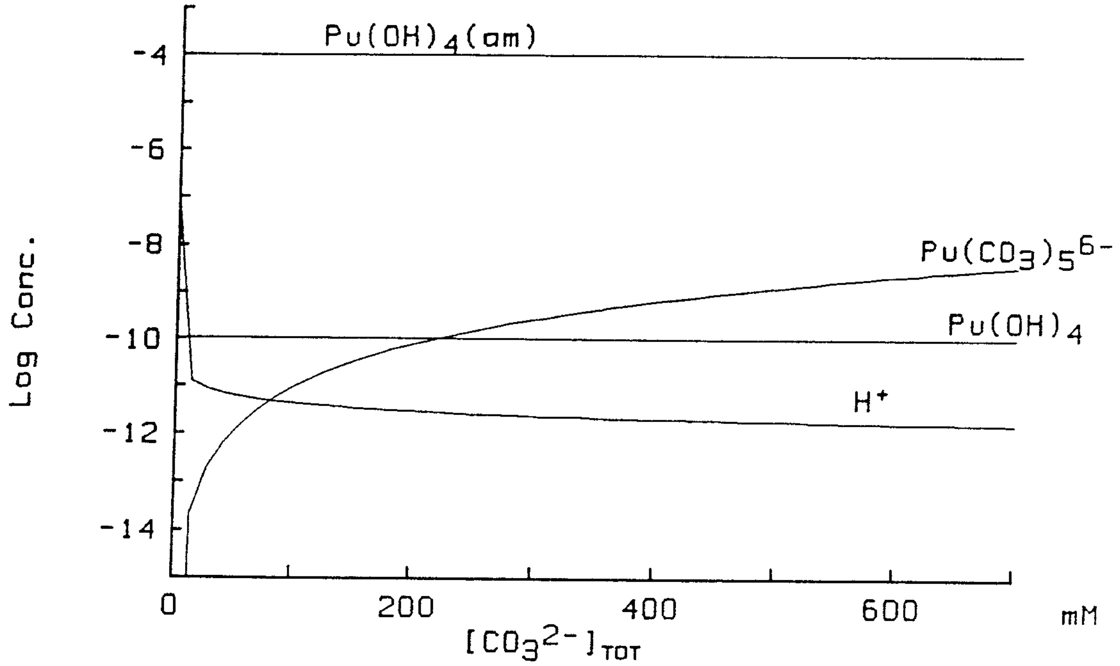

Figure 3.8 Calculated pH and concentrations of Pu-species as a function of total carbonate concentration at pe=-3 (Eh=-0.177 V), I=1 mol/l, $[Pu]_{tot}$ = 0.0001 mol/l and 25°C.

$PuO_2(OH)_2(c)$ appears in granitic groundwaters at pH$\geq$6 and saturated with oxygen. The existence of $Pu(OH)CO_3(s)$ is estimated in analogy with the americium solid, although the existence of this solid phase has not been proved. Figure 3.5 shows that according to the data base selected for this work, it precipitates in reducing granitic groundwaters (Eh$\leq$-0.15 V) of pH$\geq$7.

4 COMPARISON BETWEEN LITERATURE AND CALCULATED SOLUBILITIES

The results presented in this section include calculated plutonium solubilities for many aqueous solutions in equilibrium with several plutonium solid phases. Agreement between the results of the calculations and experimental solubilities might be taken as a validation of the data base-EQ3/6 combination.

However, a distinction must be made between validation and verification calculations. A validation of a model is only possible when the experimental data used for the validation is not related to the model, i.e., when the model has been obtained independently of the experimental values used in the validation.

We know however, that some of the experimental data used in this work have been used to develop the data base. For example, the standard free energies of formation for $Pu(OH)_4(am)$ and $Pu(OH)_4(aq)$ have been derived by Lemire and Garisto (1989) from the solubility data of Rai (1984). Therefore, agreement between EQ3/6-calculated results and the experimental data of Rai (1984) in Figure 4.4 will only give a proof of self consistency and show that no serious errors have been introduced in the procedure of developing the data base. Note, however, that in Figure 4.2, other solubility data is shown that may be used as a validation.

The solubility data that is found in the literature for the system PuO_2-H_2O-$H_2(g)$-$CO_2(g)$-H_3PO_4 will be classified into the following main groups:

- solutions free of phosphates and carbonates
- solutions containing inorganic carbon
- solutions containing inorganic phosphorus

4.1 HYDROLYSIS OF PLUTONIUM

4.1.1 Solubility of Pu(III) hydroxide

The solubility of $^{239}Pu(OH)_3(s)$ is reported by Rai et al. (1987). The same data is also given in Felmy et al. (1989). The experiments were performed in presence of Fe(s) powder, at 23±2°C. For the solubilities reached from undersaturated solutions, Pu(III) hydroxide was prepared by adjusting the pH of a Pu(III) solution to pH=12. In this report, the data for "deionized water" is used.

According to the chemical model used in this study, the stable phase in most of the solutions studied by Felmy et al. (1989) is $Pu(OH)_4(am)$ (c.f. Figure 3.3), according to

$$Pu(OH)_3(s) + H_2O = Pu(OH)_4(am) + \tfrac{1}{2} H_2(g) \qquad \log K=13.61$$

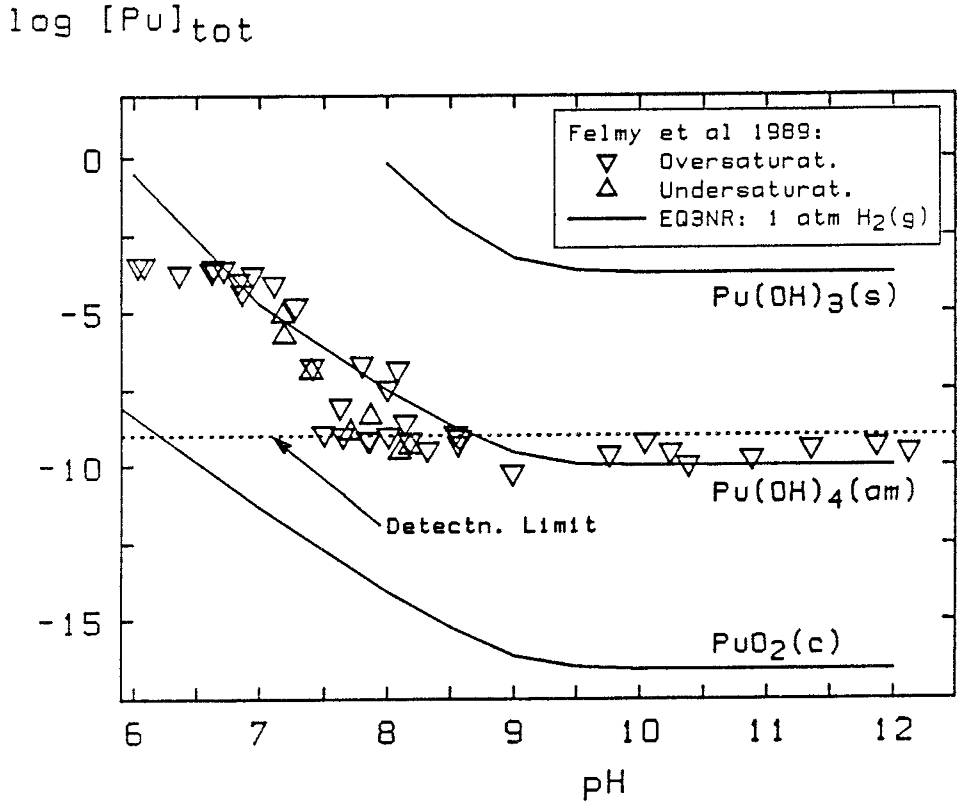

Figure 4.1 EQ3NR-calculated solubilities compared with the experimental values of Felmy et al. (1989).

Therefore, Pu(III) hydroxide is more soluble than Pu(IV) hydroxide, as shown in Figure 4.1. Because the only aqueous Pu(III) hydrolysis species in our data base is $Pu(OH)^{2+}$, $Pu(OH)_4(aq)$ is the dominating species in some of the calculated $Pu(OH)_3(s)$ solubilities, see also Figures 3.3 and 3.4.

4.1.2 Pu(IV) oxide/hydroxide

The solubility of plutonium(IV) oxide and hydroxide in water depends on the crystallinity of the solid and on the age of the chemical system. The experimental solubility of $PuO_2(c)$ and $Pu(OH)_4(am)$ reaches a steady state and becomes similar for both solids (Rai and Ryan, 1982). Nevertheless, a distinction is made here between crystalline oxide and amorphous hydroxide.

The following $Pu(OH)_4(am)$ solubility data has been used in this report

- Kraus (1944). Pu(IV) "hydroxide" in 1M Na_2SO_4
- Perez-Bustamante (1965). Dilute solutions of variable ionic strength at 24±2°C
- Rai et al. (1980a, 1980b). Data in 0.0015 M $CaCl_2$, air equilibrated. This data is also reported in Rai et al. (1977)
- Rai (1984). Data for $PuO_2{\cdot}xH_2O(am)$ in dilute HNO_3 solutions at 22±2°C. The measured redox potential varies from pe ≅ 17 to 8
- Nitsche and Edelstein (1985). Data in 0.1 M $NaClO_4$, pH=7.0±0.1, 25±1°C, inert atmosphere, the solid phase could not be identified
- Lierse (1985). Experiments in 1 M $NaClO_4$ at 25°C, inert atmosphere. The same data is given in Kim et al. (1988)
- Kim and Kanellakopulos (1989). At pH=1.09 and 1 M $HClO_4$ solutions, 20±1°C, Ar-atmosphere

The following PuO_2(c) solubility data has been used in this report

- Rai et al. (1980a, 1980b). Data in 0.0015 M $CaCl_2$, air equilibrated. This data is also reported in Rai et al. (1977)
- Kim and Kanellakopulos (1989). At 1 M $HClO_4$ solutions, 20±1°C

The following literature data has not been used in this work. Strickert and Rai (1982) Pu-solubilities in

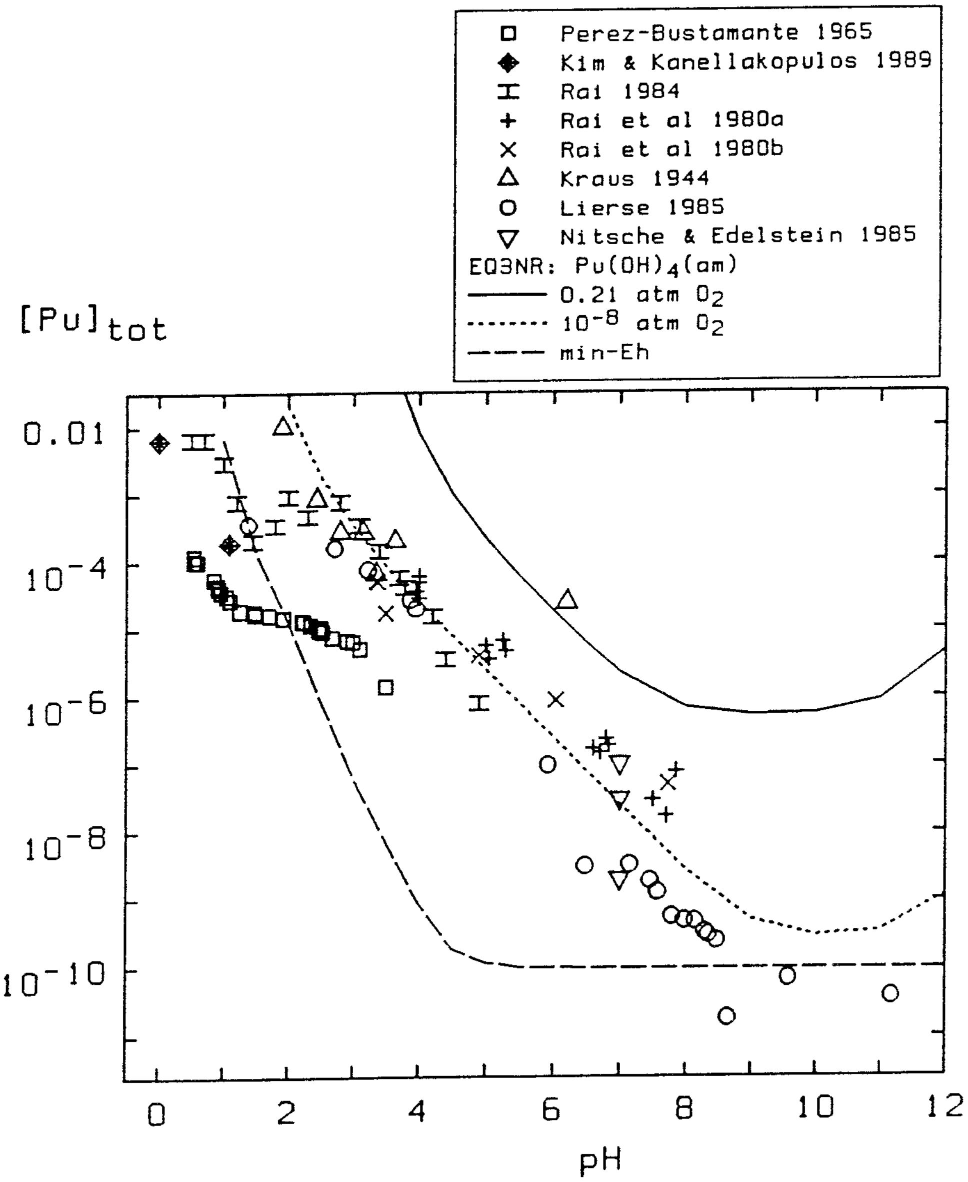

Figure 4.2 Comparison between EQ3NR-calculated solubilities and experimental literature values for $Pu(OH)_4$(am).

sediments (which show values in general lower than the PuO_2(c) solubilities of Rai et al. (1980a)). Rai and Ryan (1982) effects of ageing and crystallinity in the solubilities of PuO_2(c) and $Pu(OH)_4$(am). Rai and Swanson (1981) solubility of Pu(IV) polymer (which is between that of PuO_2(c) and $Pu(OH)_4$(am)). Delegard (1987) solubility of $Pu(OH)_4$(am) in alkaline solutions ([NaOH] $\geq$ 1 M). Kim et al. (1985) data in 0.1-5 M NaCl.

Comparisons between calculated and literature solubilities as a function of pH are given in Figure 4.2 for $Pu(OH)_4$(am), in Figure 4.3 for $Pu(OH)_4$(am) at 1 M $NaClO_4$ (data of Lierse, 1985), and in Figure 4.4 for PuO_2(c).

In Section 3.2 it was already pointed out that the solubility of Pu(IV) is dependent not only on pH but also on the redox potential (c.f. Figures 3.2 and 3.4).

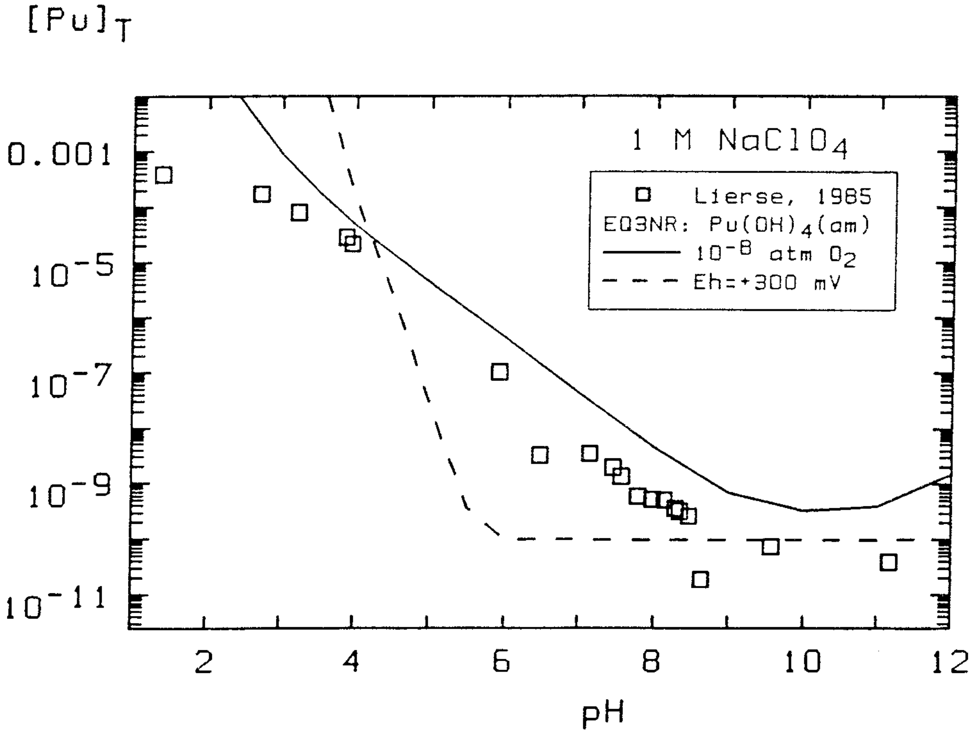

Figure 4.3 Comparison between EQ3NR-calculated solubilities and the experimental values of Lierse (1985) for $Pu(OH)_4$(am) in 1 M $NaClO_4$ and 25°C.

As most experimental work has been done under "oxygen free" atmosphere, Figure 4.2 shows the calculated solubility of $Pu(OH)_4(am)$ for solutions with an equilibrium partial pressure for $O_2(g)$ of 10^{-8} atm, as well as for air saturated solutions. Figure 4.2 also shows the minimum $Pu(OH)_4(am)$ solubility at every pH-value (obtained by varying the Eh, at a given pH, to find the minimum solubility, curve labelled "min-Eh" in Figure 4.2).

Similarly, Figure 4.4 shows the calculated solubilities of $PuO_2(c)$ both in 10^{-8} atm-$O_2(g)$, and in air and hydrogen saturated solutions.

The agreement between calculated and experimental values is good taking into consideration the uncertainties in the redox potential, the possibility of colloid formation, uncertain crystallinity, ageing effects due to alpha-radiation, etc. As Figure 4.2 shows, the calculated

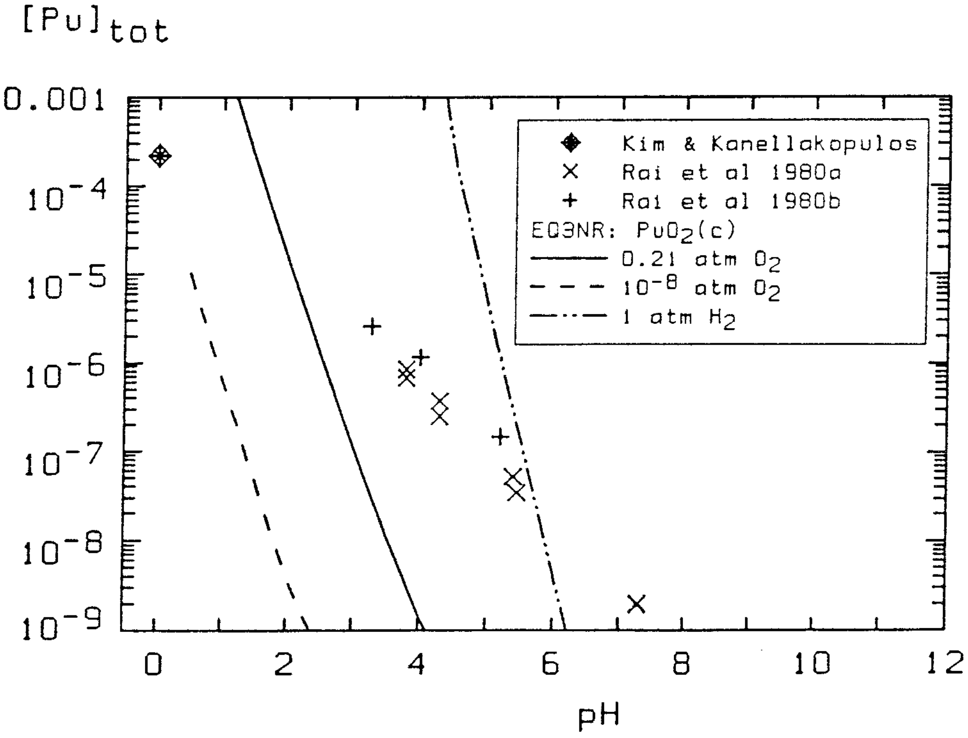

Figure 4.4 Comparison between EQ3NR-calculated solubilities and experimental literature values for $PuO_2(c)$.

solubility at a given pH is highly dependent on the specified redox conditions. At pH=7, for example, the difference between the maximum and minimum calculated $Pu(OH)_4$(am)-curves is 4.2 log-units.

Both Rai (1984) and Rai et al. (1980a, 1980b) report measured redox potentials. As the solubilities reported by Rai et al. (1980a, 1980b) were obtained in air equilibrated solutions (i.e., in equilibrium with $\cong 3.3 \cdot 10^{-4}$ atm $CO_2(g)$), these values are further discussed in Section 4.2.1.

4.1.3 Solubility of Pu(VI) oxide/hydroxide

The solubility of $^{238}PuO_2(OH)_2$ is reported by Lierse (1985) at 25°C and 0.1 M $NaClO_4$, in Ar-atmosphere. The same data is given in Kim et al. (1984).

Büppelmann and Kim (1988) discuss the effect of alpha radiolysis on the solubility of Pu(VI) solutions in 5 M NaCl. Due to the high ionic strength of their solutions, their data has not been used in this work.

Gelman et al. (1962a) report the solubility of ammonium diplutonate in distilled water. The solubilities of Pu(VI) in nitrate media of Krevinskaya et al. (1959), as well as that of ammonium diplutonate of Moskvin and Zaitseva (1962) is also reported by Gelman et al. (1962b, p.28, Tables 1 & 2). Gelman et al. (1962a and 1962b) and Moskvin and Zaitseva (1962) assume a conversion of the diplutonate ($(NH_4)_2Pu_2O_7$) into the less soluble plutonyl hydroxide $PuO_2(OH)_2(s)$.

The experimental values of Pu(VI)-solubility are given in Figure 4.5, together with the EQ3NR-calculated curve.

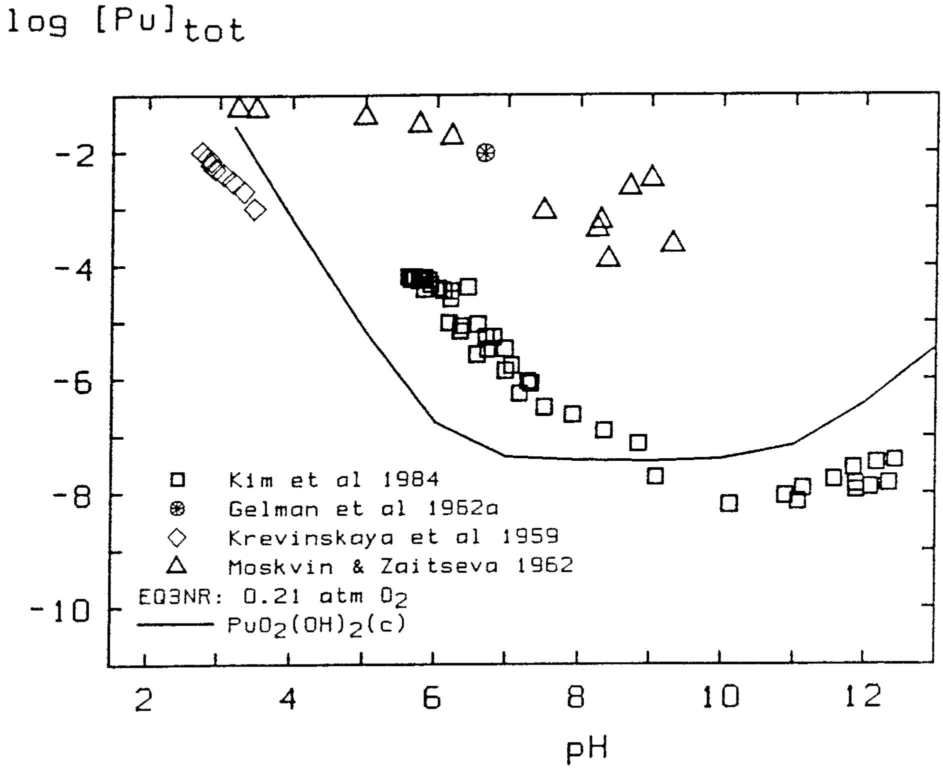

Figure 4.5 Comparison between experimental Pu(VI) solubilities and EQ3NR-calculated values.

The solubility data of Moskvin and Zaitseva (1962) is much higher than that reported by Kim et al. (1984) and Krevinskaya et al. (1959). Moskvin and Zaitseva (1962) do not state whether the solutions were filtered before the plutonium contents was determined, and therefore, the data of Kim et al. (1984) seems more reliable.

4.2 CARBONATE COMPLEXATION

4.2.1 Pu(IV) oxide/hydroxide in carbonate solutions

Rai (1984), and Rai et al. (1980a, 1980b) report measured redox potentials for their solubility experiments. The values reported by Rai et al. (1980a, 1980b) were obtained in 0.0015 M $CaCl_2$ air equilibrated solutions (i.e., with $p_{CO2} \cong 3.3 \cdot 10^{-4}$ atm), and their data is shown in Figure 4.6, where the following expressions are used to define the redox potential in the EQ3NR calculations:

$$pe = 17.0 - 0.333\ pH \quad (\text{for } 0<pH\leq 3) \qquad (4.1)$$

$$pe = 28.5 - 4.15\ pH \quad (\text{for } 3<pH\leq 5) \qquad (4.2)$$

$$pe = 12.29 - 0.921\ pH \quad (\text{for } 5<pH\leq 9) \qquad (4.3)$$

The last equation corresponds to eqn. [3] in Rai et al. (1980a), and the first two eqns. provide a fit of the Eh/pH values measured by Rai (1984, Fig.4).

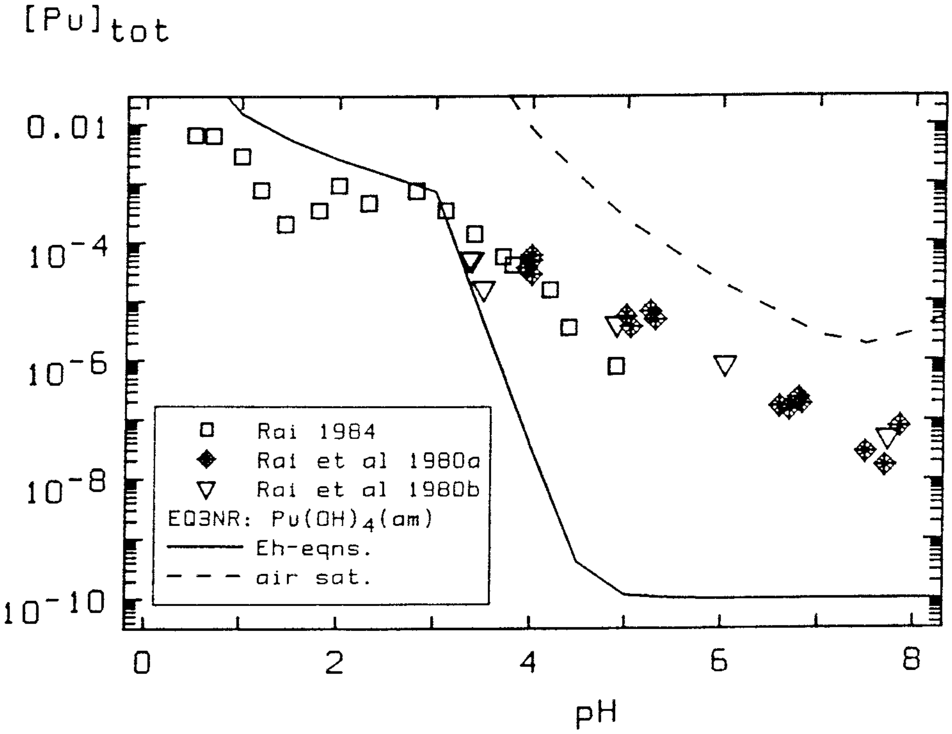

Figure 4.6 EQ3NR-calculated solubilities and experimental literature values (Rai et al.) for $Pu(OH)_4(am)$. The calculations have been performed with the redox potential specified in eqns. (4.1) to (4.3).

Figure 4.6 indicates that the data base used here requires higher redox potentials at pH≅4 to give the solubilities reported by Rai et al., or alternatively, the aqueous solutions studied by Rai et al. were more oxidised than the measured redox potentials indicate.

Pu(IV) solubility data is given in Moskvin and Gelman (1958) in concentrated solutions of alkaline carbonates. The same data is given in Gelman et al. (1962b). The experimental procedure is not very well described by these authors. We have used the 1st value (0.724 mol/l K_2CO_3) in Table V of Moskvin and Gelman (1958). They report an equilibrium pH=9.7, while the value calculated with EQ3NR is pH=11.6. Taking into account the dissociation constant of HCO_3^-, the calculated pH is more reasonable, and it has been used in Figure 4.7. The same pH value has been used for the Pu(IV)-solubility in 1M Na_2CO_3 (Cunningham and Werner, 1942).

Kim et al. (1983) report the solubility of $Pu(OH)_2CO_3(s)$ as a function of pH and $[CO_3^{2-}]$ in carbonate-bicarbonate solutions of I=1 mol/l. This data is also reported in Lierse (1985). However, $Pu(OH)_2CO_3(s)$ which is postulated by Kim et al. (1983), by analogy with a thorium solid phase, is not present in the data base used here. It is not clear to what degree these samples were in equilibrium with atmospheric $CO_2(g)$ (Lierse, 1985).

Nitsche (1985) gives plutonium solubilities at 25 and 60°C, for pH=6 and 8.5 in 0.01 M $NaClO_4$ containing 120 ppm CO_3^{2-}, in an inert-atmosphere. The same data is reported by Nitsche (1987). The solid phase in equilibrium at 25°C with the aqueous solutions could not be identified by Nitsche (1985).

Figure 4.7 shows the experimental values of Kim et al. (1983), Nitsche (1987), Moskvin and Gelman (1958) and Cunningham and Werner (1942) as a function of pH, together with solubilities of $PuO_2(c)$ and $Pu(OH)_4(am)$ calculated with EQ3NR. All literature data are plotted

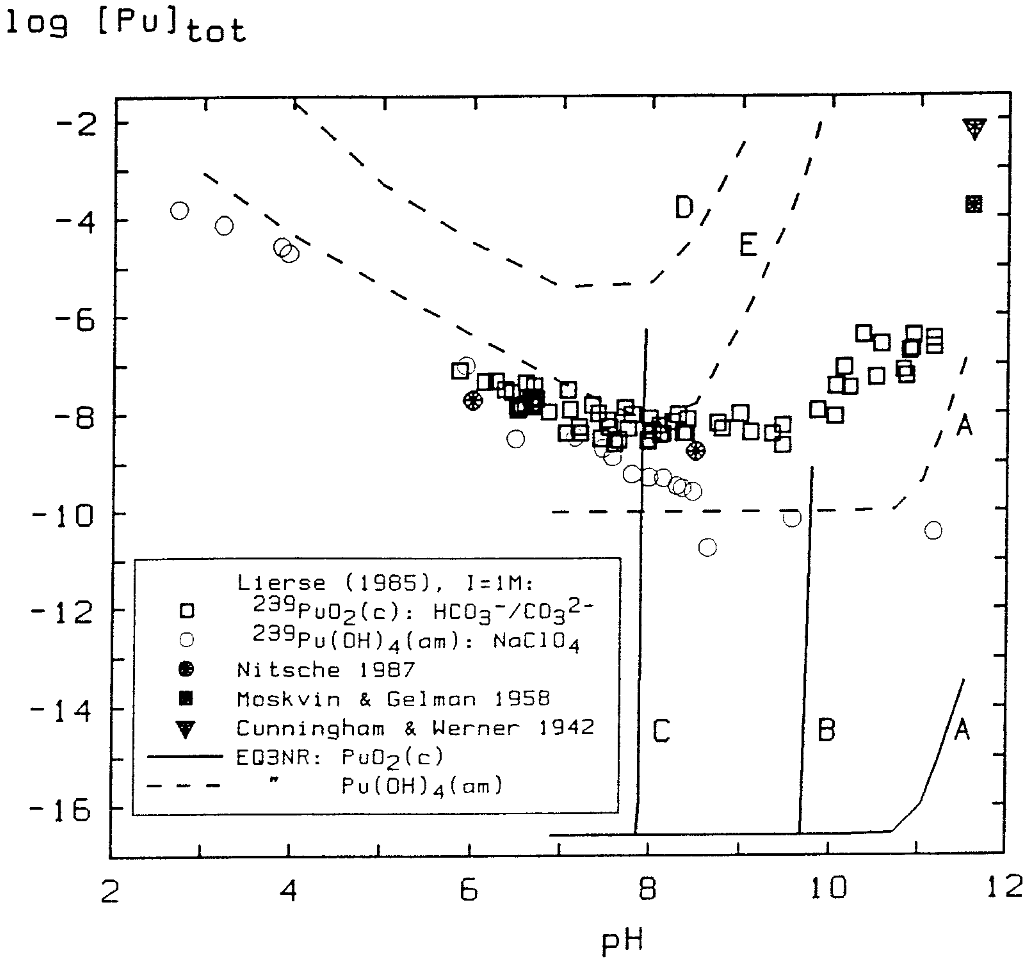

Figure 4.7 Comparison between EQ3NR-calculated solubilities and experimental literature values at 25°C for PuO_2(c) and $Pu(OH)_4$(am) in solutions containing CO_3^{2-}. See text for explanation of curves **A** to **E**.

in the same figure, even if the experimental solubilities were determined in different ionic media.

The main problem with the data of Kim et al. (1983) is that the total inorganic carbon of the solutions is not well defined. Several possibilities are offered for the EQ3NR calculations: **A**) a solubility curve is calculated for $NaClO_4/Na_2CO_3$ mixtures of I=1 mol/l, **B**) a solubility curve for $NaHCO_3/Na_2CO_3$ solutions (molar ratio 1:1) adjusted to I=1 mol/l with NaClO4, and **C**) a solubility curve for $NaClO_4/NaHCO_3$ mixtures of I=1 mol/l. In order to minimize the formation of Pu(III) and Pu(V) species in the EQ3NR calculations, the redox potential was set to Eh=+300 mV in the runs for curves **A**, **B** and **C**. The three $PuO_2(c)$-solubility curves are shown in Figure 4.7, as well as the **A**-curve for $Pu(OH)_4(am)$. Figure 4.7 shows that the pH of the solutions is well buffered for the curves **A** to **C** (pH does not change much with increasing total carbonate concentrations, and the slope of the solubility curves is very steep). The complex involved in the increase in solubility is $Pu(CO_3)_5^{6-}$. The dissolution reaction is

$$PuO_2(c) + 2H_2O + 5\ CO_3^{2-} = Pu(CO_3)_5^{6-} + 4\ OH^-$$

For the same total carbonate concentration, the Na_2CO_3 solutions are more alkaline (i.e., higher pH) than the $NaHCO_3$ solutions, and although the activity of free carbonate ions is higher in the Na_2CO_3 solutions, this is compensated by the higher activity of OH^- ions, resulting in a lower solubility.

Figure 4.7 also shows the calculated solubility of Pu(OH)4(am) versus pH both for 1 M $NaClO_4$ in equilibrium with air (0.21 atm $O_2(g)$ and $3.3 \cdot 10^{-4}$ atm $CO_2(g)$, curve D in Figure 4.7), and for 1 M $NaClO_4$ in an "inert"-atmosphere (10^{-8} atm $O_2(g)$ and $3.3 \cdot 10^{-4}$ atm $CO_2(g)$, curve **E** in Figure 4.7). The experimental solubilities of Kim et al. (1983) appear to be close to the calculated **E**-curve at $pH \leq 8$ and in between the **E** and **A** curves for pH>8.

Figure 4.8 shows the experimental (Nitsche, 1985) and calculated temperature dependence of the solubilities for Pu(IV) oxide and hydroxide at pH=6 and 8.5. Because Nitsche (1985) used an "inert"-atmosphere, it was arbitrarily assumed in the EQ3NR calculations, that the solutions were saturated with a gas phase containing 10^{-8} atm $O_2(g)$. In air saturated solutions the calculated

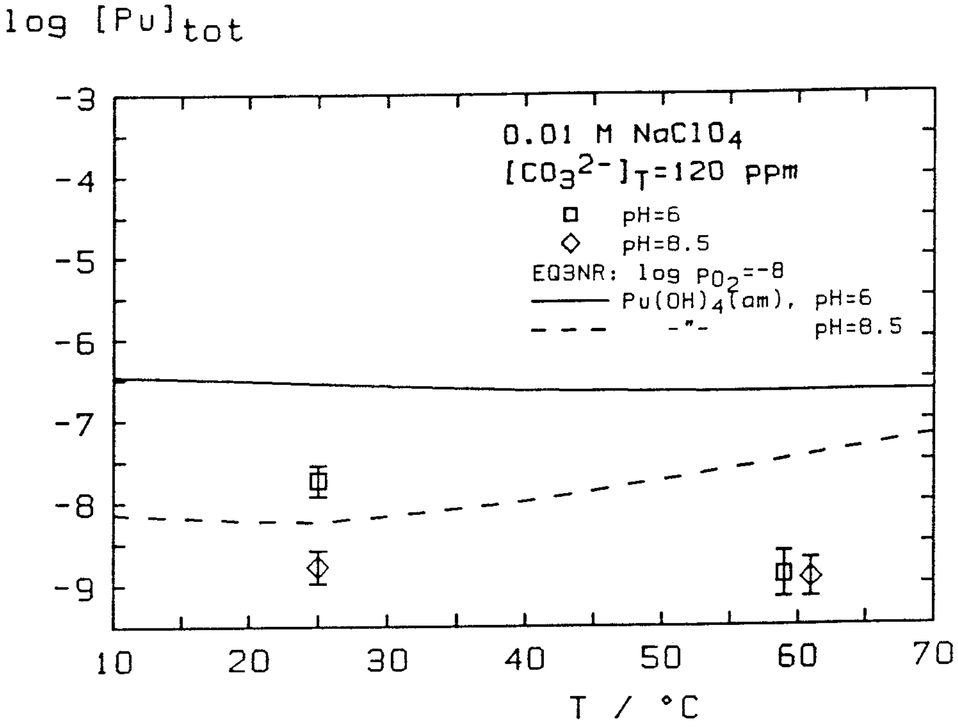

Figure 4.8 Comparison between EQ3NR-calculated solubilities and experimental Pu-solubilities (Nitsche, 1985) at 25 and 60°C for 0.01 M $NaClO_4$, 120 ppm CO_3^{2-}, pH=6 and 8.5.

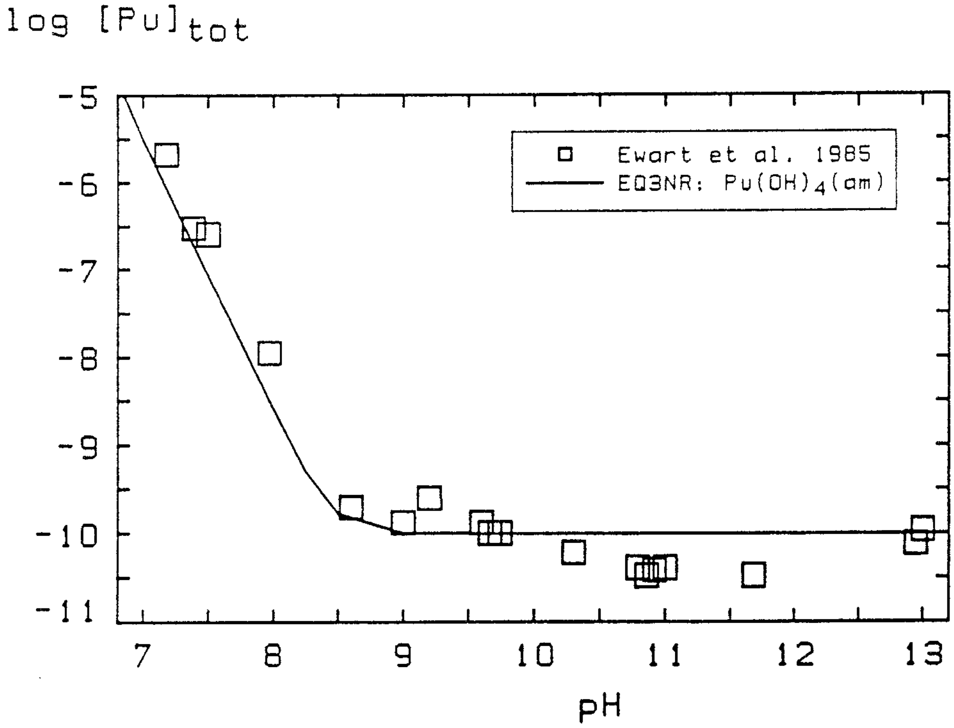

Figure 4.9 Comparison between EQ3NR-calculated solubilities and experimental Pu-solubilities for cement pore waters at 25°C and Eh=-300 mV.

solubilities would be higher. These are the only measured plutonium solubilities at T>25°C.

Ewart et al. (1985) and Pryke and Rees (1986) report Pu(IV) solubilities as function of pH in carbonate containing cement pore water and Eh=-300 mV. Their values are compared in Figure 4.9 with EQ3NR calculations. The agreement is quite satisfactory, as it is for the PHREEQE calculations reported by Ewart et al. (1985) and Pryke and Rees (1986).

4.2.2 Pu(VI) oxide/hydroxide in carbonate solutions

The following Pu(VI) solubilities have been determined in carbonate solutions:

- Moore and Werner (1944) (reported by Seaborg and Katz, 1954) determined the solubility of Pu(VI) in 5 M NaOH with increasing [K_2CO_3]. Due to the high ionic strength of these solutions, the data has not been used in this report.
- Gelman et al. (1962a) report the solubility of $(NH_4)_2Pu_2O_7$ and $(NH_4)_4PuO_2(CO_3)_3$ in ammonium carbonate solutions. These values are also reported in Gelman et al. (1962b)
- Drabkina (1960) reports the solubility of $(NH_4)_4PuO_2(CO_3)_3$ in solutions of ammonium carbonate and ammonium nitrate. The same data is reported in Gelman et al. (1962b)
- Robouch and Vitorge (1987) report the solubility of PuO_2CO_3 as a function of the free carbonate concentration at fixed partial pressure of CO_2(g). These values are discussed in Section 4.2.3.

The ammonium solid phases studied by Drabkina (1960) and Gelman et al. (1962a) are not included in our data base. Furthermore, Gelman et al. (1962a and 1962b) assume that ammonium diplutonate decomposes in the aqueous solutions to form the more stable hydroxide $PuO_2(OH)_2$, and Gelman

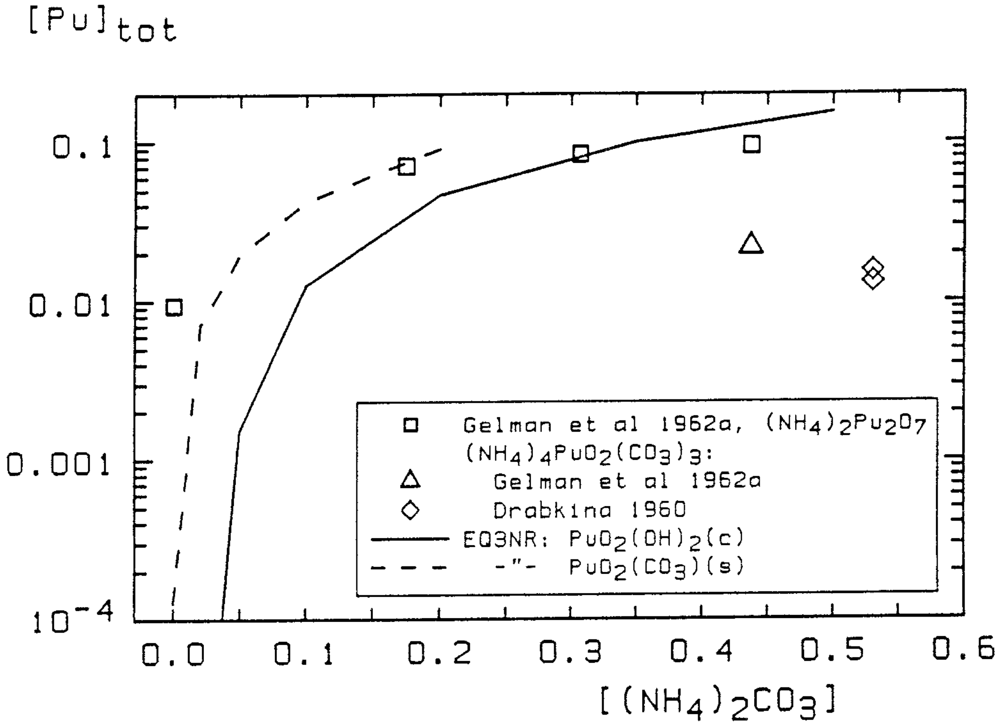

Figure 4.8 Comparison between experimental literature Pu(VI) solubilities and EQ3/6-calculated values as a function of the concentration of ammonium carbonate.

et al. (1962b) assume the decomposition in aqueous solution of ammonium plutonyl tricarbonate into the dicarbonate $(NH_4)_2PuO_2(CO_3)_2$.

Experimental solubilities of Pu(VI) in ammonium carbonate solutions are shown in Figure 4.8, together with the curves calculated with EQ3/6 for $PuO_2(OH)_2(c)$ and $PuO_2(CO_3)(s)$.

4.2.3 PuO_2CO_3

Robouch and Vitorge (1987) report the solubility of PuO_2CO_3 as a function of the free carbonate concentration in 3 M $NaClO_4$ at 20±1°C, and fixed partial pressure of $CO_2(g)$ (0.1, 0.3 and 1 atm). Figure 4.9 shows both the experimental data of Robouch and Vitorge (1987) and the solubilities calculated by EQ3NR (converted to molar units) *versus* the free carbonate ion concentration (in

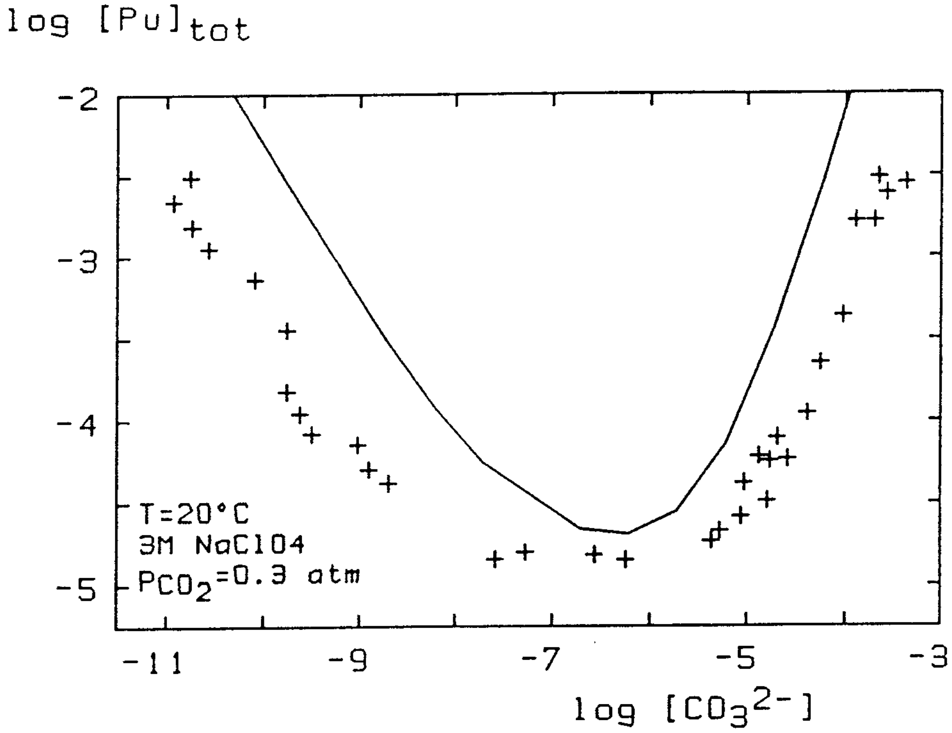

Figure 4.9 Comparison between experimental Pu(VI) solubilities (Robouch and Vitorge, 1987) and EQ3NR-calculated values as a function of the free concentration of the carbonate ion. All concentrations are given in molar units. Temperature=20°C.

molar units). The discrepancy between the calculated curve and the experimental values appears to be due to the differences between the single-ion activity coefficients calculated by Robouch and Vitorge (1987), and those calculated with the EQ3NR program.

4.3 PHOSPHATE COMPLEXATION

4.3.1 Pu(III) phosphates

O'Connor (1944a) measured the solubility of Pu(III) phosphate as a function of [HCl] in 0.8 M H_3PO_4 solutions (SO_2(g)-saturated). Due to the high acidities and ionic strengths involved, these solubilities have not been considered further in this work.

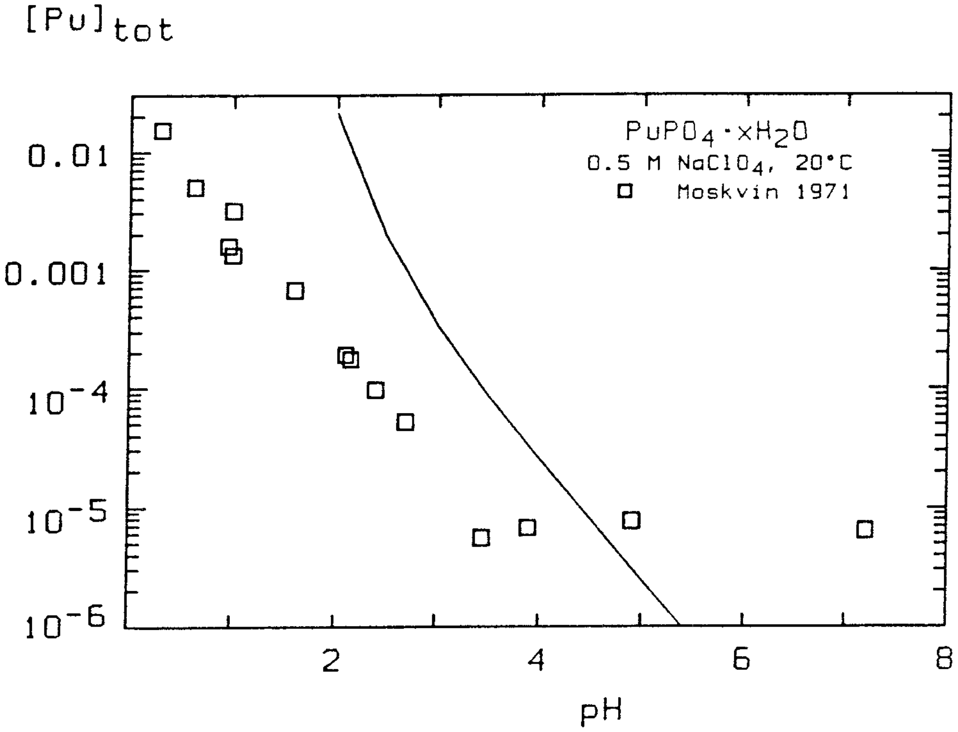

Figure 4.10 Experimental Pu(III) solubilities (Moskvin, 1971) as a function of pH. The curve shows the EQ3NR-calculated solubility of $Pu(OH)_4$(am) in 10^{-8} atm O_2(g).

Moskvin (1971) measured the solubility of $PuPO_4 \cdot xH_2O$ as a function of pH in 0.5 M $NaClO_4$ and 20±1°C. Moskvin (1971) does not specify the redox conditions of his experiments ("The experiments were conducted according to the usual procedure"). The data base used here does not include the solid $PuPO_4$(s), nevertheless, the calculated solubility of $Pu(OH)_4$(am) in diluted solutions and 10^{-8} atm O_2(g) (inert atmosphere) is compared with the experimental data of Moskvin (1971) in Figure 4.10.

4.3.2 Pu(IV) phosphates

O'Connor (1944b) measured the solubility of Pu(IV) phosphate in solutions containing H_3PO_4 and one of the following acids: H_2SO_4, HNO_3 and HCl. Due to the high acidities and ionic strengths involved, these solubilities were not considered further in this study.

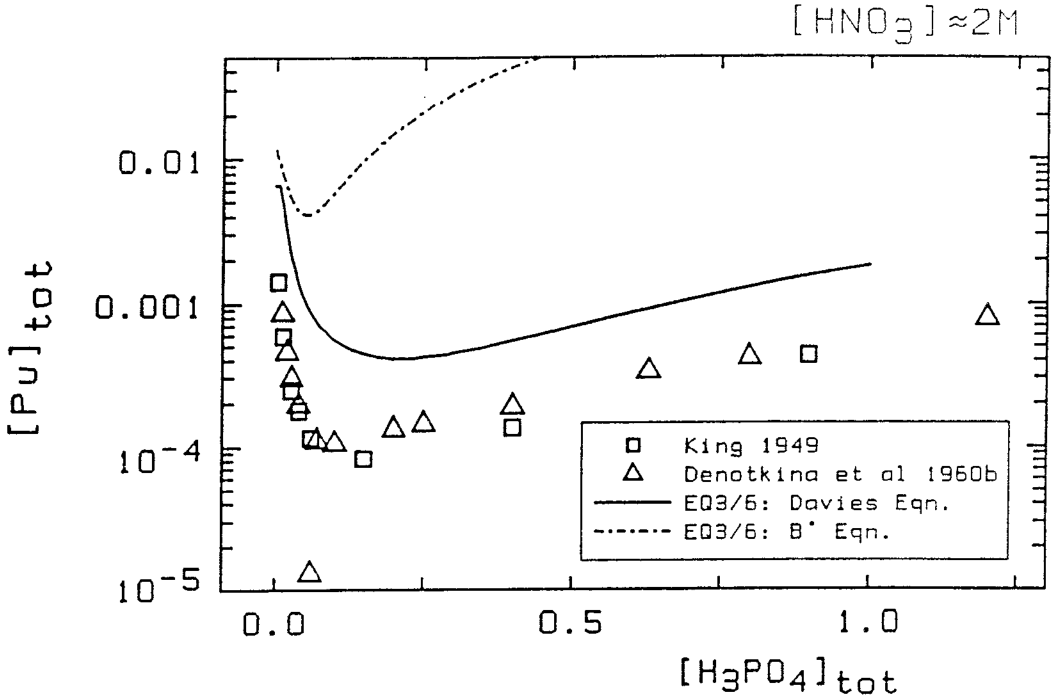

Figure 4.11 Comparison between experimental solubilities of $Pu(HPO_4)_2 \cdot xH_2O$ and EQ3/6-calculated values as a function of phosphoric acid concentration, in ≅2M HNO_3. The EQ3/6 runs were made with a fixed $p(O_2)=10^{-15}$ atm.

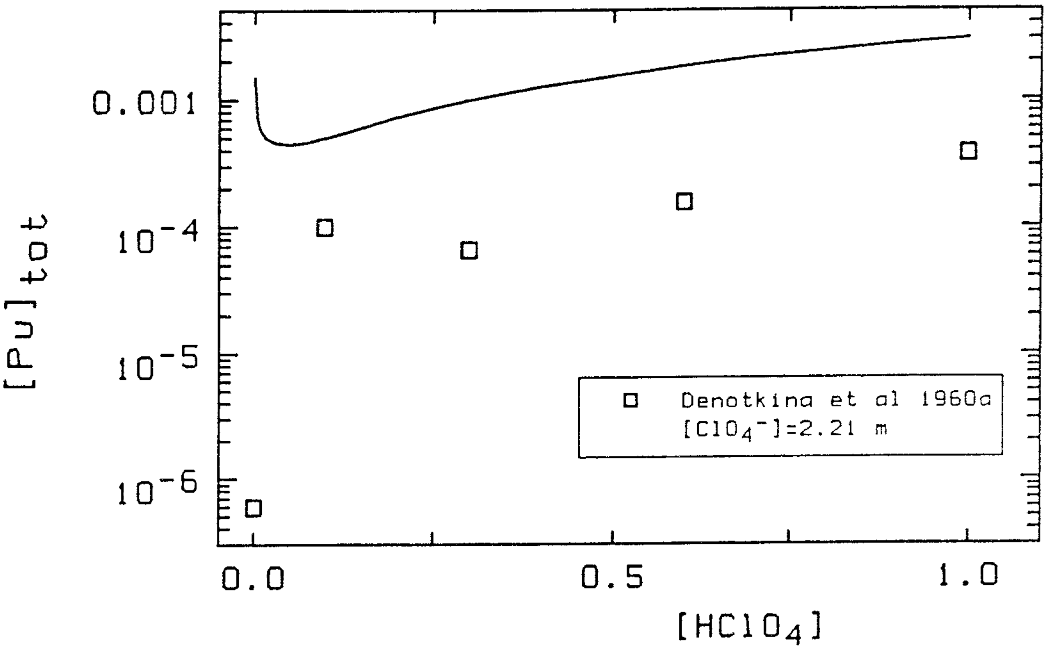

Figure 4.12 Comparison between experimental solubilities of $Pu(HPO_4)_2 \cdot xH_2O$ and EQ3/6-calculated values as a function of perchloric acid concentration in 2 M ClO_4^-. The EQ3/6 runs were made with a fixed $p(O_2)=10^{-15}$ atm, and using Davies equation (Eqn. 2.2).

The solubility of Pu(IV) phosphates was studied by King (1949) and is also reported by Seaborg and Katz (1954, p. 416). The solubility of gelatinous $Pu(HPO_4)_2 \cdot xH_2O$ as a function of $[H_3PO_4]$ at 25°C, in 2.08M HNO_3 (Table 4 in King (1949), samples with "solid III") is used in this study (Figure 4.11).

Denotkina et al. (1960a and 1960b) also studied the solubility of $Pu(HPO_4)_2 \cdot xH_2O$ at 25°C:

- solubility of the Pu(IV)-phosphate as a function of $[H_3PO_4]$ in 2M HNO_3 (Table 1 in Denotkina, 1960b)
- solubility of $Pu(HPO_4)_2 \cdot xH_2O$ in 2 M $(Na/H)ClO_4$ (Table 2 in Denotkina et al. 1960a).

these solubilities have been plotted in Figures 4.11 and 4.12.

The calculated plutonium solubilities for $Pu(HPO_4)_2(c)$ are higher than the experimental values. The dominating plutonium species in the calculations are: $Pu(HPO_4)^{2+}$ and $Pu(HPO_4)_4^{4-}$. The Pu-solubilities in Figure 4.11, calculated with the equilibrium constant for $Pu(HPO_4)_4^{4-}$ (which originates from the solubility values reported by Denotkina et al., 1960b) is higher than the experimental solubilities from which they were obtained. This appears to be due to two factors: firstly the fact that the thermodynamic data was calculated from the equilibrium constant without correction for ionic media effects (Lemire and Tremaine, 1980), and secondly, the equations used to calculate single-ion activity coefficients in EQ3NR are not well suited for ionic media of $I \geq 0.5$ m.

The last factor is illustrated in Figure 4.11, which shows the solubility of $Pu(HPO_4)_2(s)$ calculated with both Davies equation (Eq. 2.2), and Helgeson's $B^{\bullet}$ equation (Eq. 2.1). The differences are as high as a factor of 100. The solubility curve in Figure 4.12 was calculated using Davies equation.

4.3.3 Pu(VI) phosphates

Denotkina and Shevchenko (1967a) report the solubility of $PuO_2(HPO_4)\cdot4H_2O$ as $1.5\cdot10^{-5}$ mol/l at pH=4.5-4.45. The solubility of this solid at 25°C as a function of the equilibrium total phosphate concentration is also given by the same authors (Table 1 in Denotkina and Shevchenko, 1967b). A comparison between the experimental and calculated Pu-solubilities is given in Figure 4.13.

The EQ3/6 calculations were made with $p(O_2(g))=0.21$ atm, and using the Davies equation to calculate single ion activity coefficients. The calculations show that the main plutonium species in the phosphoric acid solutions are $Pu(HPO_4)_4^{4-}$ and $PuO_2(H_2PO_4)^+$. When the formation of Pu(IV) is suppressed, there is a satisfactory agreement between the EQ3/6 calculations and the experimental data of Denotkina and Shevchenko. This is hardly surprising, since the equilibrium constant for $PuO_2(H_2PO_4)^+$ used in the EQ3/6 calculations originates from the solubility data of Denotkina and Shevchenko (1967b).

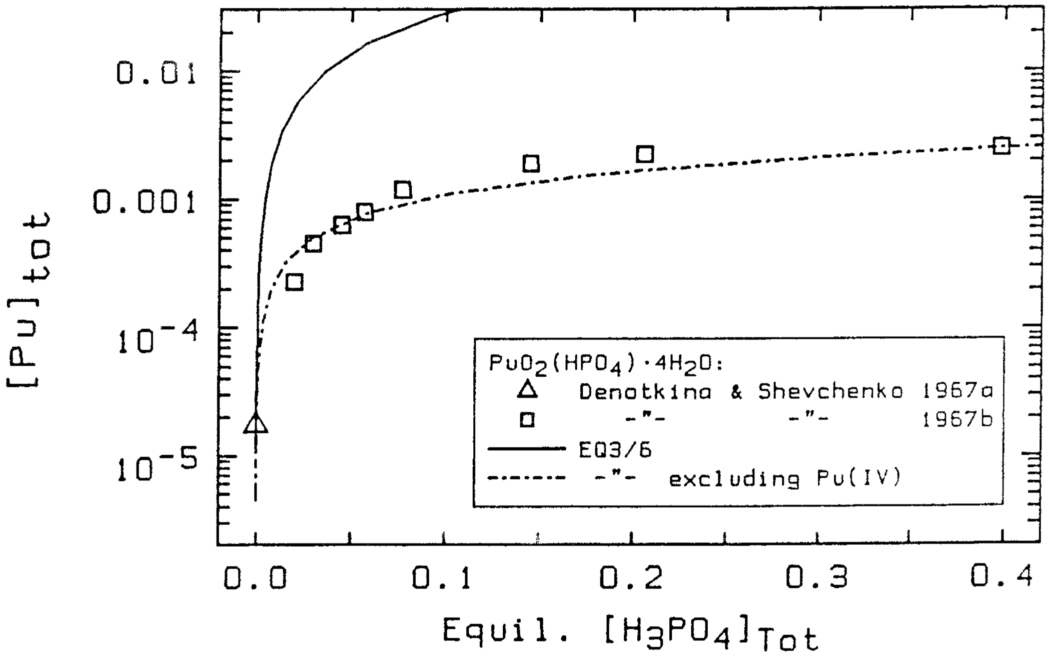

Figure 4.13 Comparison between experimental solubilities of $PuO_2(HPO_4)\cdot4H_2O$ and EQ3/6-calculated values as a function of the equilibrium concentration of $[H_3PO_4]_{tot}$.

5 CONCLUSIONS

The work presented here has three main aspects:
1) a literature survey of the plutonium solubility data,
2) a selection of thermodynamic data for plutonium, and
3) a verification/validation of a thermodynamic data base for plutonium. This allowed us to find out areas where new experimental measurements are needed. The most prominent conclusions are the following:

- The solubility of Pu(IV) has been studied by several authors (c.f. Figures 4.2-4.4, 4.6) and there is reasonable consistency between different authors in the literature. A validation of the thermodynamic data base can not be made unambiguously, because the redox potential is an important parameter in the calculation of plutonium solubilities, and because the redox potential has not been determined in most experimental studies.

- The validation of the thermodynamic data base is also difficulted by the fact that the nature of the equilibrium solid phases has seldom been studied.

- The experimental conditions used in the determination of some of the solubilities in the system Pu^{4+}/CO_3^{2-}, are such that an unambiguous interpretation is not possible. The agreement is satisfactory between calculated and experimental Pu-solubilities in alkaline cement pore waters. However, in cement pore waters the carbonate concentration is very low due to Ca-carbonate precipitation.

- For the PuO_2^{2+}/CO_3^{2-} system, the agreement between the experimental and calculated solubilities is reasonable, and can be taken as a verification of the equilibrium constants at 25°C used in the data base.

- High temperature studies on the solubility of plutonium are very scarce. Further work in this area is necessary to check assumptions on the entropies and heat capacities of plutonium species.

- Calculated solubilities are in some instances very dependent on the model used for single-ion activity coefficients. The default equation used by EQ3/6 is Helgeson's $B^{\bullet}$ equations (Eq. 2.1), and the "distance of closest approach" becomes an important parameter when this equation is used. The calculated radionuclide solubilities might show very large discrepancies when different equations for activity coefficients are used (c.f. Figure 4.11). This might be the factor behind the differences between PHREEQE and EQ3/6 calculations reported by Snellman (1989).

- The solubility of plutonium in most natural waters is too high to be useful as a barrier in a geosphere (or biosphere) submodel of any concept for nuclear waste disposal. Nevertheless, the solubility of Pu(IV) oxide/hydroxide might be useful as a conceptual barrier in the near-field model of a nuclear repository.

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APPENDIX A

Data blocks to be used in the MDAS file of the EQ3/6 package. The MDAS file is transformed by the MDAP program into a direct access file (MDAR) before it is used as input by the MCRT program. The MCRT program calculates equilibrium constants as a function of temperature, and writes the results in a DFILE. Appendix B contains the DFILE obtained with the data blocks listed here, and the data blocks for water, oxygen, phosphate, carbonate, etc.

```
mdas.3245  Pu thermodynamic data
last modified Aug29,90
+------------------------------------------------------------------------
basis species
+------------------------------------------------------------------------
pu+++                                                  date= Aug22,90
 entered by= I.Puigdomenech            quality= good
 keys   = aux              element
 subsets= plutonium
     charge=    3.0         titr. factor=    0.0 eq/mol
   ion type=  1                 ion size=    0.0 a     hydr. no.=    0.0
  1 chemical elements
       1.000 pu
          temp=     298.15 k          press=      1.013 bars
         delg0=    -138.29 kcal/mol   delh0=    -141.52 kcal/mol
            s0=     -44.22 cal/mol/k     se=       3.56 cal/mol/k
            v0=            cc/mol        cp=     -14.58 cal/mol/k
  0 species in reference reaction
  5 species in data0 reaction
     -1.000  pu+++                        -0.500  h2o
      1.000  puo2++                        1.000  h+
     -0.750  o2(g)
 t-p data grid is absent
 source=
* [lemire and tremaine, 1980]
* delH0= delG0 + 0.29815*( S0(Pu+++) - S0(Pu(c)) + 3/2 S0(H2(g)) )
*------------------------------------------------------------------------
* Directory of Pu species:
*                    Hydroxides       Carbonates      Phosphates
*
*                 +----------------+----------------+---------------+
*        Pu(III)  | pu(oh)3(s)     | pu(oh)co3(s)   |               |
*                 | pu2o3(c,beta)  |                |               |
*                 | pu+++          | pu(co3)+       | pu(h2po4)++   |
*                 | pu(oh)++       |                |               |
*                 +----------------+----------------+---------------+
*        Pu(IV)   | pu(oh)4(am)    |                | pu(hpo4)2(c)  |
*                 | puo2(c)        |                |               |
*                 | pu++++         | pu(co3)++      | pu(hpo4)++    |
*                 | pu(oh)+++      | pu(co3)5 6-    | pu(hpo4)2     |
*                 | pu(oh)2++      |                | pu(hpo4)3--   |
*                 | pu(oh)3+       |                | pu(hpo4)4 4-  |
*                 | pu(oh)4        |                |               |
*                 +----------------+----------------+---------------+
*        Pu(V)    | puo2oh(am)     |                |               |
*                 | puo2+          | puo2(co3)-     |               |
*                 | puo2oh         | puo2(co3)2 3-  |               |
*                 +----------------+----------------+---------------+
*        Pu(VI)   | puo2(oh)2(c)   | puo2(co3)(s)   | puo2hpo4(c)   |
*                 | puo2++         | puo2(co3)      | puo2(h2po4)+  |
*                 | (puo2)2(oh)2++ | puo2(co3)2--   |               |
*                 | (puo2)3(oh)5+  | puo2(co3)3 4-  |               |
*                 | puo2oh+        | puo2(oh)2hco3- |               |
*                 | puo2(oh)2      |                |               |
*                 | puo2(oh)3-     |                |               |
*                 +----------------+----------------+---------------+
*------------------------------------------------------------------------
```

```
+----------------------------------------------------------------------
pu++++                                                  date= Aug22,90
 entered by= I.Puigdomenech             quality= good
 keys    = aux               element
 subsets= plutonium
     charge=    4.0          titr. factor=    0.0 eq/mol
   ion type=  1                  ion size=    0.0 a     hydr. no.=    0.0
  1 chemical elements
       1.000 pu
          temp=     298.15 k          press=      1.013 bars
         delg0=   -115.110 kcal/mol   delh0=   -128.221 kcal/mol
            s0=     -92.97 cal/mol/k     se=       4.36 cal/mol/k
            v0=            cc/mol        cp=     -15.06 cal/mol/k
  0 species in reference reaction
  5 species in data0 reaction
     -1.000  pu++++                   -1.000  h2o
      1.000  puo2++                    2.000  h+
     -0.500  o2(g)
 t-p data grid is absent
 source=
* [lemire and tremaine, 1980]
* delH0= delG0 + 0.29815*( S0(Pu++++) - S0(Pu(c)) + 2 S0(H2(g)) )
+----------------------------------------------------------------------
puo2+                                                   date= Aug22,90
 entered by= I.Puigdomenech             quality= fair
 keys    = aux
 subsets= plutonium
     charge=    1.0          titr. factor=    0.0 eq/mol
   ion type=  1                  ion size=    0.0 a     hydr. no.=    0.0
  2 chemical elements
       1.000 pu              2.000 o
          temp=     298.15 k          press=      1.013 bars
         delg0=   -203.150 kcal/mol   delh0=   -218.607 kcal/mol
            s0=      -5.02 cal/mol/k     se=       4.57 cal/mol/k
            v0=            cc/mol        cp=      23.42 cal/mol/k
  0 species in reference reaction
  5 species in data0 reaction
     -1.000  puo2+                    -1.000  h+
      1.000  puo2++                    0.500  h2o
     -0.250  o2(g)
 t-p data grid is absent
 source=
* [lemire and tremaine, 1980]
* delH0= delG0 + 0.29815*( S0(PuO2+) - S0(Pu(c)) - S0(O2(g)) + 1/2 S0(H2(g)) )
+----------------------------------------------------------------------
puo2++                                                  date= Aug22,90
 entered by= I.Puigdomenech             quality= fair
 keys    = basis
 subsets= plutonium
     charge=    2.0          titr. factor=    0.0 eq/mol
   ion type=  1                  ion size=    5.0 a     hydr. no.=    0.0
  2 chemical elements
       1.000 pu              2.000 o
          temp=     298.15 k          press=      1.013 bars
         delg0=    -180.90 kcal/mol   delh0=   -196.478 kcal/mol
            s0=     -21.03 cal/mol/k     se=       4.36 cal/mol/k
            v0=            cc/mol        cp=       2.63 cal/mol/k
  0 species in reference reaction
  0 species in data0 reaction
 t-p data grid is absent
 source=
* [lemire and tremaine, 1980]
* delH0= delG0 + 0.29815*( S0(PuO2++) - S0(Pu(c)) - S0(O2(g)) + S0(H2(g)) )
+----------------------------------------------------------------------
```

```
+----------------------------------------------------------------------
non-basis aqueous species
+----------------------------------------------------------------------
pu(oh)++                                                date= 09-Jul90
 entered by= I.Puigdomenech            quality= good
 keys   =
 subsets= plutonium
     charge=    2.0          titr. factor=        eq/mol
   ion type=  1                 ion size=    0.0 a     hydr. no.=    0.0
  3 chemical elements
       1.000 pu              1.000 o               1.000 h
          temp=     298.15 k          press=      1.013 bars
         delg0=   -184.106 kcal/mol   delh0=       500. kcal/mol
            s0=     -21.03 cal/mol/k     se=       3.56 cal/mol/k
            v0=            cc/mol        cp=       1.67 cal/mol/k
  0 species in reference reaction
  4 species in data0 reaction
     -1.000  pu(oh)++                     -1.000  h+
      1.000  pu+++                         1.000  h2o
 t-p data grid is absent
 source=
* [lemire and garisto, 1989], see also [lemire and tremaine, 1980]
* this gives log k=-7.97 at 25 C, for Pu+++ + H2O = Pu(OH)++ + H+
+----------------------------------------------------------------------
pu(co3)+                                                date= 09-Jul90
 entered by= I.Puigdomenech            quality= speculative
 keys   =
 subsets= plutonium
     charge=   +1.0          titr. factor=    2.0 eq/mol
   ion type=  1                 ion size=    0.0 a     hydr. no.=    0.0
  3 chemical elements
       1.000 pu              3.000 o               1.000 c
          temp=    298.150 k          press=      1.000 bars
         delg0=    -276.74 kcal/mol   delh0=       500. kcal/mol
            s0=      -11.8 cal/mol/k     se=       3.56 cal/mol/k
            v0=            cc/mol        cp=            cal/mol/k
  0 species in reference reaction
  3 species in data0 reaction
     -1.000  pu(co3)+                      1.000  co3--
      1.000  pu+++
 t-p data grid is absent
 source=
* estimated log k=9(+-1) at 25 C for Pu+++ + CO3-- = Pu(CO3)+
* in analogy with Am+++ [kerrisk and silva, 1986]
* delta-S-reaction estimated as +35 from:
* correlation between
*   - entropies of reaction for ca++ and several ligands
* against
*   - entropies of reaction for m+++ and several ligands
*     (where m+++ are: la+++, pu+++, am+++, cm+++, bk+++, cf+++)
* and a entropy of reaction between ca++ and co3-- of 25.1 cal/(mol K)
+----------------------------------------------------------------------
pu(h2po4)++                                             date= 09-Jul90
 entered by= I.Puigdomenech            quality= good
 keys   =
 subsets= plutonium
     charge=    2.0          titr. factor=        eq/mol
   ion type=  1                 ion size=    0.0 a     hydr. no.=    0.0
  4 chemical elements
       1.000 pu              2.000 h               1.000 p
       4.000 o
          temp=     298.15 k          press=      1.013 bars
         delg0=   -411.807 kcal/mol   delh0=       500. kcal/mol
            s0=      15.06 cal/mol/k     se=       3.56 cal/mol/k
            v0=            cc/mol        cp=     -18.88 cal/mol/k
  0 species in reference reaction
  4 species in data0 reaction
     -1.000  pu(h2po4)++                   1.000  h+
      1.000  pu+++                         1.000  hpo4--
 t-p data grid is absent
 source=
* [lemire and garisto, 1989], see also [lemire and tremaine, 1980]
+----------------------------------------------------------------------
```

```
+----------------------------------------------------------------------
pu(oh)+++                                                date= 09-Jul90
 entered by= I.Puigdomenech            quality= fair
 keys   =
 subsets= plutonium
     charge=    3.0         titr. factor=       eq/mol
   ion type=  1                 ion size=    0.0 a     hydr. no.=    0.0
  3 chemical elements
       1.000 pu             1.000 o              1.000 h
          temp=      298.15 k         press=      1.013 bars
         delg0=     -171.10 kcal/mol  delh0=       500. kcal/mol
            s0=      -39.91 cal/mol/k    se=       4.36 cal/mol/k
            v0=             cc/mol       cp=     -16.49 cal/mol/k
  0 species in reference reaction
  4 species in data0 reaction
     -1.000  pu(oh)+++                -1.000  h+
      1.000  pu++++                    1.000  h2o
 t-p data grid is absent
 source=
* [lemire and tremaine, 1980]
+----------------------------------------------------------------------
pu(oh)2++                                                date= 09-Jul90
 entered by= I.Puigdomenech            quality= fair
 keys   =
 subsets= plutonium
     charge=    2.0         titr. factor=       eq/mol
   ion type=  1                 ion size=    0.0 a     hydr. no.=    0.0
  3 chemical elements
       1.000 pu             2.000 o              2.000 h
          temp=      298.15 k         press=      1.013 bars
         delg0=     -225.31 kcal/mol  delh0=       500. kcal/mol
            s0=      -10.52 cal/mol/k    se=       4.36 cal/mol/k
            v0=             cc/mol       cp=      -3.82 cal/mol/k
  0 species in reference reaction
  4 species in data0 reaction
     -1.000  pu(oh)2++                -2.000  h+
      1.000  pu++++                    2.000  h2o
 t-p data grid is absent
 source=
* [lemire and tremaine, 1980]
+----------------------------------------------------------------------
pu(oh)3+                                                 date= 09-Jul90
 entered by= I.Puigdomenech            quality= fair
 keys   =
 subsets= plutonium
     charge=    1.0         titr. factor=    3.0 eq/mol
   ion type=  1                 ion size=    0.0 a     hydr. no.=    0.0
  3 chemical elements
       1.000 pu             3.000 o              3.000 h
          temp=      298.15 k         press=      1.013 bars
         delg0=     -277.96 kcal/mol  delh0=       500. kcal/mol
            s0=       10.52 cal/mol/k    se=       4.36 cal/mol/k
            v0=             cc/mol       cp=      14.10 cal/mol/k
  0 species in reference reaction
  4 species in data0 reaction
     -1.000  pu(oh)3+                 -3.000  h+
      1.000  pu++++                    3.000  h2o
 t-p data grid is absent
 source=
* [lemire and tremaine, 1980]
+----------------------------------------------------------------------
```

```
+-----------------------------------------------------------------------
pu(oh)4                                                   date= 09-Jul90
 entered by= I.Puigdomenech             quality= fair
 keys   =
 subsets= plutonium
     charge=    0.0          titr. factor=    4.0 eq/mol
   ion type=  0                  ion size=    0.0 a      hydr. no.=    0.0
  3 chemical elements
       1.000 pu              4.000 o                4.000 h
          temp=     298.15 k          press=      1.013 bars
         delg0=    -329.35 kcal/mol   delh0=   -375.835 kcal/mol
            s0=       500. cal/mol/k     se=       4.36 cal/mol/k
            v0=            cc/mol        cp=            cal/mol/k
  0 species in reference reaction
  4 species in data0 reaction
     -1.000  pu(oh)4                      -4.000  h+
      1.000  pu++++                        4.000  h2o
 t-p data grid is absent
 source=
* [lemire and garisto, 1989], see also [lemire and tremaine, 1980]
* s0=17.93, delh0 calculated with s0(pu)=13.42 [lemire and garisto, 1989]
+-----------------------------------------------------------------------
pu(co3)++                                                 date= 29-Aug90
 entered by= I.Puigdomenech             quality= speculative
 keys   =
 subsets= plutonium
     charge=   +2.0          titr. factor=    2.0 eq/mol
   ion type=  1                  ion size=    0.0 a      hydr. no.=    0.0
  3 chemical elements
       1.000 pu              3.000 o                1.000 c
          temp=    298.150 k          press=      1.000 bars
         delg0=   -259.015 kcal/mol   delh0=       500. kcal/mol
            s0=       70.0 cal/mol/k     se=       4.36 cal/mol/k
            v0=            cc/mol        cp=            cal/mol/k
  0 species in reference reaction
  3 species in data0 reaction
     -1.000  pu(co3)++                     1.000  co3--
      1.000  pu++++
 t-p data grid is absent
 source=
* [silva and nitsche, 1985] log k <= 13 at 25 C for Pu++++ + CO3-- = Pu(CO3)++
* [kim et al., 1983] (I=1.0, NaClO4, temp=?) give log K=47.1,
*   they also give values for Pu(CO3)i, i=1,2,3,4, but
*   all log k values are unresonable large (see [hobart et al., 1986])
* delta-S of reaction = 36.57 cal/(mol K)
*   estimated by [lemire and tremaine, 1980]
*   equal to that of the sulphate complexation reaction.
+-----------------------------------------------------------------------
pu(co3)5 6-                                               date= 09-Jul90
 entered by= I.Puigdomenech             quality= speculative
 keys   =
 subsets= plutonium
     charge=   -6.0          titr. factor=   10.0 eq/mol
   ion type=  3                  ion size=    0.0 a      hydr. no.=    0.0
  3 chemical elements
       1.000 pu              5.000 c               15.000 o
          temp=    298.150 k          press=      1.000 bars
         delg0=   -799.240 kcal/mol   delh0=       500. kcal/mol
            s0=       4.78 cal/mol/k     se=       4.36 cal/mol/k
            v0=            cc/mol        cp=      117.6 cal/mol/k
  0 species in reference reaction
  3 species in data0 reaction
     -1.000  pu(co3)5 6-                   5.000  co3--
      1.000  pu++++
 t-p data grid is absent
 source=
* [lemire and garisto, 1989] log beta= 39+/-3
* [kim et al., 1983] (I=1.0, NaClO4, temp=?), log K=62.4 for
*    Pu++++  +  4CO3--  =  Pu(CO3)4----
*   extrapolated to I=0 with SIT as log K= 61.3 would give delg0=-829.58
* [kim et al., 1983] also give values for Pu(CO3)i, i=1,2,3,4, but
*   all log k values are unresonable large (see [hobart et al., 1986])
+-----------------------------------------------------------------------
```

```
+----------------------------------------------------------------------
pu(hpo4)++                                             date= 09-Jul90
 entered by= I.Puigdomenech            quality= fair
 keys    =
 subsets= plutonium
     charge=    2.0          titr. factor=    0.0 eq/mol
   ion type=  1                 ion size=    0.0 a     hydr. no.=    0.0
  4 chemical elements
       1.000 pu              1.000 h                1.000 p
       4.000 o
          temp=    298.150 k          press=      1.000 bars
         delg0=   -393.164 kcal/mol   delh0=       500. kcal/mol
            s0=      -9.08 cal/mol/k     se=       4.36 cal/mol/k
            v0=            cc/mol        cp=      -4.78 cal/mol/k
  0 species in reference reaction
  3 species in data0 reaction
     -1.000  pu(hpo4)++                    1.000  hpo4--
      1.000  pu++++
 t-p data grid is absent
 source=
* [lemire and garisto, 1989], see also [lemire and tremaine, 1980]
+----------------------------------------------------------------------
pu(hpo4)2                                              date= 09-Jul90
 entered by= I.Puigdomenech            quality= fair
 keys    =
 subsets= plutonium
     charge=    0.0          titr. factor=    0.0 eq/mol
   ion type=  0                 ion size=    0.0 a     hydr. no.=    0.0
  4 chemical elements
       1.000 pu              8.000 o                2.000 p
       2.000 h
          temp=    298.150 k          press=      1.000 bars
         delg0=   -668.260 kcal/mol   delh0=   -739.593 kcal/mol
            s0=       500. cal/mol/k     se=       4.36 cal/mol/k
            v0=            cc/mol        cp=            cal/mol/k
  0 species in reference reaction
  3 species in data0 reaction
     -1.000  pu(hpo4)2                     2.000  hpo4--
      1.000  pu++++
 t-p data grid is absent
 source=
* [lemire and garisto, 1989], see also [lemire and tremaine, 1980]
* s0=21.03, delh0 calculated with s0(pu)=13.42 [lemire and garisto, 1989]
+----------------------------------------------------------------------
pu(hpo4)3--                                            date= 09-Jul90
 entered by= I.Puigdomenech            quality= fair
 keys    =
 subsets= plutonium
     charge=   -2.0          titr. factor=    0.0 eq/mol
   ion type=  4                 ion size=    0.0 a     hydr. no.=    0.0
  4 chemical elements
       1.000 pu              3.000 h                3.000 p
      12.000 o
          temp=    298.150 k          press=      1.000 bars
         delg0=   -941.683 kcal/mol   delh0=       500. kcal/mol
            s0=      31.07 cal/mol/k     se=       4.36 cal/mol/k
            v0=            cc/mol        cp=      67.88 cal/mol/k
  0 species in reference reaction
  3 species in data0 reaction
     -1.000  pu(hpo4)3--                   3.000  hpo4--
      1.000  pu++++
 t-p data grid is absent
 source=
* [lemire and garisto, 1989], see also [lemire and tremaine, 1980]
+----------------------------------------------------------------------
```

```
+-----------------------------------------------------------------------
pu(hpo4)4 4-                                           date= 09-Jul90
 entered by= I.Puigdomenech             quality= fair
 keys   =
 subsets= plutonium
     charge=   -4.0         titr. factor=    0.0 eq/mol
   ion type= 4                  ion size=    0.0 a     hydr. no.=    0.0
  4 chemical elements
       1.000 pu              4.000 h               4.000 p
      16.000 o
          temp=    298.150 k          press=      1.000 bars
         delg0=  -1215.344 kcal/mol   delh0=       500. kcal/mol
            s0=      10.99 cal/mol/k     se=       4.36 cal/mol/k
            v0=            cc/mol        cp=      92.02 cal/mol/k
  0 species in reference reaction
  3 species in data0 reaction
     -1.000  pu(hpo4)4 4-             4.000  hpo4--
      1.000  pu++++
 t-p data grid is absent
 source=
* [lemire and garisto, 1989], see also [lemire and tremaine, 1980]
+-----------------------------------------------------------------------
puo2oh                                                 date= 29-Aug90
 entered by= I.Puigdomenech             quality= fair
 keys   =
 subsets= plutonium
     charge=    0.0         titr. factor=    0.0 eq/mol
   ion type= 0                  ion size=    0.0 a     hydr. no.=    0.0
  3 chemical elements
       1.000 pu              3.000 o               1.000 h
          temp=    298.150 k          press=      1.000 bars
         delg0=   -246.650 kcal/mol   delh0=   -270.392 kcal/mol
            s0=       500. cal/mol/k     se=       4.57 cal/mol/k
            v0=            cc/mol        cp=            cal/mol/k
  0 species in reference reaction
  4 species in data0 reaction
     -1.000  puo2oh                  -1.000  h+
      1.000  puo2+                    1.000  h2o
 t-p data grid is absent
 source=
* [lemire and tremaine, 1980], delta-Gr= -13.186 (log K= 9.7)
* s0=22.90, delta-Sr= -11.206
* dels0 = 22.90 - s0(Pu(c)) - 1/2 s0(H2(g)) - 3/2 s0(O2(g)) = -79.63
* delh0 = delg0 + 0.29815*dels0
* [bennett et al., 1990] give log k= 9.73 +/- 0.10
+-----------------------------------------------------------------------
puo2(co3)-                                             date= 29-Aug90
 entered by= I.Puigdomenech             quality= fair
 keys   =
 subsets= plutonium
     charge=   -1.0         titr. factor=    2.0 eq/mol
   ion type= 3                  ion size=    0.0 a     hydr. no.=    0.0
  3 chemical elements
       1.000 pu              5.000 o               1.000 c
          temp=    298.150 k          press=      1.000 bars
         delg0=   -336.277 kcal/mol   delh0=       500. kcal/mol
            s0=      47.80 cal/mol/k     se=       4.57 cal/mol/k
            v0=            cc/mol        cp=      -5.26 cal/mol/k
  0 species in reference reaction
  3 species in data0 reaction
     -1.000  puo2(co3)-               1.000  co3--
      1.000  puo2+
 t-p data grid is absent
 source=
* [bennett et al., 1987] estimate log k=4.4+/-0.7 (log k => 4.5)
* [bennett et al., 1990] give log k= 5.10 +/- 0.06
* s0 from [lemire and garisto, 1989] which give delg0=-335.33 (log k=4.4)
+-----------------------------------------------------------------------
```

```
+----------------------------------------------------------------------
puo2(co3)2---                                          date= 09-Jul90
 entered by= I.Puigdomenech            quality= speculative
 keys   =
 subsets= plutonium
     charge=   -3.0         titr. factor=    4.0 eq/mol
   ion type=  3                 ion size=    0.0 a      hydr. no.=    0.0
  3 chemical elements
       1.000 pu              8.000 o                2.000 c
          temp=     298.150 k           press=      1.000 bars
         delg0=    -465.110 kcal/mol    delh0=       500. kcal/mol
            s0=       26.29 cal/mol/k      se=       4.57 cal/mol/k
            v0=             cc/mol         cp=       35.1 cal/mol/k
  0 species in reference reaction
  3 species in data0 reaction
     -1.000  puo2(co3)2---                2.000  co3--
      1.000  puo2+
 t-p data grid is absent
 source=
* [lemire and garisto, 1989]
+----------------------------------------------------------------------
(puo2)2(oh)2++                                         date= 09-Jul90
 entered by= I.Puigdomenech            quality= fair
 keys   =
 subsets= plutonium
     charge=    2.0         titr. factor=    2.0 eq/mol
   ion type=  1                 ion size=    0.0 a      hydr. no.=    0.0
  3 chemical elements
       2.000 pu              2.000 h                6.000 o
          temp=      298.15 k           press=      1.013 bars
         delg0=    -463.910 kcal/mol    delh0=       500. kcal/mol
            s0=        0.00 cal/mol/k      se=       8.72 cal/mol/k
            v0=             cc/mol         cp=      -9.08 cal/mol/k
  0 species in reference reaction
  4 species in data0 reaction
     -1.000  (puo2)2(oh)2++              -2.000  h+
      2.000  puo2++                       2.000  h2o
 t-p data grid is absent
 source=
* [lemire and garisto, 1989], see also [lemire and tremaine, 1980]
+----------------------------------------------------------------------
(puo2)3(oh)5+                                          date= 09-Jul90
 entered by= I.Puigdomenech            quality= fair
 keys   =
 subsets= plutonium
     charge=    1.0         titr. factor=    5.0 eq/mol
   ion type=  1                 ion size=    0.0 a      hydr. no.=    0.0
  3 chemical elements
       3.000 pu             11.000 o                5.000 h
          temp=     298.150 k           press=      1.000 bars
         delg0=    -796.610 kcal/mol    delh0=       500. kcal/mol
            s0=       33.46 cal/mol/k      se=      13.08 cal/mol/k
            v0=             cc/mol         cp=       1.20 cal/mol/k
  0 species in reference reaction
  4 species in data0 reaction
     -1.000  (puo2)3(oh)5+               -5.000  h+
      3.000  puo2++                       5.000  h2o
 t-p data grid is absent
 source=
* [lemire and garisto, 1989], see also [lemire and tremaine, 1980]
+----------------------------------------------------------------------
```

```
+-------------------------------------------------------------------
puo2(oh)+                                                date= 09-Jul90
 entered by= I.Puigdomenech            quality= fair
 keys    =
 subsets= plutonium
     charge=    1.0         titr. factor=    1.0 eq/mol
   ion type=  1                ion size=    0.0 a     hydr. no.=    0.0
  3 chemical elements
      1.000 pu             3.000 o               1.000 h
         temp=    298.150 k          press=      1.000 bars
        delg0=   -229.900 kcal/mol   delh0=       500. kcal/mol
           s0=       6.21 cal/mol/k     se=       4.36 cal/mol/k
           v0=            cc/mol        cp=      15.54 cal/mol/k
  0 species in reference reaction
  4 species in data0 reaction
     -1.000  puo2(oh)+                -1.000  h+
      1.000  puo2++                    1.000  h2o
 t-p data grid is absent
 source=
* [lemire and garisto, 1989], see also [lemire and tremaine, 1980]
* This gives: log K = -5.64 for:   PuO2++ + H2O = PuO2(OH)+ + H+
*  and delta-S1=+30   cal/(mol K) for:  PuO2++ + OH- = PuO2(OH)+
*  and delta-Sr=+10.5 cal/(mol K) for:  PuO2++ + H2O = PuO2(OH)+ + H+
+-------------------------------------------------------------------
puo2(oh)2                                                date= 10-Jan91
 entered by= I.Puigdomenech            quality= fair
 keys    =
 subsets= plutonium
     charge=    0.0         titr. factor=    2.0 eq/mol
   ion type=  0                ion size=    0.0 a     hydr. no.=    0.0
  3 chemical elements
      1.000 pu             4.000 o               2.000 h
         temp=    298.150 k          press=      1.000 bars
        delg0=   -278.993 kcal/mol   delh0=    -313.21 kcal/mol
           s0=       500. cal/mol/k     se=       4.36 cal/mol/k
           v0=            cc/mol        cp=            cal/mol/k
  0 species in reference reaction
  4 species in data0 reaction
     -1.000  puo2(oh)2                -2.000  h+
      1.000  puo2++                    2.000  h2o
 t-p data grid is absent
 source=
* log K for reaction:  PuO2++ + 2H2O = 2H+ + PuO2(OH)2(aq):
*   The following data has been considered, and extrapolated to I=0 with
*   the Specific Interaction approach.
*   Ionic Medium  log K   log K(I=0)  Ref.
*    1 M NaClO4   -11.42   -11.2   [kraus and dam, 1949]
*    1 M NaClO4   -11.50           [schedin, 1975] + [kraus and dam, 1949]
*    1 M NaClO4   -11.24           [schedin, 1975] + [cassol et al., 1971]
*   0.1M NaClO4   -12.85   -12.4   [kim et al., 1984]
*   0.1M NaClO4   -11.25   -11.0   [musante and porthault, 1973]
*   Selected log K = -11.8+-1.0
* delta-S2 = deltaS1 - 6 cal/(mol K) for reaction:
*     PuO2(OH)+ + OH- = PuO2(OH)2(aq)
*   where deltaS1 is for the first hydrolysis step (see PuO2(OH)+),
*   delta-S2= 24, which gives S0=27.8
*   For PuO2++ + 2H2O = PuO2(OH)2(aq) + 2H+,  delta-Sr=15.4
* delta-Hr calculated from delta-Sr, and delh0 from delta-Hr and delh0 of
*    the reactants: delta-Hr= 15.279 + 0.29815*15.4 = 19.9
*    delh0 = 19.9 + 2*delh0(h2o) + delh0(puo2++) = -313.21
+-------------------------------------------------------------------
```

```
+--------------------------------------------------------------------
puo2(oh)3-                                                 date= 10-Jan91
 entered by= I.Puigdomenech            quality= fair
 keys    =
 subsets= plutonium
     charge=   -1.0         titr. factor=    3.0 eq/mol
   ion type=  2                ion size=    0.0 a     hydr. no.=    0.0
  3 chemical elements
      1.000 pu               5.000 o                3.000 h
         temp=    298.150 k           press=      1.000 bars
        delg0=   -322.037 kcal/mol    delh0=       500. kcal/mol
           s0=       43.2 cal/mol/k      se=       4.36 cal/mol/k
           v0=            cc/mol         cp=            cal/mol/k
  0 species in reference reaction
  4 species in data0 reaction
     -1.000  puo2(oh)3-                   -3.000  h+
      1.000  puo2++                        3.000  h2o
 t-p data grid is absent
 source=
* log K for reaction:  PuO2++ + 3H2O = 3H+ + PuO2(OH)3-:
*   The following data has been considered, and extrapolated to I=0 with
*   the Specific Interaction approach.
*   Ionic Medium   log K   log K(I=0)  Ref.
*    1 M NaClO4    -21.12    -21.2   [kraus and dam, 1949]
*   0.1M NaClO4    -24.44    -24.5   [kim et al., 1984]
*   0.1M NaClO4    -21.08    -21.1   [musante and porthault, 1973]
*   Selected log K = -22.9+-2.0
* delta-S3 = deltaS2 - 6 cal/(mol K) for reaction:
*     PuO2(OH)2(aq) + OH- = PuO2(OH)3-
*   where deltaS2 is for the 2nd hydrolysis step (see PuO2(OH)2(aq)),
*   delta-S3= 18, which gives S0=43.2
*   For PuO2++ + 3H2O = PuO2(OH)3- + 3H+,  delta-Sr=14.1
+--------------------------------------------------------------------
puo2(co3)                                                  date= Aug22,90
 entered by= I.Puigdomenech            quality= good
 keys    =
 subsets= plutonium
     charge=    0.0         titr. factor=    2.0 eq/mol
   ion type=  0                ion size=    0.0 a     hydr. no.=    0.0
  3 chemical elements
      1.000 pu               5.000 o                1.000 c
         temp=    298.150 k           press=      1.000 bars
        delg0=   -319.621 kcal/mol    delh0=   -352.994 kcal/mol
           s0=       500. cal/mol/k      se=       4.36 cal/mol/k
           v0=            cc/mol         cp=            cal/mol/k
  0 species in reference reaction
  3 species in data0 reaction
     -1.000  puo2(co3)                     1.000  co3--
      1.000  puo2++
 t-p data grid is absent
 source=
* [robouch and vitorge, 1987] log k= 9.2 (delta-Gr= -12.551 kcal/mol)
* entropy: delta-Sr for PuO2++ + CO3-- = PuO2CO3(aq) is set equal to delta-Sr
*   for UO2++ reaction [puigdomenech and bruno, 1988] = 60 (+-5) cal/(mol k)
*   which results in S0= 25 (+-5) cal/(mol k).
* delta-Hr calculated from delta-Sr, and delh0 from delta-Hr and delh0 of
*   the reactants: delta-Hr= -12.551 + 0.29815*60 = 5.338
*   delh0 = 5.338 + delh0(co3--) + delh0(puo2++) = -352.994
+--------------------------------------------------------------------
```

```
+----------------------------------------------------------------------
puo2(co3)2--                                               date= 09-Jul90
 entered by= I.Puigdomenech                  quality= good
 keys   =
 subsets= plutonium
     charge=   -2.0          titr. factor=    4.0 eq/mol
   ion type=  3                  ion size=    0.0 a     hydr. no.=    0.0
  3 chemical elements
       1.000 pu              8.000 o                 2.000 c
          temp=    298.150 k            press=      1.000 bars
         delg0=   -453.430 kcal/mol   delh0=       500. kcal/mol
            s0=      42.20 cal/mol/k     se=        4.36 cal/mol/k
            v0=            cc/mol        cp=       -90.6 cal/mol/k
  0 species in reference reaction
  3 species in data0 reaction
     -1.000  puo2(co3)2--                 2.000  co3--
      1.000  puo2++
 t-p data grid is absent
 source=
* [robouch and vitorge, 1987] log k= 14.8,  and  [lemire and tremaine, 1980]
* [sullivan et al., 1982] give delta-S=+244 J/(K mol)  (I=0.1 NaClO4)  for
*        PuO2++  +  2 CO3--  =  PuO2(CO3)2--
* s0 calculated from [sullivan et al., 1982]-value
+----------------------------------------------------------------------
puo2(co3)3 4-                                              date= 09-Jul90
 entered by= I.Puigdomenech                  quality= good
 keys   =
 subsets= plutonium
     charge=   -4.0          titr. factor=    6.0 eq/mol
   ion type=  3                  ion size=    0.0 a     hydr. no.=    0.0
  3 chemical elements
       1.000 pu             11.000 o                 3.000 c
          temp=    298.150 k            press=      1.000 bars
         delg0=   -583.150 kcal/mol   delh0=       500. kcal/mol
            s0=     -13.17 cal/mol/k     se=        4.36 cal/mol/k
            v0=            cc/mol        cp=            cal/mol/k
  0 species in reference reaction
  3 species in data0 reaction
     -1.000  puo2(co3)3 4-                3.000  co3--
      1.000  puo2++
 t-p data grid is absent
 source=
* [robouch and vitorge, 1987] log k= 17.4,  which combined with
* [ullman and schreiner, 1988] delta-h = -38.6 +/- 1 kj/mol (i=0.3 to 1.1 m)
* gives delta-s of reaction = -(-99.317 + 38.6)/298.15 = 203.6 j/(mol k)
* which is an approximate value (no ionic medium correction on delta-h)
* s0 = (-88)+3*(-56.90)+203.6 = -55.1 j/(mol k)
+----------------------------------------------------------------------
puo2(h2po4)+                                               date= 09-Jul90
 entered by= I.Puigdomenech                  quality= good
 keys   =
 subsets= plutonium
     charge=    1.0          titr. factor=    0.0 eq/mol
   ion type=  1                  ion size=    0.0 a     hydr. no.=    0.0
  4 chemical elements
       1.000 pu              6.000 o                 2.000 h
       1.000 p
          temp=    298.150 k            press=      1.000 bars
         delg0=   -456.501 kcal/mol   delh0=       500. kcal/mol
            s0=      16.97 cal/mol/k     se=       4.360 cal/mol/k
            v0=            cc/mol        cp=        9.32 cal/mol/k
  0 species in reference reaction
  4 species in data0 reaction
     -1.000  puo2(h2po4)+                 1.000  hpo4--
      1.000  puo2++                       1.000  h+
 t-p data grid is absent
 source=
* [lemire and garisto, 1989], see also [lemire and tremaine, 1980]
+----------------------------------------------------------------------
```

```
+--------------------------------------------------------------------
puo2(oh)2hco3-                                      date= 09-Jul90
 entered by= I.Puigdomenech              quality= fair
 keys    =
 subsets= plutonium
     charge=   -1.0         titr. factor=         eq/mol
   ion type=  3                ion size=    0.0 a     hydr. no.=    0.0
  4 chemical elements
       1.000 pu              7.000 o                3.000 h
       1.000 c
          temp=    298.150 k          press=       1.000 bars
         delg0=   -423.674 kcal/mol   delh0=        500. kcal/mol
            s0=       1.84 cal/mol/k     se=        4.36 cal/mol/k
            v0=            cc/mol        cp=             cal/mol/k
  0 species in reference reaction
  4 species in data0 reaction
     -1.000  puo2(oh)2hco3-              2.000  oh-
      1.000  puo2++                      1.000  hco3-
 t-p data grid is absent
 source=
* [sullivan et al., 1982] (see [newton and sullivan, 1985] p.396 & Table 2)
* give log k = 20, at I=0.1 for
*       PuO2++  +  2OH-  +  HCO3-  =  PuO2(OH)2HCO3-
* [sullivan et al., 1982] give delta-S=-151+/-50 J/(K mol) (at I=0.1)  for
*       PuO2(CO3)2--  +  2H2O  =  PuO2(OH)2HCO3-  +  HCO3-
*   which combined with S0(=110) of PuO2(CO3)2-- ([lemire and garisto, 1989])
*   and S0 for water(=69.95) and bicarbonate(=91.21), gives S0 listed above.
+--------------------------------------------------------------------
solids
+--------------------------------------------------------------------
pu2o3(c,beta)                                       date= 09-Jul90
 entered by= I.Puigdomenech              quality= fair
 keys    =
 subsets= plutonium
  2 chemical elements
       2.000 pu              3.000 o
          temp=     298.15 k          press=       1.013 bars
         delg0=    -380.98 kcal/mol   delh0=        500. kcal/mol
            s0=      30.35 cal/mol/k     v0=             cc/mol
  1 heat capacity range(s) follow
      equation=  0                  cp or a=       21.48 cal/mol/k
             b=      38.48                c=       -3.00
             d=       0.                  e=        0.
         limit=       600. k
  0 species in reference reaction
  4 species in data0 reaction
     -1.000  pu2o3(c,beta)              -6.000  h+
      2.000  pu+++                       3.000  h2o
 t-p data grid is absent
 source=
* [lemire and tremaine, 1980]
+--------------------------------------------------------------------
pu(oh)3(s)                                          date= 09-Jul90
 entered by= I.Puigdomenech              quality= fair
 keys    =
 subsets= plutonium
  3 chemical elements
       1.000 pu              3.000 o                3.000 h
          temp=     298.15 k          press=       1.013 bars
         delg0=    -277.72 kcal/mol   delh0=        500. kcal/mol
            s0=      21.99 cal/mol/k     v0=             cc/mol
  1 heat capacity range(s) follow
      equation=  0                  cp or a=       25.10 cal/mol/k
             b=       0.                  c=        0.
             d=       0.                  e=        0.
         limit=       600. k
  0 species in reference reaction
  4 species in data0 reaction
     -1.000  pu(oh)3(s)                 -3.000  h+
      1.000  pu+++                       3.000  h2o
 t-p data grid is absent
 source=
* [lemire and tremaine, 1980]
* this gives log k=-22.45 at 25 C, for Pu+++ + 3H2O = Pu(OH)3(s) + 3H+
+--------------------------------------------------------------------
```

```
+----------------------------------------------------------------------
puo2(c)                                                date= 09-Jul90
 entered by= I.Puigdomenech            quality= good
 keys   =
 subsets= plutonium
  2 chemical elements
       1.000 pu              2.000 o
          temp=     298.15 k          press=      1.013 bars
         delg0=   -238.528 kcal/mol   delh0=       500. kcal/mol
            s0=      15.81 cal/mol/k     v0=            cc/mol
  1 heat capacity range(s) follow
      equation=  0                  cp or a=      11.79 cal/mol/k
             b=      19.23                c=      -1.50
             d=       0.                  e=       0.
         limit=       600. k
  0 species in reference reaction
  4 species in data0 reaction
     -1.000  puo2(c)                      -4.000  h+
      1.000  pu++++                        2.000  h2o
 t-p data grid is absent
 source=
* [lemire and tremaine, 1980]
* [rai and ryan, 1982] believe puo2 more soluble than log k suggests due
* to radiation damage.
+----------------------------------------------------------------------
pu(oh)4(am)                                            date= 09-Jul90
 entered by= I.Puigdomenech            quality= fair
 keys   =
 subsets= plutonium
  3 chemical elements
       1.000 pu              4.000 o               4.000 h
          temp=     298.15 k          press=      1.013 bars
         delg0=   -342.973 kcal/mol   delh0=       500. kcal/mol
            s0=      25.57 cal/mol/k     v0=            cc/mol
  1 heat capacity range(s) follow
      equation=  0                  cp or a=      31.31 cal/mol/k
             b=       0.                  c=       0.
             d=       0.                  e=       0.
         limit=       600. k
  0 species in reference reaction
  4 species in data0 reaction
     -1.000  pu(oh)4(am)                  -4.000  h+
      1.000  pu++++                        4.000  h2o
 t-p data grid is absent
 source=
* [lemire and tremaine, 1980]
+----------------------------------------------------------------------
puo2oh(am)                                             date= 09-Jul90
 entered by= I.Puigdomenech            quality= fair
 keys   =
 subsets= plutonium
  3 chemical elements
       1.000 pu              3.000 o               1.000 h
          temp=     298.15 k          press=      1.013 bars
         delg0=    -252.39 kcal/mol   delh0=       500. kcal/mol
            s0=      20.79 cal/mol/k     v0=            cc/mol
  1 heat capacity range(s) follow
      equation=  0                  cp or a=      20.55 cal/mol/k
             b=       0.                  c=       0.
             d=       0.                  e=       0.
         limit=       600. k
  0 species in reference reaction
  4 species in data0 reaction
     -1.000  puo2oh(am)                   -1.000  h+
      1.000  puo2+                         1.000  h2o
 t-p data grid is absent
 source=
* [lemire and tremaine, 1980]
+----------------------------------------------------------------------
```

```
+----------------------------------------------------------------------
puo2(oh)2(c)                                           date= 09-Jul90
 entered by= I.Puigdomenech             quality= fair
 keys   =
 subsets= plutonium
  3 chemical elements
       1.000 pu              4.000 o              2.000 h
          temp=    298.150 k          press=      1.000 bars
         delg0=   -288.305 kcal/mol   delh0=       500. kcal/mol
            s0=      24.86 cal/mol/k     v0=            cc/mol
  1 heat capacity range(s) follow
      equation=  0                  cp or a=     26.77  cal/mol/k
             b=      0.                  c=      0.
             d=      0.                  e=      0.
         limit=     600.   k
  0 species in reference reaction
  4 species in data0 reaction
     -1.000  puo2(oh)2(c)                -2.000  h+
      1.000  puo2++                       2.000  h2o
 t-p data grid is absent
 source=
* [lemire and tremaine, 1980]
* PuO2(OH)2(c) = PuO2++ + 2 OH-, log Ksp=-23 at 0.1 M NaClO4 [Kim et al., 1984]
*   log K0 = log Ksp + log y(PuO2++) + 2 log y(OH-), where y(i) are act. coeff.
*          = -23.0    + (-0.3908)     + 2 (-0.1052) = -23.601
* delta-G0 of reaction is 32197. cal/mol
+----------------------------------------------------------------------
pu(oh)co3(s)                                           date= 09-Jul90
 entered by= I.Puigdomenech             quality= speculative
 keys   =
 subsets= plutonium
  4 chemical elements
       1.000 pu              4.000 o              1.000 h
       1.000 c
          temp=     298.15 k          press=      1.013 bars
         delg0=    -332.06 kcal/mol   delh0=       500. kcal/mol
            s0=       500. cal/mol/k     v0=            cc/mol
  0 heat capacity range(s) follow
  0 species in reference reaction
  5 species in data0 reaction
     -1.000  pu(oh)co3(s)                -1.000  h+
      1.000  pu+++                        1.000  h2o
      1.000  co3--
 t-p data grid is absent
 source=
* estimated log k=22(+-2) at 25 C for Pu+++ + CO3-- + OH- = Pu(OH)CO3(s)
*          (log k=8(+-2) at 25 C  for Pu+++ + CO3-- + H2O = Pu(OH)CO3(s) + H+)
* in analogy with Am+++ [kerrisk and silva, 1986]
* the existence of this solid phase has not been proven
+----------------------------------------------------------------------
puo2(co3)(s)                                           date= 09-Jul90
 entered by= I.Puigdomenech             quality= fair
 keys   =
 subsets= plutonium
  3 chemical elements
       1.000 pu              1.000 c              5.000 o
          temp=    298.150 k          press=      1.000 bars
         delg0=    -326.45 kcal/mol   delh0=       500. kcal/mol
            s0=       48.4 cal/mol/k     v0=            cc/mol
  1 heat capacity range(s) follow
      equation=  0                  cp or a=     28.00 cal/mol/k
             b=      0.                  c=       0.
             d=      0.                  e=       0.
         limit=     600.   k
  0 species in reference reaction
  3 species in data0 reaction
     -1.000  puo2(co3)(s)                 1.000  co3--
      1.000  puo2++
 t-p data grid is absent
 source=
* [robouch and vitorge, 1987] log ksp= -14.2
* entropy from delta-S= 83 cal/(mol k) of reaction UO2++ + CO3-- = UO2CO3(s)
*   [lemire, 1988]
* Cp from Kopp's law (according to Sturtevant, 1959)
+----------------------------------------------------------------------
```

```
+-------------------------------------------------------------------
pu(hpo4)2(c)                                            date= 09-Jul90
 entered by= I.Puigdomenech              quality= fair
 keys   =
 subsets= plutonium
  4 chemical elements
      1.000 pu              2.000 h               8.000 o
      2.000 p
         temp=     298.15 k          press=      1.013 bars
        delg0=   -673.520 kcal/mol   delh0=       500. kcal/mol
           s0=      44.69 cal/mol/k    v0=            cc/mol
  1 heat capacity range(s) follow
     equation=  0                   cp or a=     53.54 cal/mol/k
           b=      0.                    c=       0.
           d=      0.                    e=       0.
        limit=     600.   k
  0 species in reference reaction
  3 species in data0 reaction
     -1.000  pu(hpo4)2(c)              2.000  hpo4--
      1.000  pu++++
 t-p data grid is absent
 source=
* [lemire and tremaine, 1980]
+-------------------------------------------------------------------
puo2hpo4(c)                                             date= 09-Jul90
 entered by= I.Puigdomenech              quality= fair
 keys   =
 subsets= plutonium
  4 chemical elements
      1.000 pu              6.000 o               1.000 h
      1.000 p
         temp=    298.150 k          press=      1.000 bars
        delg0=   -458.413 kcal/mol   delh0=       500. kcal/mol
           s0=      36.81 cal/mol/k    v0=            cc/mol
  1 heat capacity range(s) follow
     equation=  0                   cp or a=     38.00 cal/mol/k
           b=      0.                    c=       0.
           d=      0.                    e=       0.
        limit=     600.   k
  0 species in reference reaction
  3 species in data0 reaction
     -1.000  puo2hpo4(c)               1.000  hpo4--
      1.000  puo2++
 t-p data grid is absent
 source=
* [lemire and tremaine, 1980]
+-------------------------------------------------------------------
stop.
```

APPENDIX B

The data blocks to be used in the DATA0 file of the EQ3/6 package are listed below. This data blocks were produced by the MCRT program with the thermodynamic data listed in Appendix A. The DATA0 file is reformatted into DATA1, DATA2 and DATA3 files before the equilibrium constants may be used as input for the EQ3NR and EQ6 programs.

For users requiring redox reactions involving "e^-" rather than "$O_2(g)$", the necessary reactions and equilibrium constants may be obtained from the data blocks listed below. As an example, the following equilibrium at 100°C,

$$Pu^{4+} + H_2O + \tfrac{1}{2}O_2(g) = PuO_2^{2+} + 2H^+ \qquad \log K_{eq}=6.6437 \tag{B.1}$$

will be converted into,

$$Pu^{4+} + 2H_2O = PuO_2^{2+} + 4H^+ + 2e^- \tag{B.2}$$

using the equilibrium,

$$H_2O = \tfrac{1}{2}O_2(g) + 2H^+ + 2e^- \tag{B.3}$$

The equilibrium constant at 100°C for the last reaction may be obtained from the apparent standard partial molal Gibbs free energies of formation of the reactants involved,

$$\Delta G^\circ_a = \Delta G^\circ_f + (G^\circ_{P,T} - G^\circ_{P_r,T_r})$$

which for H^+ is zero at all temperatures, and for $O_2(g)$ and H_2O are listed in the MDAS file of the EQ3/6 package, and in Table B.1. The equilibrium constant is given by

$$\log K_{eq} = - \Delta_r\bar{G}^\circ \;/\; (R\ T\ 2.303)$$

for example, at 100°C:

$$\log K_{eq}(B.3) = - (\tfrac{1}{2}(-3.737)-(-58.097))/1.7074 = -32.932$$

and for reaction B.1, the equilibrium constant at 100°C is therefore,

$$\begin{aligned}\log K_{eq}(B.2) &= \log K_{eq}(B.1) + \log K_{eq}(B.3)\\ &= 6.644 - 32.932 = -26.288\end{aligned}$$

Table B.1

Temp.	Pressure	ΔG°_a / (kcal/mol)		$\log K_{eq}$
(°C)	(bars)	H_2O	$O_2(g)$	(B.3)
0	1.0	-56.288	1.218	-45.523
25	1.0	-56.686	-.000	-41.553
60	1.0	-57.307	-1.729	-37.026
100	1.0	-58.097	-3.737	-32.932
150	4.8	-59.192	-6.291	-28.946
200	15.5	-60.393	-8.888	-25.843
250	39.8	-61.689	-11.524	-23.364
300	85.9	-63.069	-14.197	-21.342

The data blocks to be used in the DATA0 file of the EQ3/6 package are listed below. This data blocks were produced by the MCRT program with the thermodynamic data listed in Appendix A.

```
dfile
 MCRT.3245R65
+----------------------------------------------------------------------
pu+++
    entered by= MCRT (see below)        date= Jan11,91
        source= MCRT.3245R65         quality= fair
        charge=   3.0           titr. factor=   0.0 eq/mol
      ion size=   8.0 a         hydr. number=   0.0
     1 chemical elements=
       1.000 pu
     5 species in reaction=
      -1.000 pu+++          -0.500 h2o             1.000 puo2++
       1.000 h+             -0.750 o2(g)
*    log k grid (0-25-60-100/150-200-250-300 c) =
        11.8440   10.4563    8.8508    7.3893
         5.9652    4.8552    3.9793    3.2785
*    delvr grid (0-25-60-100/150-200-250-300 c) =
       500.0000  500.0000  500.0000  500.0000
       500.0000  500.0000  500.0000  500.0000
* MCRT file mdas.3245 Pu, rev.   Jan11,91, criss-cobble method
*   (quality of pu+++              data = good        )
+----------------------------------------------------------------------
pu++++
    entered by= MCRT (see below)        date= Jan11,91
        source= MCRT.3245R65         quality= fair
        charge=   4.0           titr. factor=   0.0 eq/mol
      ion size=  11.0 a         hydr. number=   0.0
     1 chemical elements=
       1.000 pu
     5 species in reaction=
      -1.000 pu++++         -1.000 h2o             1.000 puo2++
       2.000 h+             -0.500 o2(g)
*    log k grid (0-25-60-100/150-200-250-300 c) =
         6.6523    6.6707    6.6626    6.6437
         6.6184    6.5934    6.5873    6.5986
*    delvr grid (0-25-60-100/150-200-250-300 c) =
       500.0000  500.0000  500.0000  500.0000
       500.0000  500.0000  500.0000  500.0000
* MCRT file mdas.3245 Pu, rev.   Jan11,91, criss-cobble method
*   (quality of pu++++             data = good        )
+----------------------------------------------------------------------
```

```
+-----------------------------------------------------------------------
puo2+
    entered by= MCRT (see below)        date= Jan11,91
        source= MCRT.3245R65         quality= fair
        charge=   1.0           titr. factor=   0.0 eq/mol
      ion size=   4.0 a         hydr. number=   0.0
     2 chemical elements=
       1.000 pu              2.000 o
     5 species in reaction=
      -1.000 puo2+          -1.000 h+                1.000 puo2++
       0.500 h2o            -0.250 o2(g)
*    log k grid (0-25-60-100/150-200-250-300 c) =
         5.2748    4.4673    3.5321    2.6451
         1.7218    0.9478    0.2722   -0.3318
*    delvr grid (0-25-60-100/150-200-250-300 c) =
       500.0000  500.0000  500.0000  500.0000
       500.0000  500.0000  500.0000  500.0000
* MCRT file mdas.3245 Pu, rev.   Jan11,91, criss-cobble method
*   (quality of puo2+             data = fair        )
+-----------------------------------------------------------------------
pu(co3)+
    entered by= MCRT (see below)        date= Jan11,91
        source= MCRT.3245R65         quality= speculative
        charge=   1.0           titr. factor=   2.0 eq/mol
      ion size=   4.0 a         hydr. number=   0.0
     3 chemical elements=
       1.000 pu              3.000 o                1.000 c
     3 species in reaction=
      -1.000 pu(co3)+        1.000 co3--             1.000 pu+++
*    log k grid (0-25-60-100/150-200-250-300 c) =
        -8.9956   -9.0010   -9.2625   -9.8233
       -10.7259  -11.7961  -13.0320  -14.3784
*    delvr grid (0-25-60-100/150-200-250-300 c) =
       500.0000    0.0000  500.0000  500.0000
       500.0000  500.0000  500.0000  500.0000
* MCRT file mdas.3245 Pu, rev.   Jan11,91, criss-cobble method
*   (quality of pu(co3)+          data = speculative )
+-----------------------------------------------------------------------
pu(co3)++
    entered by= MCRT (see below)        date= Jan11,91
        source= MCRT.3245R65         quality= speculative
        charge=   2.0           titr. factor=   2.0 eq/mol
      ion size=   5.0 a         hydr. number=   0.0
     3 chemical elements=
       1.000 pu              3.000 o                1.000 c
     3 species in reaction=
      -1.000 pu(co3)++       1.000 co3--             1.000 pu++++
*    log k grid (0-25-60-100/150-200-250-300 c) =
       -10.7252  -12.9995  -15.7695  -18.4304
       -21.1245  -23.3594  -25.3166  -27.0557
*    delvr grid (0-25-60-100/150-200-250-300 c) =
       500.0000    0.0000  500.0000  500.0000
       500.0000  500.0000  500.0000  500.0000
* MCRT file mdas.3245 Pu, rev.   Jan11,91, criss-cobble method
*   (quality of pu(co3)++         data = speculative )
+-----------------------------------------------------------------------
pu(co3)5 6-
    entered by= MCRT (see below)        date= Jan11,91
        source= MCRT.3245R65         quality= speculative
        charge=  -6.0           titr. factor=  10.0 eq/mol
      ion size=   4.0 a         hydr. number=   0.0
     3 chemical elements=
       1.000 pu              5.000 c               15.000 o
     3 species in reaction=
      -1.000 pu(co3)5 6-     5.000 co3--             1.000 pu++++
*    log k grid (0-25-60-100/150-200-250-300 c) =
       -39.7192  -39.0534  -39.4263  -41.2001
       -44.5065  -48.7114  -53.7637  -59.3872
*    delvr grid (0-25-60-100/150-200-250-300 c) =
       500.0000    0.0000  500.0000  500.0000
       500.0000  500.0000  500.0000  500.0000
* MCRT file mdas.3245 Pu, rev.   Jan11,91, criss-cobble method
*   (quality of pu(co3)5 6-       data = speculative )
+-----------------------------------------------------------------------
```

```
+-----------------------------------------------------------------------
pu(h2po4)++
    entered by= MCRT (see below)        date= Jan11,91
        source= MCRT.3245R65         quality= good
        charge=   2.0          titr. factor=   0.0 eq/mol
      ion size=   5.0 a        hydr. number=   0.0
     4 chemical elements=
       1.000 pu              2.000 h               1.000 p
       4.000 o
     4 species in reaction=
      -1.000 pu(h2po4)++     1.000 h+              1.000 pu+++
       1.000 hpo4--
*    log k grid (0-25-60-100/150-200-250-300 c) =
        -9.2594   -9.6585  -10.2744  -10.9952
       -11.8994  -12.8186  -13.7465  -14.6806
*    delvr grid (0-25-60-100/150-200-250-300 c) =
       500.0000    0.0000  500.0000  500.0000
       500.0000  500.0000  500.0000  500.0000
* MCRT file mdas.3245 Pu, rev.   Jan11,91, criss-cobble method
*   (quality of pu(h2po4)++        data = good        )
+-----------------------------------------------------------------------
pu(hpo4)++
    entered by= MCRT (see below)        date= Jan11,91
        source= MCRT.3245R65         quality= fair
        charge=   2.0          titr. factor=   0.0 eq/mol
      ion size=   5.0 a        hydr. number=   0.0
     4 chemical elements=
       1.000 pu              1.000 h               1.000 p
       4.000 o
     3 species in reaction=
      -1.000 pu(hpo4)++      1.000 hpo4--          1.000 pu++++
*    log k grid (0-25-60-100/150-200-250-300 c) =
       -12.4012  -12.9841  -13.8293  -14.7987
       -16.0014  -17.2047  -18.4126  -19.6233
*    delvr grid (0-25-60-100/150-200-250-300 c) =
       500.0000    0.0000  500.0000  500.0000
       500.0000  500.0000  500.0000  500.0000
* MCRT file mdas.3245 Pu, rev.   Jan11,91, criss-cobble method
*   (quality of pu(hpo4)++         data = fair        )
+-----------------------------------------------------------------------
pu(hpo4)2
    entered by= MCRT (see below)        date= Jan11,91
        source= MCRT.3245R65         quality= fair
        charge=   0.0          titr. factor=   0.0 eq/mol
      ion size=   4.0 a        hydr. number=   0.0
     4 chemical elements=
       1.000 pu              8.000 o               2.000 p
       2.000 h
     3 species in reaction=
      -1.000 pu(hpo4)2       2.000 hpo4--          1.000 pu++++
*    log k grid (0-25-60-100/150-200-250-300 c) =
       -23.5257  -23.8000  -24.5441  -25.8635
       -28.2443  -31.6284  500.0000  500.0000
*    delvr grid (0-25-60-100/150-200-250-300 c) =
       500.0000    0.0000  500.0000  500.0000
       500.0000  500.0000  500.0000  500.0000
* MCRT file mdas.3245 Pu, rev.   Jan11,91, dquant method
*   (quality of pu(hpo4)2          data = fair        )
+-----------------------------------------------------------------------
pu(hpo4)3--
    entered by= MCRT (see below)        date= Jan11,91
        source= MCRT.3245R65         quality= fair
        charge=  -2.0          titr. factor=   0.0 eq/mol
      ion size=   4.0 a        hydr. number=   0.0
     4 chemical elements=
       1.000 pu              3.000 h               3.000 p
      12.000 o
     3 species in reaction=
      -1.000 pu(hpo4)3--     3.000 hpo4--          1.000 pu++++
*    log k grid (0-25-60-100/150-200-250-300 c) =
       -33.6921  -33.3896  -33.6255  -34.5823
       -36.4598  -38.8612  -41.6652  -44.7666
*    delvr grid (0-25-60-100/150-200-250-300 c) =
       500.0000    0.0000  500.0000  500.0000
       500.0000  500.0000  500.0000  500.0000
* MCRT file mdas.3245 Pu, rev.   Jan11,91, criss-cobble method
*   (quality of pu(hpo4)3--        data = fair        )
+-----------------------------------------------------------------------
```

```
+-----------------------------------------------------------------------
pu(hpo4)4 4-
    entered by= MCRT (see below)        date= Jan11,91
        source= MCRT.3245R65         quality= fair
        charge=  -4.0           titr. factor=   0.0 eq/mol
      ion size=   4.0 a         hydr. number=   0.0
     4 chemical elements=
       1.000 pu              4.000 h               4.000 p
      16.000 o
     3 species in reaction=
      -1.000 pu(hpo4)4 4-    4.000 hpo4--          1.000 pu++++
*    log k grid (0-25-60-100/150-200-250-300 c) =
       -44.6522  -43.1537  -42.1906  -42.2814
       -43.6229  -45.9108  -48.8955  -52.3959
*    delvr grid (0-25-60-100/150-200-250-300 c) =
       500.0000    0.0000  500.0000  500.0000
       500.0000  500.0000  500.0000  500.0000
* MCRT file mdas.3245 Pu, rev.   Jan11,91, criss-cobble method
*   (quality of pu(hpo4)4 4-      data = fair        )
+-----------------------------------------------------------------------
(puo2)2(oh)2++
    entered by= MCRT (see below)        date= Jan11,91
        source= MCRT.3245R65         quality= fair
        charge=   2.0           titr. factor=   2.0 eq/mol
      ion size=   5.0 a         hydr. number=   0.0
     3 chemical elements=
       2.000 pu              2.000 h               6.000 o
     4 species in reaction=
      -1.000 (puo2)2(oh)2   -2.000 h+              2.000 puo2++
       2.000 h2o
*    log k grid (0-25-60-100/150-200-250-300 c) =
          9.2276    8.2597    7.2552    6.4651
          5.8342    5.4742    5.2924    5.2319
*    delvr grid (0-25-60-100/150-200-250-300 c) =
       500.0000   36.1364  500.0000  500.0000
       500.0000  500.0000  500.0000  500.0000
* MCRT file mdas.3245 Pu, rev.   Jan11,91, criss-cobble method
*   (quality of (puo2)2(oh)2++     data = fair        )
+-----------------------------------------------------------------------
(puo2)3(oh)5+
    entered by= MCRT (see below)        date= Jan11,91
        source= MCRT.3245R65         quality= fair
        charge=   1.0           titr. factor=   5.0 eq/mol
      ion size=   4.0 a         hydr. number=   0.0
     3 chemical elements=
       3.000 pu             11.000 o               5.000 h
     4 species in reaction=
      -1.000 (puo2)3(oh)5   -5.000 h+              3.000 puo2++
       5.000 h2o
*    log k grid (0-25-60-100/150-200-250-300 c) =
        23.9786   21.6497   19.2035   17.2144
        15.5260   14.4469   13.7616   13.3430
*    delvr grid (0-25-60-100/150-200-250-300 c) =
       500.0000   90.3411  500.0000  500.0000
       500.0000  500.0000  500.0000  500.0000
* MCRT file mdas.3245 Pu, rev.   Jan11,91, criss-cobble method
*   (quality of (puo2)3(oh)5+      data = fair        )
+-----------------------------------------------------------------------
puo2(co3)
    entered by= MCRT (see below)        date= Jan11,91
        source= MCRT.3245R65         quality= fair
        charge=   0.0           titr. factor=   2.0 eq/mol
      ion size=   4.0 a         hydr. number=   0.0
     3 chemical elements=
       1.000 pu              5.000 o               1.000 c
     3 species in reaction=
      -1.000 puo2(co3)       1.000 co3--           1.000 puo2++
*    log k grid (0-25-60-100/150-200-250-300 c) =
        -8.9086   -9.1997   -9.7297  -10.5099
       -11.7773  -13.4720  500.0000  500.0000
*    delvr grid (0-25-60-100/150-200-250-300 c) =
       500.0000    0.0000  500.0000  500.0000
       500.0000  500.0000  500.0000  500.0000
* MCRT file mdas.3245 Pu, rev.   Jan11,91, dquant method
*   (quality of puo2(co3)          data = good        )
+-----------------------------------------------------------------------
```

```
+----------------------------------------------------------------------
puo2(co3)-
    entered by= MCRT (see below)        date= Jan11,91
        source= MCRT.3245R65         quality= fair
        charge=  -1.0           titr. factor=   2.0 eq/mol
      ion size=   4.0 a         hydr. number=   0.0
     3 chemical elements=
       1.000 pu              5.000 o               1.000 c
     3 species in reaction=
      -1.000 puo2(co3)-      1.000 co3--           1.000 puo2+
*    log k grid (0-25-60-100/150-200-250-300 c) =
        -4.2934   -5.0994   -6.1668   -7.2886
        -8.5171   -9.6347  -10.7131  -11.7492
*    delvr grid (0-25-60-100/150-200-250-300 c) =
       500.0000    0.0000  500.0000  500.0000
       500.0000  500.0000  500.0000  500.0000
* MCRT file mdas.3245 Pu, rev.   Jan11,91, criss-cobble method
*   (quality of puo2(co3)-        data = fair        )
+----------------------------------------------------------------------
puo2(co3)2--
    entered by= MCRT (see below)        date= Jan11,91
        source= MCRT.3245R65         quality= fair
        charge=  -2.0           titr. factor=   4.0 eq/mol
      ion size=   4.0 a         hydr. number=   0.0
     3 chemical elements=
       1.000 pu              8.000 o               2.000 c
     3 species in reaction=
      -1.000 puo2(co3)2--    2.000 co3--           1.000 puo2++
*    log k grid (0-25-60-100/150-200-250-300 c) =
       -14.4951  -14.7990  -15.5595  -16.7524
       -18.4450  -20.3256  -22.4253  -24.6621
*    delvr grid (0-25-60-100/150-200-250-300 c) =
       500.0000    0.0000  500.0000  500.0000
       500.0000  500.0000  500.0000  500.0000
* MCRT file mdas.3245 Pu, rev.   Jan11,91, criss-cobble method
*   (quality of puo2(co3)2--      data = good        )
+----------------------------------------------------------------------
puo2(co3)2---
    entered by= MCRT (see below)        date= Jan11,91
        source= MCRT.3245R65         quality= speculative
        charge=  -3.0           titr. factor=   4.0 eq/mol
      ion size=   4.0 a         hydr. number=   0.0
     3 chemical elements=
       1.000 pu              8.000 o               2.000 c
     3 species in reaction=
      -1.000 puo2(co3)2--    2.000 co3--           1.000 puo2+
*    log k grid (0-25-60-100/150-200-250-300 c) =
        -6.6642   -7.0513   -7.8757   -9.0951
       -10.7903  -12.6423  -14.6808  -16.8360
*    delvr grid (0-25-60-100/150-200-250-300 c) =
       500.0000    0.0000  500.0000  500.0000
       500.0000  500.0000  500.0000  500.0000
* MCRT file mdas.3245 Pu, rev.   Jan11,91, criss-cobble method
*   (quality of puo2(co3)2---     data = speculative )
+----------------------------------------------------------------------
puo2(co3)3 4-
    entered by= MCRT (see below)        date= Jan11,91
        source= MCRT.3245R65         quality= fair
        charge=  -4.0           titr. factor=   6.0 eq/mol
      ion size=   4.0 a         hydr. number=   0.0
     3 chemical elements=
       1.000 pu             11.000 o               3.000 c
     3 species in reaction=
      -1.000 puo2(co3)3 4    3.000 co3--           1.000 puo2++
*    log k grid (0-25-60-100/150-200-250-300 c) =
       -18.2029  -17.4011  -16.9870  -17.2377
       -18.1682  -19.6010  -21.4811  -23.6701
*    delvr grid (0-25-60-100/150-200-250-300 c) =
       500.0000    0.0000  500.0000  500.0000
       500.0000  500.0000  500.0000  500.0000
* MCRT file mdas.3245 Pu, rev.   Jan11,91, criss-cobble method
*   (quality of puo2(co3)3 4-     data = good        )
+----------------------------------------------------------------------
```

```
+--------------------------------------------------------------------
puo2(h2po4)+
    entered by= MCRT (see below)        date= Jan11,91
        source= MCRT.3245R65        quality= fair
        charge=   1.0          titr. factor=   0.0 eq/mol
      ion size=   4.0 a        hydr. number=   0.0
     4 chemical elements=
       1.000 pu              6.000 o               2.000 h
       1.000 p
     4 species in reaction=
      -1.000 puo2(h2po4)+    1.000 hpo4--          1.000 puo2++
       1.000 h+
*    log k grid (0-25-60-100/150-200-250-300 c) =
       -11.3562  -11.1861  -11.1641  -11.3335
       -11.7399  -12.3070  -12.9861  -13.7478
*    delvr grid (0-25-60-100/150-200-250-300 c) =
       500.0000    0.0000  500.0000  500.0000
       500.0000  500.0000  500.0000  500.0000
* MCRT file mdas.3245 Pu, rev.   Jan11,91, criss-cobble method
*   (quality of puo2(h2po4)+      data = good        )
+--------------------------------------------------------------------
puo2oh
    entered by= MCRT (see below)        date= Jan11,91
        source= MCRT.3245R65        quality= fair
        charge=   0.0          titr. factor=   0.0 eq/mol
      ion size=   4.0 a        hydr. number=   0.0
     3 chemical elements=
       1.000 pu              3.000 o               1.000 h
     4 species in reaction=
      -1.000 puo2oh         -1.000 h+              1.000 puo2+
       1.000 h2o
*    log k grid (0-25-60-100/150-200-250-300 c) =
         10.7646    9.6675    8.3730    7.1351
          5.8235    4.6592  500.0000  500.0000
*    delvr grid (0-25-60-100/150-200-250-300 c) =
       500.0000   18.0682  500.0000  500.0000
       500.0000  500.0000  500.0000  500.0000
* MCRT file mdas.3245 Pu, rev.   Jan11,91, dquant method
*   (quality of puo2oh            data = fair        )
+--------------------------------------------------------------------
puo2(oh)+
    entered by= MCRT (see below)        date= Jan11,91
        source= MCRT.3245R65        quality= fair
        charge=   1.0          titr. factor=   1.0 eq/mol
      ion size=   4.0 a        hydr. number=   0.0
     3 chemical elements=
       1.000 pu              3.000 o               1.000 h
     4 species in reaction=
      -1.000 puo2(oh)+      -1.000 h+              1.000 puo2++
       1.000 h2o
*    log k grid (0-25-60-100/150-200-250-300 c) =
          6.3744    5.6361    4.8135    4.0744
          3.3540    2.7913    2.3300    1.9402
*    delvr grid (0-25-60-100/150-200-250-300 c) =
       500.0000   18.0682  500.0000  500.0000
       500.0000  500.0000  500.0000  500.0000
* MCRT file mdas.3245 Pu, rev.   Jan11,91, criss-cobble method
*   (quality of puo2(oh)+         data = fair        )
+--------------------------------------------------------------------
puo2(oh)2
    entered by= MCRT (see below)        date= Jan11,91
        source= MCRT.3245R65        quality= fair
        charge=   0.0          titr. factor=   2.0 eq/mol
      ion size=   4.0 a        hydr. number=   0.0
     3 chemical elements=
       1.000 pu              4.000 o               2.000 h
     4 species in reaction=
      -1.000 puo2(oh)2      -2.000 h+              1.000 puo2++
       2.000 h2o
*    log k grid (0-25-60-100/150-200-250-300 c) =
         13.1759   11.8044   10.1815    8.6230
          6.9613    5.4726  500.0000  500.0000
*    delvr grid (0-25-60-100/150-200-250-300 c) =
       500.0000   36.1364  500.0000  500.0000
       500.0000  500.0000  500.0000  500.0000
* MCRT file mdas.3245 Pu, rev.   Jan11,91, dquant method
*   (quality of puo2(oh)2         data = fair        )
+--------------------------------------------------------------------
```

```
+--------------------------------------------------------------------
puo2(oh)3-
    entered by= MCRT (see below)        date= Jan11,91
        source= MCRT.3245R65         quality= fair
        charge=  -1.0           titr. factor=   3.0 eq/mol
      ion size=   4.0 a         hydr. number=   0.0
     3 chemical elements=
       1.000 pu              5.000 o               3.000 h
     4 species in reaction=
      -1.000 puo2(oh)3-     -3.000 h+             1.000 puo2++
       3.000 h2o
*    log k grid (0-25-60-100/150-200-250-300 c) =
        25.3758   22.9057   20.2982   18.1372
        16.2598   15.0372   14.2554   13.7996
*    delvr grid (0-25-60-100/150-200-250-300 c) =
       500.0000   54.2047  500.0000  500.0000
       500.0000  500.0000  500.0000  500.0000
* MCRT file mdas.3245 Pu, rev.   Jan11,91, criss-cobble method
*   (quality of puo2(oh)3-        data = fair        )
+--------------------------------------------------------------------
puo2(oh)2hco3-
    entered by= MCRT (see below)        date= Jan11,91
        source= MCRT.3245R65         quality= fair
        charge=  -1.0           titr. factor=   0.0 eq/mol
      ion size=   4.0 a         hydr. number=   0.0
     4 chemical elements=
       1.000 pu              7.000 o               3.000 h
       1.000 c
     4 species in reaction=
      -1.000 puo2(oh)2hco    2.000 oh-             1.000 puo2++
       1.000 hco3-
*    log k grid (0-25-60-100/150-200-250-300 c) =
       -21.7357  -19.9990  -17.9531  -15.9489
       -13.8629  -12.1476  -10.8275  -10.2271
*    delvr grid (0-25-60-100/150-200-250-300 c) =
       500.0000    9.0298  500.0000  500.0000
       500.0000  500.0000  500.0000  500.0000
* MCRT file mdas.3245 Pu, rev.   Jan11,91, criss-cobble method
*   (quality of puo2(oh)2hco3-    data = fair        )
+--------------------------------------------------------------------
pu(oh)++
    entered by= MCRT (see below)        date= Jan11,91
        source= MCRT.3245R65         quality= good
        charge=   2.0           titr. factor=   0.0 eq/mol
      ion size=   5.0 a         hydr. number=   0.0
     3 chemical elements=
       1.000 pu              1.000 o               1.000 h
     4 species in reaction=
      -1.000 pu(oh)++       -1.000 h+             1.000 pu+++
       1.000 h2o
*    log k grid (0-25-60-100/150-200-250-300 c) =
         8.8400    7.9699    6.9930    6.1070
         5.2336    4.5425    3.9705    3.4830
*    delvr grid (0-25-60-100/150-200-250-300 c) =
       500.0000   18.0682  500.0000  500.0000
       500.0000  500.0000  500.0000  500.0000
* MCRT file mdas.3245 Pu, rev.   Jan11,91, criss-cobble method
*   (quality of pu(oh)++          data = good        )
+--------------------------------------------------------------------
pu(oh)+++
    entered by= MCRT (see below)        date= Jan11,91
        source= MCRT.3245R65         quality= fair
        charge=   3.0           titr. factor=   0.0 eq/mol
      ion size=   8.0 a         hydr. number=   0.0
     3 chemical elements=
       1.000 pu              1.000 o               1.000 h
     4 species in reaction=
      -1.000 pu(oh)+++      -1.000 h+             1.000 pu++++
       1.000 h2o
*    log k grid (0-25-60-100/150-200-250-300 c) =
         1.3030    0.5126   -0.3510   -1.0898
        -1.7555   -2.2259   -2.5689   -2.8209
*    delvr grid (0-25-60-100/150-200-250-300 c) =
       500.0000   18.0682  500.0000  500.0000
       500.0000  500.0000  500.0000  500.0000
* MCRT file mdas.3245 Pu, rev.   Jan11,91, criss-cobble method
*   (quality of pu(oh)+++         data = fair        )
+--------------------------------------------------------------------
```

```
+-----------------------------------------------------------------------
pu(oh)2++
    entered by= MCRT (see below)        date= Jan11,91
        source= MCRT.3245R65         quality= fair
        charge=   2.0           titr. factor=   0.0 eq/mol
      ion size=   5.0 a         hydr. number=   0.0
     3 chemical elements=
       1.000 pu               2.000 o               2.000 h
     4 species in reaction=
      -1.000 pu(oh)2++       -2.000 h+              1.000 pu++++
       2.000 h2o
*    log k grid (0-25-60-100/150-200-250-300 c) =
         3.5523    2.3298    0.9966   -0.1559
        -1.2171   -1.9899   -2.5801   -3.0418
*    delvr grid (0-25-60-100/150-200-250-300 c) =
       500.0000   36.1364  500.0000  500.0000
       500.0000  500.0000  500.0000  500.0000
* MCRT file mdas.3245 Pu, rev.   Jan11,91, criss-cobble method
*   (quality of pu(oh)2++          data = fair        )
+-----------------------------------------------------------------------
pu(oh)3+
    entered by= MCRT (see below)        date= Jan11,91
        source= MCRT.3245R65         quality= fair
        charge=   1.0           titr. factor=   3.0 eq/mol
      ion size=   4.0 a         hydr. number=   0.0
     3 chemical elements=
       1.000 pu               3.000 o               3.000 h
     4 species in reaction=
      -1.000 pu(oh)3+        -3.000 h+              1.000 pu++++
       3.000 h2o
*    log k grid (0-25-60-100/150-200-250-300 c) =
         6.8813    5.2906    3.5549    2.0379
         0.6119   -0.4549   -1.2996   -1.9900
*    delvr grid (0-25-60-100/150-200-250-300 c) =
       500.0000   54.2047  500.0000  500.0000
       500.0000  500.0000  500.0000  500.0000
* MCRT file mdas.3245 Pu, rev.   Jan11,91, criss-cobble method
*   (quality of pu(oh)3+           data = fair        )
+-----------------------------------------------------------------------
pu(oh)4
    entered by= MCRT (see below)        date= Jan11,91
        source= MCRT.3245R65         quality= fair
        charge=   0.0           titr. factor=   4.0 eq/mol
      ion size=   4.0 a         hydr. number=   0.0
     3 chemical elements=
       1.000 pu               4.000 o               4.000 h
     4 species in reaction=
      -1.000 pu(oh)4         -4.000 h+              1.000 pu++++
       4.000 h2o
*    log k grid (0-25-60-100/150-200-250-300 c) =
        10.8471    9.1749    7.1134    5.0129
         2.5790    0.1492  500.0000  500.0000
*    delvr grid (0-25-60-100/150-200-250-300 c) =
       500.0000   72.2729  500.0000  500.0000
       500.0000  500.0000  500.0000  500.0000
* MCRT file mdas.3245 Pu, rev.   Jan11,91, dquant method
*   (quality of pu(oh)4            data = fair        )
+-----------------------------------------------------------------------
pu2o3(c,beta)
    entered by= MCRT (see below)        date= Jan11,91
        source= MCRT.3245R65         quality= fair
        volume=     0.000 cc/mol
     2 chemical elements=
       2.000 pu               3.000 o
     4 species in reaction=
      -1.000 pu2o3(c,beta    -6.000 h+              2.000 pu+++
       3.000 h2o
*    log k grid (0-25-60-100/150-200-250-300 c) =
        53.9349   48.1335   41.5136   35.4587
        29.4458   24.6621   20.7231   17.3947
*    delvr grid (0-25-60-100/150-200-250-300 c) =
       500.0000   54.2047  500.0000  500.0000
       500.0000  500.0000  500.0000  500.0000
* MCRT file mdas.3245 Pu, rev.   Jan11,91, heat capacity integration
*   (quality of pu2o3(c,beta)      data = fair        )
+-----------------------------------------------------------------------
```

```
+-----------------------------------------------------------------------
pu(hpo4)2(c)
    entered by= MCRT (see below)         date= Jan11,91
        source= MCRT.3245R65         quality= fair
        volume=     0.000 cc/mol
     4 chemical elements=
       1.000 pu               2.000 h                  8.000 o
       2.000 p
     3 species in reaction=
      -1.000 pu(hpo4)2(c)     2.000 hpo4--            1.000 pu++++
*    log k grid (0-25-60-100/150-200-250-300 c) =
       -27.2877  -27.6555  -28.5381  -29.8616
       -31.8169  -33.9986  -36.3272  -38.7570
*    delvr grid (0-25-60-100/150-200-250-300 c) =
       500.0000    0.0000  500.0000  500.0000
       500.0000  500.0000  500.0000  500.0000
* MCRT file mdas.3245 Pu, rev.   Jan11,91, heat capacity integration
*   (quality of pu(hpo4)2(c)      data = fair        )
+-----------------------------------------------------------------------
puo2(c)
    entered by= MCRT (see below)         date= Jan11,91
        source= MCRT.3245R65         quality= good
        volume=     0.000 cc/mol
     2 chemical elements=
       1.000 pu               2.000 o
     4 species in reaction=
      -1.000 puo2(c)        -4.000 h+                1.000 pu++++
       2.000 h2o
*    log k grid (0-25-60-100/150-200-250-300 c) =
        -6.5064   -7.3587   -8.2994   -9.1451
        -9.9812  -10.6410  -11.2001  -11.6924
*    delvr grid (0-25-60-100/150-200-250-300 c) =
       500.0000   36.1364  500.0000  500.0000
       500.0000  500.0000  500.0000  500.0000
* MCRT file mdas.3245 Pu, rev.   Jan11,91, heat capacity integration
*   (quality of puo2(c)           data = good        )
+-----------------------------------------------------------------------
puo2(co3)(s)
    entered by= MCRT (see below)         date= Jan11,91
        source= MCRT.3245R65         quality= fair
        volume=     0.000 cc/mol
     3 chemical elements=
       1.000 pu               1.000 c                  5.000 o
     3 species in reaction=
      -1.000 puo2(co3)(s)    1.000 co3--              1.000 puo2++
*    log k grid (0-25-60-100/150-200-250-300 c) =
       -13.9434  -14.2052  -14.7641  -15.5591
       -16.6349  -17.7814  -19.0100  -20.2856
*    delvr grid (0-25-60-100/150-200-250-300 c) =
       500.0000    0.0000  500.0000  500.0000
       500.0000  500.0000  500.0000  500.0000
* MCRT file mdas.3245 Pu, rev.   Jan11,91, heat capacity integration
*   (quality of puo2(co3)(s)      data = fair        )
+-----------------------------------------------------------------------
puo2hpo4(c)
    entered by= MCRT (see below)         date= Jan11,91
        source= MCRT.3245R65         quality= fair
        volume=     0.000 cc/mol
     4 chemical elements=
       1.000 pu               6.000 o                  1.000 h
       1.000 p
     3 species in reaction=
      -1.000 puo2hpo4(c)     1.000 hpo4--             1.000 puo2++
*    log k grid (0-25-60-100/150-200-250-300 c) =
       -12.5149  -12.5875  -12.9108  -13.4677
       -14.3466  -15.3594  -16.4533  -17.6034
*    delvr grid (0-25-60-100/150-200-250-300 c) =
       500.0000    0.0000  500.0000  500.0000
       500.0000  500.0000  500.0000  500.0000
* MCRT file mdas.3245 Pu, rev.   Jan11,91, heat capacity integration
*   (quality of puo2hpo4(c)       data = fair        )
+-----------------------------------------------------------------------
```

```
+-----------------------------------------------------------------------
puo2(oh)2(c)
    entered by= MCRT (see below)       date= Jan11,91
        source= MCRT.3245R65         quality= fair
        volume=      0.000 cc/mol
     3 chemical elements=
       1.000 pu            4.000 o                  2.000 h
     4 species in reaction=
      -1.000 puo2(oh)2(c)   -2.000 h+             1.000 puo2++
       2.000 h2o
*     log k grid (0-25-60-100/150-200-250-300 c) =
         5.0417     4.3785     3.6503     3.0178
         2.4240     1.9883     1.6580     1.4001
*     delvr grid (0-25-60-100/150-200-250-300 c) =
       500.0000    36.1364   500.0000   500.0000
       500.0000   500.0000   500.0000   500.0000
* MCRT file mdas.3245 Pu, rev.   Jan11,91, heat capacity integration
*   (quality of puo2(oh)2(c)      data = fair        )
+-----------------------------------------------------------------------
puo2oh(am)
    entered by= MCRT (see below)       date= Jan11,91
        source= MCRT.3245R65         quality= fair
        volume=      0.000 cc/mol
     3 chemical elements=
       1.000 pu            3.000 o                  1.000 h
     4 species in reaction=
      -1.000 puo2oh(am)     -1.000 h+             1.000 puo2+
       1.000 h2o
*     log k grid (0-25-60-100/150-200-250-300 c) =
         6.1507     5.4602     4.6986     4.0565
         3.4897     3.1086     2.8617     2.7107
*     delvr grid (0-25-60-100/150-200-250-300 c) =
       500.0000    18.0682   500.0000   500.0000
       500.0000   500.0000   500.0000   500.0000
* MCRT file mdas.3245 Pu, rev.   Jan11,91, heat capacity integration
*   (quality of puo2oh(am)        data = fair        )
+-----------------------------------------------------------------------
pu(oh)3(s)
    entered by= MCRT (see below)       date= Jan11,91
        source= MCRT.3245R65         quality= fair
        volume=      0.000 cc/mol
     3 chemical elements=
       1.000 pu            3.000 o                  3.000 h
     4 species in reaction=
      -1.000 pu(oh)3(s)     -3.000 h+             1.000 pu+++
       3.000 h2o
*     log k grid (0-25-60-100/150-200-250-300 c) =
        24.8594    22.4571    19.7576    17.3343
        14.9801    13.1570    11.6936    10.4869
*     delvr grid (0-25-60-100/150-200-250-300 c) =
       500.0000    54.2047   500.0000   500.0000
       500.0000   500.0000   500.0000   500.0000
* MCRT file mdas.3245 Pu, rev.   Jan11,91, heat capacity integration
*   (quality of pu(oh)3(s)        data = fair        )
+-----------------------------------------------------------------------
pu(oh)4(am)
    entered by= MCRT (see below)       date= Jan11,91
        source= MCRT.3245R65         quality= fair
        volume=      0.000 cc/mol
     3 chemical elements=
       1.000 pu            4.000 o                  4.000 h
     4 species in reaction=
      -1.000 pu(oh)4(am)    -4.000 h+             1.000 pu++++
       4.000 h2o
*     log k grid (0-25-60-100/150-200-250-300 c) =
         0.1851    -0.8106    -1.8685    -2.7645
        -3.5807    -4.1601    -4.5996    -4.9467
*     delvr grid (0-25-60-100/150-200-250-300 c) =
       500.0000    72.2729   500.0000   500.0000
       500.0000   500.0000   500.0000   500.0000
* MCRT file mdas.3245 Pu, rev.   Jan11,91, heat capacity integration
*   (quality of pu(oh)4(am)       data = fair        )
+-----------------------------------------------------------------------
```

```
+-----------------------------------------------------------------------
pu(oh)co3(s)
    entered by= MCRT (see below)        date= Jan11,91
        source= MCRT.3245R65         quality= speculative
        volume=     0.000 cc/mol
     4 chemical elements=
       1.000 pu              4.000 o               1.000 h
       1.000 c
     5 species in reaction=
      -1.000 pu(oh)co3(s)   -1.000 h+              1.000 pu+++
       1.000 h2o             1.000 co3--
*    log k grid (0-25-60-100/150-200-250-300 c) =
        -7.9974   -7.9974  500.0000  500.0000
       500.0000  500.0000  500.0000  500.0000
*    delvr grid (0-25-60-100/150-200-250-300 c) =
       500.0000   18.0682  500.0000  500.0000
       500.0000  500.0000  500.0000  500.0000
* MCRT file mdas.3245 Pu, rev.   Jan11,91, insufficient data
*   (quality of pu(oh)co3(s)       data = speculative )
+-----------------------------------------------------------------------
stop.


 there were
       0 errors encountered and
       0 warnings about g-h-s inconsistencies
```

List of SKB reports

Annual Reports

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KBS Technical Reports 1 – 120
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KBS Technical Reports 79-01 – 79-27
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Summaries
Stockholm, June 1984

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TR 85-01
Annual Research and Development Report 1984
Including Summaries of Technical Reports Issued during 1984. (Technical Reports 84-01 – 84-19)
Stockholm, June 1985

1985
TR 85-20
Annual Research and Development Report 1985
Including Summaries of Technical Reports Issued during 1985. (Technical Reports 85-01 – 85-19)
Stockholm, May 1986

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SKB Annual Report 1986
Including Summaries of Technical Reports Issued during 1986
Stockholm, May 1987

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SKB Annual Report 1987
Including Summaries of Technical Reports Issued during 1987
Stockholm, May 1988

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SKB Annual Report 1988
Including Summaries of Technical Reports Issued during 1988
Stockholm, May 1989

1989
TR 89-40
SKB Annual Report 1989
Including Summaries of Technical Reports Issued during 1989
Stockholm, May 1990

Technical Reports

List of SKB Technical Reports 1991

TR 91-01
Description of geological data in SKB's database GEOTAB
Version 2
Stefan Sehlstedt, Tomas Stark
SGAB, Luleå
January 1991

TR 91-02
Description of geophysical data in SKB database GEOTAB
Version 2
Stefan Sehlstedt
SGAB, Luleå
January 1991

TR 91-03
1. The application of PIE techniques to the study of the corrosion of spent oxide fuel in deep-rock ground waters
2. Spent fuel degradation
R S Forsyth
Studsvik Nuclear
January 1991