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AN ASSESSMENT OF THE THERMODYNAMIC BEHAVIOUR

OF NEPTUNIUM IN WATER AND MODEL GROUNDWATERS FROM 25 TO 150°C

UNE EVALUATION DU COMPORTEMENT THERMODYNAMIQUE

DU NEPTUNIUM DANS L'EAU

ET DANS DES EAUX SOUTERRAINES MODELES DE 25°C A 150°C

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RÉSUMÉ

Le présent rapport examine d'une manière critique les valeurs de l'énergie de Gibbs standard de formation et l'entropie des solides simples de neptunium et des complexes du neptunium avec l'OH^-, le Cl^-, le F^-, le CO_3^{2-}, le PO_4^{3-}, le SO_4^{2-} et le Na^+ en milieu aqueux. On a utilisé des valeurs sélectionnées avec des valeurs de capacité calorifique estimées afin de dériver des expressions analytiques pour la dépendance avec la température entre 25°C et 150°C des énergies de Gibbs standard de formation des espèces.

On a utilisé les énergies de Gibbs pour évaluer l'effet de différentes concentrations de ligands sur la solubilité des solides de neptunium en fonction de la température. On donne des diagrammes tension-pH pour le neptunium dans l'eau pure et dans deux eaux souterraines modèles. Le rapport traite du manque important de données thermodynamiques disponibles pour les espèces de neptunium.

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ABSTRACT

Standard molal Gibbs energy of formation and entropy data for simple neptunium solids and aqueous neptunium complexes with OH^-, Cl^-, F^-, CO_3^{2-}, PO_4^{3-}, SO_4^{2-} and Na^+ have been critically reviewed. Selected values are used with estimated heat capacity values to derive self-consistent analytical expressions for the temperature dependence of the standard molal Gibbs energies of formation of the species from 25 to 150°C.

The Gibbs energies have been used to evaluate the effect of different concentrations of ligands on the solubility of neptunium solids as a function of temperature. Potential-pH diagrams are given for neptunium in pure water and in two model groundwaters. Important deficiencies in the available thermodynamic data for neptunium species are discussed.

CONTENTS

GLOSSARY

$a(x)$ — solution activity of species x (infinite dilution standard state)

C_p°, $\bar{C}_p^\circ$ — standard molar and partial molal heat capacities, at 25°C unless the temperature is noted $(\bar{C}_p^\circ(H^+,T) \equiv 0)$

$\bar{C}_p^\circ|_{25}^{150}$ — effective constant partial molal heat capacity over the temperature range 25 to 150°C $(\bar{C}_p^\circ|_{25}^{150}(H^+) \equiv 0)$, calculated by a least-squares fit to Equation (13) using values for $\bar{S}^\circ(T)$ at 25, 60, 100 and 150°C

$\Delta_r C_p^\circ$ — heat capacity change for reaction

E — potential (versus a standard hydrogen electrode at T)

$\Delta_f G^\circ$ — standard molal Gibbs energy of formation, at 25°C unless the temperature is noted

$\Delta_r G^\circ$ — standard Gibbs energy of reaction

$\Delta_f H^\circ$ — standard molal enthalpy of formation, at 25°C unless the temperature is noted

$\Delta_r H^\circ$ — standard enthalpy of reaction

$\Delta_{sln} H$ — enthalpy of dissolution of a solid in a specified solution

$\Delta_n H$, $\Delta_n H^*$ — enthalpies of reaction for reactions with equilibrium constants K_n, K_n^*

I — ionic strength $(mol.dm^{-3})$

k   Boltzman constant

K   equilibrium constant for the reaction as written

K_s solubility product for salts (metal ion M, charge p+(= nq+), ligand L, charge q-) $ML_{p/q} \rightleftharpoons M^{p+} + \frac{p}{q} L^{q-}$, $K_s = [M^{p+}] [L^{q-}]^{p/q}$. For solid hydroxides $L \equiv OH^-$.

K_w ionic dissociation product of water

K_n stepwise stoichiometric formation constant for the reaction $ML_{n-1}^{(p-qn+q)} + L^{q-} \rightleftharpoons ML_n^{(p-nq)}$, $K_n = [ML_n^{p-nq}]/[ML_{n-1}^{(p-qn+q)}][L^{q-}]$. If the ionic strength is not stated, then K_n is the value at infinite dilution.

K_n^* formation constants similar to K_n but involving complexation of protonated ligands with loss of protons

$$ML_{n-1}^{(p-qn+q)} + HL^{(q-1)-} \rightleftharpoons ML_n^{(p-nq)} + H^+$$

K_{mn} cumulative stoichiometric formation constant for the hydrolysis reaction

$$mM^{p+} + nH_2O \rightleftharpoons M_m(OH)_n^{mp-n} + nH^+,$$

$$K_{mn} = [M_m(OH)_n^{mp-n}][H^+]^n/[M^{p+}]^m$$

If the ionic strength is not stated, then K_{mn} is the value at infinite dilution.

P(x)   pressure of the gas x

$S°$, $\bar{S}°$ standard and partial molal entropies, at 25°C unless the temperature is noted ($\bar{S}°(H^+,T) \equiv 0$)

$\Delta_f S°$ standard entropy of formation

$\Delta_r S°$ standard molal entropy of reaction at T

$\Delta_{mn} S$ entropy of the hydrolysis reaction with cumulative equilibrium constant K_{mn}

$\bar{S}°_e$ contribution to the partial molal entropy from the ground-state electronic degeneracy of the aqueous species

$\bar{S}°_{adj}$ temperature-dependent portion of the partial molal entropy

T absolute temperature in Kelvin

β_n cumulative stoichiometric formation constant for the reaction $M^{p+} + nL^{q-} \rightleftharpoons ML_n^{(p-nq)}$, $\beta_n = [ML_n^{(p-qn)}]/[M][L]^n$. If the ionic strength is not stated, then the β_n is the value at infinite dilution.

β_n^* formation constants similar to β_n but involving complexation of protonated ligands with loss of protons
$M^{p+} + nHL^{(q-1)-} \rightleftharpoons ML_n^{(p-nq)} + nH^+$,
$\beta_n^* = [ML_n^{(p-nq)}][H^+]^n/[M^{p+}][HL^{(q-1)-}]^n$

$\gamma(x)$ molal activity coefficient for the species x (infinite dilution standard state).

1. INTRODUCTION

Preliminary nuclear fuel waste management assessments [1,2] have emphasized the importance of limiting the release of ^{237}Np to the environment. Indeed, it has been suggested [2] that in some cases the dose-equivalent for an individual will be considerably greater from ^{237}Np than from ^{239}Pu. Therefore, it is important to obtain information on the sorption behaviour of neptunium and to demonstrate experimentally its behaviour in solution when exposed to "real" geological materials. However, to properly interpret the results of such experiments, it is also necessary to understand the behaviour at thermodynamic equilibrium and, therefore, to have thermodynamic data for neptunium species in aqueous solution and fo neptunium-containing solids. Such data will be needed not only for 25°C but also for the higher temperatures, 100 to 150°C, expected in a nuclear fuel waste-disposal vault. The equilibrium constant for a reaction at 150°C can be calculated knowing $\Delta_r G°$ and $\Delta_r S°$ at 25°C as well as the value for $\Delta_r C_p \big|_{25}^{150}$; however, an uncertainty of ± 65 J.K^{-1}.mol^{-1} in $\Delta_r S°(25°C)$ or ± 350 J.K^{-1}.mol^{-1} in $\Delta_r C_p \big|_{25}^{150}$ will lead to an uncertainty of ± 1 in the value of $\log_{10} K$ at 150°C.

Less critical assessment has been done for the thermodynamic data available for neptunium species than for the data of uranium or plutonium species [3]. The detailed work of Fuger and Oetting [4] dealt only with the simple neptunium ions. Patil et al. [5] provided a review of neptunium complexation, covering the literature to the end of 1976. In addition, recent general reviews of actinide behaviour [6-8] contain assessments of data for selected neptunium species. Nevertheless, aside from a report by Phillips and Silvester [9] that discusses the predicted temperature dependence of the reaction

$$Np^{4+} + HF \rightleftarrows NpF^{3+} + H^+, \tag{1}$$

little has been written about the behaviour of neptunium solution species and solubility as a function of temperature.

This report presents a critical review of thermodynamic data available in the literature for neptunium oxide, hydroxide, phosphate, fluoride, sulphate, carbonate and chloride equilibria. The results for 25°C have been used, primarily in a modified Criss-Cobble extrapolation scheme [3,10], to estimate thermodynamic constants for neptunium equilibria for temperatures as high as 150°C. Potential-pH diagrams and neptunium species distributions have been calculated for pure water and model groundwaters. Finally, types of experimental data most needed to improve our understanding of the thermodynamics of neptunium in aqueous solutions have been noted.

2. THERMODYNAMIC DATA ASSESSMENT

2.1 GIBBS ENERGY AND ENTROPY DATA FOR 25°C

2.1.1 Aqueous Ligand Species

Gibbs energies of formation and entropies were estimated as discussed in a previous paper [3]. Minor changes have been made in the values used in reference 3 for the Gibbs energies of the sulphate species to ensure consistency with the CODATA compilation [11]. Except for $H_2CO_3(aq)$, only 25°C protonation reaction data have been used to calculate the values of $\bar{S}^\circ$. Heat capacities at elevated temperatures were determined by the Criss-Cobble principle (HPO_4^{2-}, PO_4^{3-}, F^-, Cl^-, Na^+, SO_4^{2-}) or from the temperature dependence (25 to ~ 150°C) of the appropriate protonation or deprotonation equilibria (HF, HSO_4^-, $H_2PO_4^-$, H_3PO_4, HCO_3^-, CO_3^{2-}). $\bar{S}^\circ$ and $\bar{C}_p^\circ$ for $H_2CO_3(aq)$ were estimated from a least-squares fit of reported measurements of CO_2 solubility in water as a function of temperature.

2.1.2 Simple Neptunium Ions

Values for the 25°C Gibbs energies of formation and entropies of the simple neptunium ions, Np^{3+}, Np^{4+}, NpO_2^+ and NpO_2^{2+}, were taken from the

careful assessment by Fuger and Oetting [4]. Their values are consistent with auxiliary data from the CODATA data base [11,12], and we have attempted to maintain consistency with that compilation. In aqueous solution, Np(VII) is reported to be reduced by water, except in the presence of high concentrations of hydroxide ions [13]. Also, Np(VII) in solution is more readily reduced at higher temperature [14]. Since good thermodynamic data are not available for aqueous Np(VII) species, they will not be considered further in this report.

2.1.3   Oxides, Hydroxides and Oxy-hydroxides

The enthalpy of formation of NpO_2 ((-1074.0 ± 2.5) $kJ.mol^{-1}$) at 298.15 K was taken from the work of Huber and Holley [15], who determined the heat of combustion of α-Np. Combining this with the entropy of NpO_2((80.3 ± 0.4) $J.K^{-1}.mol^{-1}$) reported by Westrum et al. [16] leads to $\Delta_f G°(NpO_2$, 298.15 K) = (-1021.8 ± 2.5) $kJ.mol^{-1}$.

Moskvin [17] reported $\log_{10}K = 0.8$ for the reaction

$$Np^{4+} + 4H_2O \rightleftharpoons Np(OH)_4(s) + 4H^+ , \qquad (2)$$
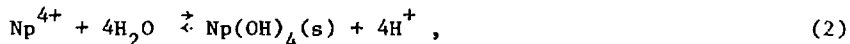
based on solubility measurements on an uncharacterized sample of the solid hydroxide. Similar measurements on $Pu(OH)_4(s)$ give equilibrium constants spanning many orders of magnitude [18,19]. We have assumed Moskvin's value is correct within four orders of magnitude and derive $\Delta_r G° = (-4.6 \pm 20)$ $kJ.mol^{-1}$. This leads to $\Delta_f G°(Np(OH)_4(s)) = (-1447 \pm 20)$ $kJ.mol^{-1}$. Latimer suggested [20] that the entropy contribution of a hydroxide ion attached to a central metal ion decreases from 21 to 13 $J.K^{-1}.mol^{-1}$ as the charge on the metal increases from 1+ to 3+. As the contribution per anion is often slightly larger for 4+ ions than for 3+ ions, an entropy contribution of (17 ± 5) $J.K^{-1}.mol^{-1}$ per hydroxyl group has been estimated for $Np(OH)_4$. A value of 72 $J.K^{-1}.mol^{-1}$ was derived for the contribution of Np to NpO_2 using Latimer's rules [20] and this, combined with the contribution for the OH^- groups, leads to an estimate of $S°(Np(OH)_4(s)$, 298.15 K) = (139 ± 25) $J.K^{-1}.mol^{-1}$.

Several papers have given values for the solubility product of the amorphous solid $NpO_2OH \cdot xH_2O$. Kraus and Nelson [21] estimated $\log_{10}K_s$ to be -9.2 (by potentiometry) which, as noted by Baes and Mesmer [18], is probably an upper limit. Moskvin [17] reported $\log_{10}K_s = -9.0$ from solubility measurements, but his value appears to drift systematically with the equilibrium pH of his solutions. Sevost'yanova and Khalturin [22] obtained -9.73 ± 0.10 for $\log_{10}K_s$, also from solubility measurements. In none of these experiments was the solid phase characterized. The somewhat lower solubility values of Sevost'yanova and Khalturin have been used (neglecting their value for pH 6.6 for which the pH and calculated hydroxyl ion concentrations are not in good agreement). Thus $\Delta_r G° = (55.7 \pm 0.8)$ kJ.mol^{-1} for

$$NpO_2OH \cdot xH_2O(am) \overset{\rightarrow}{\leftarrow} NpO_2^+ + OH^- + xH_2O \ . \tag{3}$$
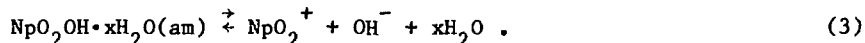
As the actual nature of the solid is not known, we have treated it simply as $NpO_2(OH)$ (am) ($= 0.5 \ [Np_2O_5 \cdot H_2O]$). The Gibbs energy of formation of this solid is calculated to be (-1128.0 ± 5.5) kJ.mol^{-1} using the value of $\Delta_f G°(NpO_2^+)$ from reference 4. $S°(NpO_2OH(am), 298.15 \ K)$ was estimated as the sum of $S°(NpO_2)$ and an entropy contribution ($20._9$ J.K^{-1}.mol^{-1}) suggested by Latimer [20] for an OH$^-$ group attached to a singly charged metal ion.

Belyaev et al. [23] have obtained $\Delta_f H°(Np_2O_5, 298.15 \ K) = (-2147 \pm 12)$ kJ.mol^{-1} from a cycle involving the reduction of Np_2O_5 with Fe(II) in acid solution. $S°(Np_2O_5, 298.15 \ K) = (163 \pm 23)$ J.K^{-1}.mol^{-1} was estimated as twice $S°(NpO_2OH, 298.15 \ K)$ minus 39 J.K^{-1}.mol^{-1} for the entropy of a water of hydration, as suggested by Latimer [20]. These lead to $\Delta_f G°(Np_2O_5, 298.15 \ K) = (-2013 \pm 14)$ kJ.mol^{-1}.

Two groups have reported calorimetric results leading to estimates of $\Delta_f H°(NpO_2(OH)_2)$. The more straightforward experiment, by Fuger et al. [24], measured $\Delta_r H = (-53.1 \pm 1.2)$ kJ.mol^{-1} for the dissolution of $NpO_2(OH)_2$ in 1 mol.dm^{-3} aqueous hydrochloric acid. Although $\Delta_f H°(NpO_2^{2+}, 1 \ mol.dm^{-3}$ HCl) is not known, the value of $\Delta_f H°(UO_2^{2+}, 1 \ mol.dm^{-3}$ HCl) differs from the

value in pure water by < 1 kJ.mol^{-1} [4]. Accepting that $\Delta_f H(NpO_2^{2+})$ in 1 mol.dm^{-3} HCl is the same as the value in water (i.e., $\Delta_f H°(NpO_2^{2+}, H_2O)$ - $\Delta_f H(NpO_2^{2+}, 1$ mol.dm^{-3} HCl) = (0 ± 4) kJ.mol^{-1}), a value of $\Delta_f H°(NpO_2(OH)_2(s))$ = (-1379 ± 5) kJ.mol^{-1} can be calculated. Belyaev et al. [23] have determined the heat of reaction of $NpO_2(OH)_2(s)$ in aqueous HCl (6 mol.dm^{-3}) containing 0.04 mol.dm^{-3} FeCl$_2$ and 0.004 mol.dm^{-3} Na$_2$SiF$_6$. Fuger and Oetting [4] gave $\Delta_f H(Np^{4+}, 1$ mol.dm^{-3} HCl) = -551.9 kJ.mol^{-1}, while Fuger and Brown [25] have determined $\Delta_{sln} H$ of Cs$_2$NpCl$_6$ in both 6 mol.dm^{-3} HCl and 1 mol.dm^{-3} HCl. Using appropriate values for $\Delta_{sln} H(CsCl,$ 6 mol.dm^{-3} HCl) [24], $\Delta_{sln} H(CsCl, 1$ mol.dm^{-3} HCl), $\Delta_f H(Cl^-, 6$ mol.dm^{-3} HCl) [4] and $\Delta_f H(Cl^-, 1$ mol.dm^{-3} HCl) [4] gives $\Delta_f H(Np^{4+}, 6$ mol.dm^{-3} HCl) = (-532.3 ± 1.9) kJ.mol^{-1}. This is combined with the experimental enthalpy data in the paper of Belyaev et al. [23] and the literature enthalpy of dilution data for HCl [26], and by assuming the experimental enthalpy of the reaction of the $NpO_2(OH)_2$ includes an exothermic contribution of -1.7 ± 0.8 kJ.mol^{-1} from the effect of the 0.004 mol.dm^{-3} Na$_2$SiF$_6$ (i.e. the same contribution as given for 0.005 mol.dm^{-3} Na$_2$SiF$_6$ by Fuger and Oetting [4]), $\Delta_f H°(NpO_2(OH)_2(s))$ = (-1369 ± 13) kJ.mol^{-1} can be calculated. Combining the results of Belyaev et al. with those of Fuger et al, gives $\Delta_f H°(NpO_2(OH)_2(s), 298.15$ K) = (-1378 ± 6) kJ.mol^{-1}.

Moskvin [17] has reported the solubility of $NpO_2(OH)_2$ (at 20°C?) as a function of pH ($I < 0.1$). Although this solid was well characterized initially, it does not appear that the material was re-examined after equilibration with the aqueous solutions. Higher hydrates have been reported to form under similar conditions after long periods of time [27]. Moskvin reported $\log_{10} K_s$ = -22.1 for the reaction

$$NpO_2(OH)_2(s) \rightleftarrows NpO_2^{2+} + 2OH^-, \qquad (4)$$

but his experimental data are inconsistent with data on the hydrolysis of NpO_2^{2+} obtained from potentiometric measurements [28] (see Figure 1). Attempts to apply activity corrections and/or modify the hydrolysis constants did not significantly improve the agreement. Recalculation of
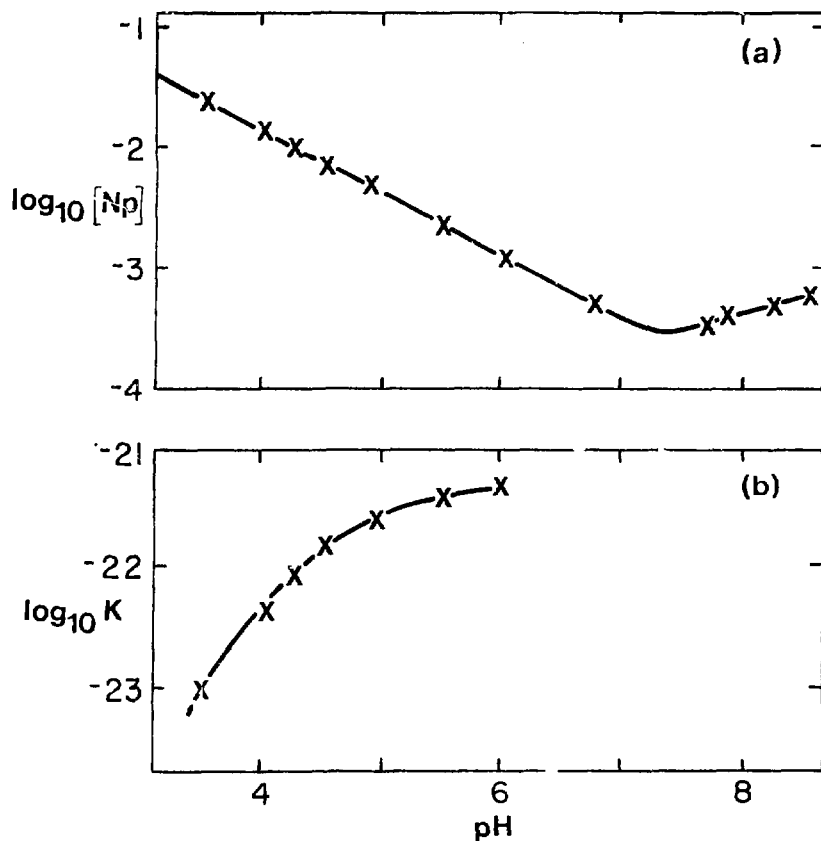
FIGURE 1: The solubility of $NpO_2(OH)_2$

(a) experimental data from reference 17;

(b) values of $K_s = \{NpO_2^{2+}\}\{OH^-\}^2$ calculated from the same data using hydrolysis constants (25.0°C) from reference 28

Moskvin's data (pH 3.5 to 6) demonstrates a regular drift in $\log_{10}K_s$ from −23.05 to −21.32. Data in Cassol et al. [28] lead to an estimate of $\log_{10}K_s$ < −21.3. It is probable that $\log_{10}K_s \sim -22 \pm 2$; hence, $\Delta_f G°(NpO_2(OH)_2(s))$ is calculated to be (-1236 ± 12) kJ.mol^{-1}. Combining this with the value derived above for $\Delta_f H°(NpO_2(OH)_2(s))$ gives $\Delta_f S°(NpO_2(OH)_2(s)) = (-473 \pm 44)$ J.K^{-1}mol^{-1}. Using $S°(Np) = 50.46$ J.K^{-1}.mol^{-1} [29] and CODATA values for $S°(H_2)$ and $S°(O_2)$ leads to $S°(NpO_2(OH)_2(s)) = 118 \pm 44$ J.K^{-1}.mol^{-1}. This value is in good agreement with the estimate based on $S°(NpO_2(OH)_2(s))$ = $S°(NpO_2) + 2S°(OH^-) = 118$ J.K^{-1}.mol^{-1} using Latimer's [20] value of 18.8 J.K^{-1}.mol^{-1} per OH$^-$ group attached to a 2+ central ion. The value $S°(NpO_2(OH)_2) = (118 \pm 20)$ J.K^{-1}.mol^{-1} has been chosen for use in this report.

2.1.4   Hydrolytic Solution Species

Mefod'eva et al. [30] have measured the ratio of the first hydrolysis constants, $K_{11}(Np^{3+})/K_{11}(Pr^{3+}) = 14 \pm 3$ and $K_{11}(Np^{3+})/K_{11}(Nd^{3+})$ = 10 ± 2, at I = 0.1 and 20°C. Within the experimental uncertainties, the derived ratio of $K_{11}(Nd^{3+})/K_{11}(Pr^{3+})$ (= 1.4 ± 0.2) is the same as the ratio of the hydrolysis constants (I → 0, 25°C) given in Baes and Mesmer's compilation [18]. Taking the lanthanide ion hydrolysis constants from that source, and assuming the differences in the ratios caused by the different ionic strengths and temperatures are small, lead to $\log_{10}K_{11} = -7.0 \pm 0.3$ for the first hydrolysis constant of Np^{3+}. A major portion of the uncertainty is attributable to the uncertainties in the lanthanide ion hydrolysis constants. Using $\Delta_f G°(Np^{3+})$ from Fuger and Oetting [4] gives $\Delta_f G°(NpOH^{2+}) = (-714.3 \pm 3.7)$ kJ.mol^{-1}. The value of K_{11} and Equation (18-11) of reference 18 are used to calculate a value of (-20.5 ± 0.3) for Baes and Mesmer's parameter A for Np^{3+}. Use of Equation (18-13) of reference 18 thus gives a value $\Delta_{11}S = (34._5 \pm 30)$ J.K^{-1}.mol^{-1} for the entropy of the first hydrolysis step of Np^{3+}, and hence, $\bar{S}°(NpOH^{2+})$ = (-75 ± 30) J.K^{-1}mol^{-1}.

Three quantitative studies of the first hydrolysis step for Np(IV) (reaction (5)) have been reported.

$$Np^{4+} + H_2O \xrightleftharpoons{K_{11}} NpOH^{3+} + H^+ \tag{5}$$

Sullivan and Hindman [31] reported $K_{11} = (5.0 \pm 0.3) \times 10^{-3}$ in aqueous per-chlorate solutions (2 mol.dm^{-3}) from spectrophotometry. Paul [32] also used spectrophotometry and reported a value of "β_{Hydr}" = $(1.24 \pm 0.02) \times 10^{-2}$ (I = 1.0). This "β_{Hydr}" incorporates the hydrogen ion activity (as pH) whereas Sullivan and Hindman's "constant" is purely a concentration quotient. This difference in definition accounts in part for the difference in the numbers reported, as does the difference in ionic strength. Paul agrees with Sullivan and Hindman that $\log_{10}K_{11}$ for Np(IV) is approximately 0.5 lower than $\log_{10}K_{11}$ for U(IV). These results are in contrast to those of Duplessis and Guillaumont [33] who reported $K_{11} = 0.3$ (1 mol.dm^{-3} LiClO$_4$) from extraction experiments involving tracer quantities of ^{239}Np. This is more than an order of magnitude larger than the other results. As noted by Duplessis and Guillaumont, the same problem occurs when potentiometric [34] and tracer studies [35] of Pu(IV) hydrolysis are compared.

Baes and Mesmer [18] estimated $\log_{10}K_{11} = -0.65$ and -0.5 at I = 0 for U(IV) and Pu(IV) hydrolysis, respectively. The value $\log_{10}K_{11} = (-1.0 \pm 1.0)$ has been chosen for K_{11} for neptunium (I → 0), which leads to $\Delta_f G°(NpOH^{3+}) = (-734 \pm 9)$ kJ.mol^{-1}. On the basis of hydrolysis data for other metals with a 4+ charge [18,36], polymeric neptunium hydrolysis species would be expected to predominate above pH 1 to 2 at 25°C if neptunium is present in greater than tracer quantities. Furthermore, Sullivan and Hindman [31] reported evidence for polymerization of Np(IV) at 2×10^{-3} mol.dm^{-3} near pH 2. For this reason Schmidt et al.'s [37] value of $\log_{10}K = -4.5$ for the reaction

$$NpOH^{3+} + H_2O \xrightleftharpoons{K} Np(OH)_2^{2+} + H^+, \tag{6}$$
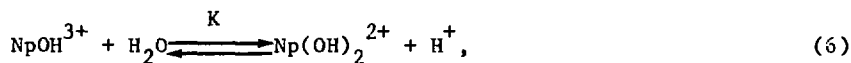
obtained with solutions 10^{-3} to 10^{-4} mol.dm^{-3} in neptunium, must be consid-ered suspect. No good quantitative data are available for the formation constants of the polymeric Np(IV) species.

For U^{4+}, $\log_{10}K_{14}$ can be estimated as -9.7 using the UO$_2$ solubil-ity data of Tremaine et al. [38] to calculate K_{15} and the method of Baes and

Mesmer [18] to estimate the values of formation constants for sequential (monomeric) hydrolysis products. Baes and Mesmer [18] also deduced a value of $\log_{10}K_{14} = -9.5$ for $Pu^{4+} + 4 H_2O \rightleftharpoons Pu(OH)_4(aq) + 4H^+$ from the data of Metivier [39]. When the same Baes and Mesmer method is applied assuming $\log_{10}K_{14} = -9.6$ and $\log_{10}K_{11} = -1.0$ for neptunium, values of -2.9, -5.8 and -14.3 are obtained for $\log_{10}K_{12}$, $\log_{10}K_{13}$ and $\log_{10}K_{15}$, respectively. It should be noted that the value for $\log_{10}K_{12}$ is markedly more negative than the -0.91 reported by Duplessis and Guillaumont, although the values for $\log_{10}K$ for reaction (6) agree within about 0.5. Furthermore, there does not appear to be any unequivocal evidence for the formation of anionic Np(IV) hydrolysis species. Nevertheless, we have used the interpolated and extrapolated equilibrium constants noted above to calculate $\Delta_f G^\circ(Np(OH)_2^{2+})$ = (-961 ± 15) kJ.mol^{-1}, $\Delta_f G^\circ(Np(OH)_3^+) = (-1181 \pm 20)$ kJ.mol^{-1}, $\Delta_f G^\circ(Np(OH)_4(aq)) = (-1397 \pm 20)$ kJ.mol^{-1} and $\Delta_f G^\circ(Np(OH)_5^-) = (-1607 \, {}^{+40}_{-20})$ kJ.mol^{-1} in the expectation that, within the noted estimated uncertainties, these may serve as a guide to the probable behaviour of Np(IV) in solution. Ryan and Rai [40] have recently reported solubility results (21°C) for uncharacterized samples of "hydrous" UO_2. Their data indicate that UO_2 is probably less soluble than reported by Tremaine et al. [38]. If the behaviour of the U(IV) and Np(IV) oxides, hydroxides and hydrolysis species are similar, then $Np(OH)_4(aq)$ and $Np(OH)_5^-$ are less stable than assumed here. The differences may be as little as 5 to 15 kJ.mol^{-1} if the "hydrous" UO_2 is similar to crystalline UO_2, or the difference may be > 40 kJ.mol^{-1} if the "hydrous" UO_2 is much less stable than UO_2. The stability of $Np(OH)_5^-$ is especially likely to be overestimated if the noted value is used, as little experimental evidence was found for increased solubility of U(IV) in basic solutions.

Approximate values for the entropies of the $Np(OH)_n^{4-n}$ species were calculated by assuming values of $\Delta_r S^\circ$ for the hydrolysis reactions are equal to those estimated by Langmuir [41] for the corresponding reactions of U(IV).

Three groups have determined a value for the first hydrolysis constant of NpO_2^+. Kraus and Nelson [21] gave $\log_{10}K_{11} = -8.9$ for $NpO_2^+ + H_2O \rightleftharpoons NpO_2OH(aq) + H^+$ in 0.1 mol.dm^{-3} chloride, and the value can be

assumed to be approximately equal to the value at zero ionic strength. Sevost'yanova and Khalturin [22] did spectrophotometric (20°C) and potentiometric (23°C) studies that gave an average value of $\log_{10}K_{11}$ = -8.90 ± 0.04. If the small differences in the temperatures used by the two groups are neglected, the values are in excellent agreement - and in marked disagreement with $\log_{10}K_{11}$ = -10.1 obtained by Moskvin [17]. The value -8.90 ± 0.10 has been chosen for $\log_{10}K_{11}$ at 25°C, with the uncertainty increased because of the differences in the temperatures of the measurements and the lack of correction to $I = 0$. This gives a value for Δ_rG of (50.8 ± 0.6) kJ.mol^{-1}, and hence, $\Delta_fG°(NpO_2OH(aq))$ = (-1101 ± 5) kJ.mol^{-1}. The entropy of the first hydrolysis step for NpO_2^+ would be expected to be less positive than for the reaction $UO_2^{2+} + H_2O \leftrightarrows UO_2OH^+ + H^+$ because the reaction of NpO_2^+ does not involve separation of ions of like charge. Baes and Mesmer [18] suggested an empirical formula for calculating the entropy of reaction for the first hydrolysis step for metal cations. This formula (Equation (18-13) of reference 18) includes parameters related to the hardness of the cations and their charge-to-radius ratio. Assuming identical parameters for UO_2^{2+} and NpO_2^+, except for the charge difference, leads to $\Delta_{11}S$ = -22 J.K^{-1}.mol^{-1} and $\bar{S}°(NpO_2OH(aq))$ = (25 ± 60) J.K^{-1}.mol^{-1} (the noted uncertainty is an estimate). This value is considerably smaller than the value of $\bar{S}°$ for many other neutral aqueous species [20].

Cassol et al. [28] obtained hydrolysis constants for NpO_2^{2+} in 1 mol.dm^{-3} NaClO$_4$ at 25°C. Baes and Mesmer [18] used the data to calculate $\log_{10}K_{11}$ = -5.15, $\log_{10}K_{22}$ = -6.39 and $\log_{10}K_{35}$ = -17.49 for zero ionic strength. The value for $\log_{10}K_{11}$ is in fair agreement with the value -5.45 ± 0.1 ($I \rightarrow 0$) recently reported by Schmidt et al. [42]. For the sake of consistency, the values from reference 18 have been used here. These lead to $\Delta_fG°$ values of (-1004 ± 5), (-2030 ± 11) and (-3474 ± 17) kJ.mol^{-1} for NpO_2OH^+, $(NpO_2)_2(OH)_2^{2+}$ and $(NpO_2)_3(OH)_5^+$, respectively. Baes and Meyer [43] measured the hydrolysis equilibrium constants for the corresponding U(VI) species at 25 and 94.4°C, and thus derived values for the entropies of the hydrolysis reactions. The entropies of reaction for the hydrolysis of NpO_2^{2+} are probably equal to those for UO_2^{2+} within 20 J.K^{-1}.mol^{-1}. The entropy values given by Baes and Meyer are actually average values for the

temperature range 25 to 94.4°C, and are for an aqueous solution containing 0.5 mol.dm^{-3} KNO$_3$. By assuming that the lack of correction of $\Delta_r S$ to 25°C and to zero ionic strength would eac. introduce an uncertainty of approximately 30 J.K^{-1}.mol^{-1}, the values $\bar{S}°(NpO_2OH^+)$ = (24 ± 50) J.K^{-1}.mol^{-1}, $\bar{S}°((NpO_2)_2(OH)_2^{2+})$ = (-14 ± 50) J.K^{-1}.mol^{-1} and $\bar{S}°((NpO_2)_3(OH)_5^+)$ = (116 ± 50) J.K^{-1}.mol^{-1} were estimated.

2.1.5   Fluoride Complexes

Bond and Hefter [44] have recently critically reviewed literature values for the stability constants of metal fluoride complexes in aqueous solution. For the complexation of neptunium, it appears that there is little to choose between many of the experimental values. Most of the experiments were done in highly acidic solutions and at high ionic strength and the constants refer to reactions of the form

$$NpO_a^{+x} + nHF \underset{}{\overset{\beta_n^*}{\rightleftharpoons}} NpO_a F_n^{+(x-n)} + nH^+. \qquad (7)$$
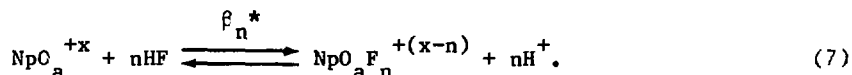
Arbitrarily, the values $\log_{10}\beta_1^*$ = 4.70 and $\log_{10}\beta_2^*$ = 7.38, in HClO$_4$(aq, 2 mol.dm^{-3}) of Bagawde et al. [45] were selected for the formation constants of the Np(IV) complexes NpF_n^{4-n}. For the Th(IV) fluoride complexes, $\log_{10}K_1^*$ and $\log_{10}K_2^*$ are 4.43 and ~ 2.7, respectively, in HClO$_4$(aq, 2 mol.dm^{-3}) but 5.27 and 3.45 at I = 0 [44]. If these same differences are applied for the medium effects in the Np(IV) system, then $\log_{10}\beta_1^*$ = 5.5 ± 0.3 and $\log_{10}\beta_2^*$ = 9.0 ± 0.6 at I = 0, where the error limits have been chosen to reflect errors both in the reported values and in the corrections to "zero ionic strength". Therefore, using $\log_{10}K$ = 3.19 for reaction (8) [44],

$$H^+ + F^- \overset{K}{\rightleftharpoons} HF, \qquad (8)$$

gives $\log_{10}\beta_1$ = 8.7 ± 0.3, $\log_{10}\beta_2$ = 15.4 ± 0.6, $\Delta_f G°(NpF^{3+})$ = (-834.3 ± 7.7) kJ.mol^{-1} and $\Delta_f G°(NpF_2^{2+})$ = (-1154.3 ± 8.1) kJ.mol^{-1}.

Choppin and Unrein [46] have reported values for β_1^* at 10, 25 and 40°C for solutions containing ~ 1 mol.dm^{-3} HClO$_4$. They calculated $\Delta_1 H$ = (3.2 ± 1.8) kJ.mol^{-1}, which leads to $\bar{S}$(NpF^{3+}, HClO$_4$(aq) 1 mol.dm^{-3}) = -247 J.K^{-1}.mol^{-1}. Since there is no simple method of converting this value to a value at zero ionic strength, a value of $\bar{S}°$(NpF^{3+}, I = 0) = -247 ± 50 J.K^{-1}.mol^{-1} has been used in the calculations described in this report.

There are no reported values for $\bar{S}°$(NpF$_2^{2+}$), although the lower charge would suggest [20] a less negative value than that of $\bar{S}°$(NpF^{3+}). The value of $\bar{S}°$(NpF$_2^{2+}$) has been chosen to be (-100 ± 100) J.K^{-1}.mol^{-1}.

Rao and coworkers [47] have shown that NpO$_2^+$ forms a complex with fluoride and report K$_1$ = 9.8 (25°C, 2 mol.dm^{-3} NaClO$_4$). In the absence of any data on the ionic strength dependence of the constant, the zero ionic strength value has been estimated as equal to the reported value. Therefore, $\Delta_r G°$ = (-5.7 ± 2.0) kJ.mol^{-1}, where the error limits have been chosen to reflect the lack of proper medium correction. This leads to $\Delta_f G°$(NpO$_2$F) = (-1202 ± 6) kJ.mol^{-1}. No experimental data are available for calculating $\bar{S}°$(NpO$_2$F). $\Delta_r S$ for the complexation reaction of NpO$_2^+$ with F$^-$ should probably be positive, and the entropy of reaction of a fluoride with metal cations generally ranges from 50 to 200 J.K^{-1}.mol^{-1} [44]. Therefore, $\bar{S}°$(NpO$_2$F) probably lies in the range 20 to 170 J.K^{-1}.mol^{-1} and a value of $\bar{S}°$(NpO$_2$F) = (100 ± 100) J.K^{-1}.mol^{-1} has been chosen.

For NpO$_2^{2+}$ fluoride complexes, the values for K$_1^*$ and K$_2^*$ (I = 0) reported by Al-Niaimi et al. [48] have been chosen. As noted by Bond and Hefter [44], the errors in the K$_n^*$ values are probably considerably larger than estimated by the original authors. The values log$_{10}\beta_1$ = 4.6 ± 0.3 and log$_{10}\beta_2$ = 7.8 ± 0.5 have been used and these give $\Delta_f G°$(NpO$_2$F$^+$) = (-1103.8 ± 5.7) kJ.mol^{-1} and $\Delta_f G°$(NpO$_2$F$_2$(aq)) = (-1403.8 ± 6.1) kJ.mol^{-1}. The two sets of reported entropy values for the formation of NpO$_2$F$^+$ are in marked disagreement [5]. The value for the entropy of the first fluoride-complexation step for UO$_2^{2+}$, as given by Ahrland and Kullberg [49], is between the

two reported values for the neptunium system. Therefore, the entropies for the first and second complexation steps of NpO_2^{2+} have been assumed the same as for the corresponding reactions of UO_2^{2+}. This gives $\bar{S}°(NpO_2F^+) =$ (-14 ± 80) $J.K^{-1}.mol^{-1}$ and $\bar{S}°(NpO_2F_2(aq)) = (40 \pm 80)$ $J.K^{-1}.mol^{-1}$, where the error limits are estimates.

No adequate 25°C values appear to be available for the thermo-dynamic parameters for the simple, solid neptunium fluorides, NpF_3 and NpF_4. Values for $\Delta_f H°$ for these compounds given in reference 50 can be traced to an undocumented calculation first reported in reference 51.

2.1.6   Sulphate Complexes

The experimental work on complexation of neptunium ions with sul-phate has recently been summarized [5]. For the reactions

$$Np^{4+} + nHSO_4^- \xrightleftharpoons{\beta_n^*} Np(SO_4)_n^{4-2n} + nH^+, \qquad (9)$$
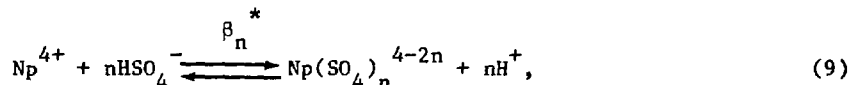
values for $\log_{10}\beta_1^* = 2.53$ and $\log_{10}\beta_2^* = 4.04$ have been selected from the work of Bagawde et al. [45]. Wagman et al. [52] estimated corrections to zero ionic strength for the analogous Th(IV) complexation reactions. Applying these corrections to the neptunium results, and using the Gibbs energies of formation for the sulphate and hydrogen sulphate ions given in reference 12, values of $\log_{10}\beta_1 = 5.5 \pm 1.1$ and $\log_{10}\beta_2 = 9.9 \pm 1.1$ are obtained. These give $\Delta_f G°(NpO_2SO_4^{2+}) = (-1279 \pm 10)$ $kJ.mol^{-1}$ and $\Delta_f G°(NpO_2(SO_4)_2(aq)) = (-2048 \pm 10)$ $kJ.mol^{-1}$.

Using calorimetry, Zielen [53] obtained values for the enthalpies of the first and second steps of complexation of Th(IV) with HSO_4^- (I = 2). The value of $\Delta_1 H^* = -2.3$ $kJ.mol^{-1}$ is within a few kilojoules per mole of the values for the neptunium system obtained by Patil and Ramakrishna [54] from the temperature variation of the association constants over a small tempera-ture range. The latter method is relatively inaccurate and completely unreliable for $\Delta_2 H^*$ [54]. Therefore, the enthalpies of complex formation in the Np(IV) system (I = 2) have been assumed to be equal to those determined

experimentally by Zielen for the Th(IV) system. Zielen's enthalpy of protonation of $SO_4{}^{2-}$ at I = 2 [53] has been used. The enthalpy of each complexation reaction has been assumed to be independent of the ionic strength. Large uncertainties ($\pm$ 15 kJ.mol^{-1} for each complexation step) were chosen to reflect this crude approximation. These assumptions lead to $\Delta_r S^\circ$ = (180 $\pm$ 50) J.K^{-1}.mol^{-1} and (150 $\pm$ 50) J.K^{-1}.mol^{-1} for the first and second complexation reactions, respectively, and $\bar{S}^\circ(NpSO_4{}^{2+})$ = (-195 $\pm$ 50) J.K^{-1}.mol^{-1} and $\bar{S}^\circ(Np(SO_4)_2(aq))$ = (-27 $\pm$ 70) J.K^{-1}.mol^{-1}.

Rao et al. [47] used an extraction technique to obtain a value of 2.8 for the association constant of $NpO_2{}^+$ with $SO_4{}^{2-}$ (I = 2). Other workers [55,56] have obtained higher or lower values, but all results agree within an order of magnitude in K_1. In the absence of data at low ionic strength, the value of Rao et al. has been used for I = 0 but with uncertainties of $\pm$1 in $\log_{10} K_1$, to reflect the possible errors using this approximation. Thus $\Delta_r G^\circ$ = (-3 $\pm$ 6) kJ.mol^{-1} and $\Delta_f G^\circ(NpO_2SO_4{}^-)$ = (-1662 $\pm$ 8) kJ.mol^{-1}. The entropy of the reaction

$$UO_2{}^{2+} + SO_4{}^{2-} \rightleftarrows UO_2SO_4(aq) \tag{10}$$

is 130 J.K^{-1}.mol^{-1} [3]. The entropy of the corresponding reaction of $NpO_2{}^+$ would be expected to be less positive because of the difference in charge types. A value of $\Delta_r S^\circ$ = (70 $\pm$ 50) J.K^{-1}.mol^{-1} is estimated, giving $\bar{S}^\circ(NpO_2SO_4{}^-)$ = (70 $\pm$ 50) J.K^{-1}.mol^{-1}.

Al-Niaimi et al. [48] reported $K_1{}^*$ = 18.9 (I = 0) for the reaction

$$NpO_2{}^{2+} + HSO_4{}^- \xrightarrow{K_1{}^*} NpO_2SO_4(aq) + H^+. \tag{11}$$
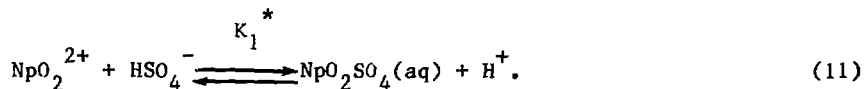
In their analysis, Np(V) was assumed not to form a sulphate complex, but the inclusion of this species would not have resulted in a significant difference ($\sim$ 0.1) in the value of $K_1{}^*$. If the uncertainty in $K_1{}^*$ is increased from the authors' value to $\pm$3, because of the magnitude of

the correction of the experimental values from $I = 0.1$ to $I = 0$, this leads to $\log_{10} K_1 = 3.3 \pm 0.5$ and $\Delta_f G^\circ(NpO_2SO_4(aq)) = (-1559 \pm 6)$ kJ.mol^{-1}. The entropy of sulphate complexation with NpO_2^{2+} to form $NpO_2SO_4(aq)$ has been taken as 130 J.K^{-1}.mol^{-1}, i.e., identical to the value of the entropy of the corresponding reaction for UO_2^{2+} [3]. This gives $S^\circ(NpO_2SO_4(aq)) = (57 \pm 100)$ J.K^{-1}.mol^{-1}.

2.1.7   Carbonate Complexes

The solubility work of Moskvin [57] is the only quantitative study of Np(IV) complexation with carbonate. Unfortunately, the solid phase does not appear to have been properly characterized, nor is it definitely established that the predominant Np(IV) hydrolysis species at the pH of the experiments is the assumed $Np(OH)_4(aq)$, and not $Np(OH)_5^-$ or some polymeric species. Because of the limited pH range used by Moskvin, the data could equally well be explained by species other than Moskvin's $Np(OH)_4CO_3^{2-}$. As noted by Moskvin, assuming the analogous $Pu(OH)_4CO_3^{2-}$, instead of the often criticized species $PuCO_3^{2+}$, could better explain the Pu(IV) carbonate data of Moskvin and Gel'man [58].

Recently Ciavatta et al. [59] have reported spectroscopic and potentiometric evidence for the formation of $U(CO_3)_5^{6-}$ in the corresponding uranium system (3 mol.dm^{-3} NaClO$_4$(aq)). They also obtained an estimate of $\log_{10}\beta_5 = 40$. This value is dependent on the value chosen for the formation constant of $UO_2(CO_3)_3^{4-}$. Using the β_3 value for $UO_2(CO_3)_3^{4-}$ from reference 3 gives $\log_{10}\beta_5 = 38.3$. If the formation constant for $Np(CO_3)_5^{6-}$ is assumed equal (within two orders of magnitude) to that of the U(IV) complex, $\Delta_f G^\circ(Np(CO_3)_5^{6-}) = (-3361 \pm 14)$ kJ.mol^{-1} is obtained. Calculations of neptunium solubility for total carbonate concentrations < 1 mol.dm^{-3}, based on this Gibbs energy of formation and the Gibbs energy of formation of $Np(OH)_4(s)$ (discussed in Section 2.1.3), lead to lower values than found experimentally for the conditions of Moskvin [57]. This may indicate that $Np(CO_3)_5^{6-}$ is not the major Np(IV) carbonate complex for the noted conditions, but is more likely the result of medium effects and the lack of

proper characterization of the solid and solution species in Moskvin's experiments. The entropy for $Np(CO_3)_5^{6-}$ was estimated to be (160 ± 200) $J.K^{-1}.mol^{-1}$ using the method of Cobble [60] by assuming Np^{4+} to be ten-coordinate and all carbonate ligands to be bidentate ligands in this complex. $Np(OH)_4CO_3^{2-}$ has not been retained in the data base.

Various species and equilibrium constants have been reported for the Np(V) carbonate system. Moskvin's constants [57], based on solubility measurements, cannot be used because of the lack of characterization of the solid phase and because the measurements were made over an extremely small pH range. The results of the coprecipitation experiments of Moskvin and Poznyakov [55] and the solubility experiments of Moskvin et al. [61] for the formation constant of $NpO_2HCO_3(aq)$ are consistent, but in marked disagreement with the preliminary work of Edelstein et al. [62]. This last reference also provides a value for the formation constant of $NpO_2(CO_3)_3^{5-}$, a species for which there is reasonably good spectroscopic evidence [63].

Maya [64] has recently reported data for the solubility of $NaNpO_2CO_3 \cdot 3.5H_2O$ as a function of pH and carbonate concentration ($I = 1.0$ $mol \cdot dm^{-3}$). From his data, values were obtained for the formation constants of $NpO_2(CO_3)_n^{1-2n}$ ($n = 1-3$), the solubility product of $NaNpO_2CO_3 \cdot 3.5H_2O$ and the first hydrolysis constant of NpO_2^+. The values of the other four constants are not very sensitive to the value selected for the hydrolysis constant for NpO_2^+. The difference between the value -9.12 for this constant from Maya ($I = 1$) and the value -8.9 ($I = 0$) selected in Section 2.1.4 is probably the result of medium effects. From $K_s(NaNpO_2CO_3 \cdot 3.5H_2O)$ $= 10.14$, taking $\gamma(Na^+)$ and $\gamma(CO_3^{2-})$ from the work of Whitfield [65] and estimating $\gamma(NpO_2^+, 1 \text{ mol.dm}^{-3} \text{ NaClO}_4(aq)) = 0.6$, a value of $K_s = -11.6 \pm 1.5$ is obtained (corrected to $I = 0$). This leads to $\Delta_fG°(NaNpO_2CO_3 \cdot 3.5H_2O, I \to 0) = (-2601 \pm 10) \text{ kJ.mol}^{-1}$. Also, from the values of β_1, $\Delta_fG°(NpO_2CO_3^-) = (-1469 \pm 7) \text{ kJ.mol}^{-1}$, $\Delta_fG°(NpO_2(CO_3)_2^{3-}) =$ $(-2011 \pm 7) \text{ kJ.mol}^{-1}$ and $\Delta_fG°(NpO_2(CO_3)_3^{5-}) = (-2547 \pm 7) \text{ kJ.mol}^{-1}$. The uncertainties in the Gibbs energies of formation of the complexes include $\pm 5 \text{ kJ.mol}^{-1}$ introduced in assuming the experimental values ($I = 1$) can be used for $I \to 0$. It should be noted that the value $\log_{10}\beta_3 = 16.3$ ($I = 0.05$, 294 K) from Edelstein et al. [62] is completely inconsistent with the solu-

bility data. The values of the slopes from the plots shown in reference 62 are ambiguous, and therefore the nature of the complexes involved is uncertain. It appears that the complexation constants based on the solubility measurements are to be preferred.

$\Delta_r S = 274$ J.K^{-1}.mol^{-1} [3] for the reaction of UO_2^{2+} and CO_3^{2-} to form $UO_2(CO_3)_3^{4-}$. Assuming that the same entropy change occurs in a similar reaction to form $NpO_2(CO_3)_3^{5-}$ gives $\overline{S}^\circ(NpO_2(CO_3)_3^{5-}) = 80 \pm 50$ J.K^{-1}.mol^{-1}. This value agrees within 30 J.K^{-1}.mol^{-1} with the value calculated by the method of Cobble [60]. Cobble's method was used to calculate $\overline{S}^\circ(NpO_2CO_3^-)$ = (200 ± 200) J.K^{-1}.mol^{-1} and $\overline{S}^\circ(NpO_2(CO_3)_2^{3-}) = (110 \pm 200)$ J.K^{-1}.mol^{-1}. The entropy of $NaNpO_2CO_3 \cdot 3.5H_2O$ has been estimated as $S^\circ(NpO_2)$ plus the entropy contributions for Na, CO_3^{2-} (attached to 1+ cations) and water of hydration suggested by Latimer [20].

Moskvin's solubility work [57] demonstrated the formation of a Np(VI) carbonate complex in aqueous solution. Lack of control of the ionic strength and lack of proper characterization of the equilibrium solids in these experiments could lead to errors in the nature of the reported species and/or the reported equilibrium constants. Madic et al. [63] reported some spectroscopic evidence for $NpO_2(CO_3)_3^{4-}$ at high concentrations, while Moskvin claimed the existence of $NpO_2(OH)_2CO_3^{2-}$ and $NpO_2(CO_3)_2^{2-}$. In the absence of other quantitative information, $NpO_2(CO_3)_2^{2-}$ has been accepted strictly as a representative species, and Moskvin's value for $\log_{10}\beta_2 = 14$ is used with the assumption that the value is correct within two orders of magnitude. This leads to $\Delta_f G^\circ(NpO_2(CO_3)_2^{2-}) = (-1933 \pm 11)$ kJ.mol^{-1}. By assuming $\Delta_r S$ is the same for the uranium [3] and neptunium complexation reactions, a value of $\overline{S}^\circ(NpO_2(CO_3)_2^{2-}) = (170 \pm 130)$ J.K^{-1}.mol^{-1} has been chosen. The large uncertainty reflects lack of confidence in the value for the uranium species as well as the fact that Cobble's method [60] leads to a considerably more positive value for the entropy.

Maya [64] has estimated $\log_{10}\beta_3 = 20.37$ for the formation constant of $NpO_2(CO_3)_3^{4-}$. This gives $\Delta_f G^\circ(NpO_2(CO_3)_3^{4-}) = (-2496 \pm 10)$ kJ.mol^{-1} where the uncertainty is an estimate. For high carbonate concentrations in

basic solution, this species would then be predicted to be more important than $NpO_2(CO_3)_2^{2-}$ - even under Moskvin's experimental conditions. Until further data become available (see also reference 66), it seems reasonable to retain both $NpO_2(CO_3)_2^{2-}$ and $NpO_2(CO_3)_3^{4-}$ in the data base. $\bar{S}°(NpO_2(CO_3)_3^{4-}) = (12 \pm 50)$ J.K.$^{-1}$.mol^{-1} was calculated by assuming $\Delta_r S$ is the same for the neptunium and uranium [3] complexation reactions.

2.1.8   Phosphate Complexes

Moskvin [67] has estimated values of the formation constants (β_i, I = 0) to be 2.5×10^2, 5.4×10^3 and 4.4×10^5 for $Np(H_2PO_4)_i^{3-i}$(i = 1-3). These lead to $\Delta_f G°(NpH_2PO_4^{2+}) = (-1661 \pm 10)$ kJ.mol^{-1}, $\Delta_f G°(Np(H_2PO_4)_2^+)$ = (-2799 ± 10) kJ.mol^{-1} and $\Delta_f G°(Np(H_2PO_4)_3(aq)) = (-3941 \pm 20)$ kJ.mol^{-1}. The entropies of the 1:1, 1:2 and 1:3 complexes were estimated, respectively, as (-146 ± 200), (-180 ± 200) and (-245 ± 200) J.K^{-1}.mol^{-1} using Cobble's method [60], and assuming each phosphate displaces two water molecules from around the Np^{3+} ion.

Values of the formation constants of the Np(IV) monohydrogen phosphate complexes (I = 0) were assumed equal to the experimental values (I ~ 2) for the corresponding Pu(IV) species [68]. No attempt has been made here to "correct" the experimental values to I = 0. Instead, large uncertainties (± 20 kJ.mol^{-1}) have been assumed for the calculated values of $\Delta_f G°(NpHPO_4^{2+}) = -1666$ kJ.mol^{-1}, $\Delta_f G°(Np(HPO_4)_2(aq)) = -2817$ kJ.mol^{-1}, $\Delta_f G°(Np(HPO_4)_3^{2-}) = -3962$ kJ.mol^{-1}, $\Delta_f G°(Np(HPO_4)_4^{4-}) = -5107$ kJ.mol^{-1} and $\Delta_f G°(Np(HPO_4)_5^{6-}) = -6246$ kJ.mol^{-1}. Values of (-150 ± 200), (-120 ± 200), (0 ± 200), (80 ± 200) and (160 ± 200) J.K^{-1}.mol^{-1} were estimated [60] for the entropies of these species.

Moskvin and Poznyakov [55] reported coprecipitation results that gave a value of $\log_{10}K_1 = 2.90 \pm 0.11$ (I = 0.1, 20°C; or 3.3 $\pm$ 0.4 corrected to I = 0) for the association of NpO_2^+ with HPO_4^{2-}. This is in good agreement with the value of $\log_{10}K_1 = 3.4 \pm 0.5$ (20°C, corrected to I = 0) obtained on recalculating the results of the ion-exchange study of Moskvin and Peretrukhin [69]. There are difficulties with the analysis of the sparse

data from the coprecipitation study, a study that also proposes, but presents little evidence for, the existence of the species $NpO_2PO_4^{2-}$. The complexation constant from the ion-exchange study has been chosen here and leads to $\Delta_f G°(NpO_2HPO_4) = (-2024 \pm 6)$ kJ.mol^{-1} at 20°C. Moskvin and Peretrukhin's results also suggested that the species $NpO_2H_2PO_4(aq)$ is formed. A value of $\log_{10}K_1 = 0.7 \pm 0.2$ (20°C, I → 0) was obtained by recalculating the data in reference 69, and thus $\Delta_f G°(NpO_2H_2PO_4(aq), 20°C)$ = (-2049 ± 6) kJ.mol^{-1} was calculated. Entropies for these two phosphate complexes have been estimated [60] as $\bar{S}°(NpO_2HPO_4^-) = (180 \pm 200)$ J.K^{-1}.mol^{-1} and $\bar{S}°(NpO_2H_2PO_4(aq)) = (20 \pm 200)$ J.K^{-1}.mol^{-1}. These were then used with the values of $\Delta_f G°$ for 20°C to obtain the 25°C values $\Delta_f G°(NpO_2HPO_4^-) = (-2025 \pm 6)$ kJ.mol^{-1} and $\Delta_f G°(NpO_2H_2PO_4(aq)) = (-2049 \pm 6)$ kJ.mol^{-1}.

Moskvin [67] has reported the stability constants of $NpO_2HPO_4(aq)$ and $NpO_2H_2PO_4^+$ to be 1.5×10^7 and 50, respectively, at I = 1. Moskvin estimates that at I = 0 these imply values of 8.2 and 2.3 for $\log_{10}K_1$ and $\log_{10}K_2$. Using these values, and assuming them correct within an order of magnitude, give $\Delta_f G°(NpO_2HPO_4(aq)) = (-1932 \pm 8)$ kJ.mol^{-1} and $\Delta_f G°(NpO_2H_2PO_4^+) = (-1940 \pm 8)$ kJ.mol^{-1}. The treatment of Cobble [60] gives estimates of $\bar{S}°(NpO_2HPO_4(aq)) = (10 \pm 200)$ J.K^{-1}.mol^{-1} and $\bar{S}°(NpO_2H_2PO_4^+)$ = (-50 ± 200) J.K^{-1}.mol^{-1}.

Although neptunium phosphate solids are expected for several oxidation states on the basis of comparison with the uranium and plutonium systems, little has been reported on these compounds. Moskvin et al. [70] estimated $K_s = 10^{-28}$ for $Np(HPO_4)_2 \cdot xH_2O$ (at I = 0.35) on the basis of comparison with the corresponding phosphates of other actinides. A later paper by Moskvin [71] suggested $K_s = 10^{-30.9}$ (I → 0). The later value has been assumed correct within two orders of magnitude and gives $\Delta_f G°(Np(HPO_4)_2(s)) = (-2858 \pm 14)$ kJ.mol^{-1}. $S°(Np(HPO_4)_2)$ = (200 ± 20) J.K^{-1}.mol^{-1} has been calculated from Langmuir's estimate [41] for $U(HPO_4)_2$, as discussed previously for the corresponding plutonium compound [3].

2.1.9   Chloride Complexes

Many studies have been done on the complexation of chloride with neptunium ions [5]. Most of the experiments were done in the presence of a high concentration of supporting electrolyte (I = 0.5 to 4), and the results are reasonably consistent. For use in this report, the values of $\log_{10}\beta_1$ = -0.05 and $\log_{10}\beta_2$ = -0.2 (I = 2) from the extraction study of Patil and Ramakrishna [72] have been selected for complexation of chloride with Np(IV). The value of $\log_{10}\beta_1$ = -0.4 (I = 2.0) of Rao et al. [47] has been selected for NpO_2^+/Cl^- association, and a value of $\log_{10}\beta_1$ = -0.3 (I = 0.3) obtained by potentiometry [73] has been chosen for NpO_2^{2+}/Cl^- complexation. For the Np(IV) and Np(VI) complexes, the values have been corrected to I = 0 using the same parameters estimated for the corresponding hydrolysis constants [18]. Values for $M(OH)_2^{2+}$ (M = Zr, Hf) were used for $NpCl_2^{2+}$. No medium correction is available for the formation constant of $NpO_2Cl(aq)$, but the constant at I = 0 has been assumed equal to the value at I = 2, which is probably correct within ±1 for $\log_{10}\beta_1$. Errors in the correction of the constants to I = 0 are likely to be of the order of the size of the corrections and, hence, larger than the error limits in the constants. The corrected values of $\log_{10}\beta_1$ for $NpCl^{3+}$, $NpCl_2^{2+}$ and NpO_2Cl^+ are (0.2 ± 1.0), (-0.1 ± 1.0) and (-0.2 ± 0.2), respectively. Hence, $\Delta_f G°(NpCl^{3+})$ = (-636 ± 9) kJ.mol^{-1}, $\Delta_f G°(NpCl_2^{2+})$ = (-765 ± 9) kJ.mol^{-1}, $\Delta_f G°(NpO_2Cl(aq))$ = (-1044 ± 8) kJ.mol^{-1} and $\Delta_f G°(NpO_2Cl^+)$ = (-926 ± 6) kJ.mol^{-1}.

$\bar{S}°(NpCl_3^+)$ = (-260 ± 150) J.K^{-1}.mol^{-1} and $\bar{S}°(NpO_2Cl^+)$ = (0 ± 150) J.K^{-1}.mol^{-1} were estimated by assuming the same entropy of complexation as for the corresponding uranium species [3]. $\bar{S}°(NpO_2Cl(aq))$ = (80 ± 200) J.K^{-1}.mol^{-1} and $\bar{S}°(NpCl_2^{2+})$ = (40 ± 200) J.K^{-1}.mol^{-1} were estimated by the methods of Cobble [60].

2.2   HEAT CAPACITIES

2.2.1   Heat Capacities of Neptunium Solids

Two sets of experimental data are available for NpO_2. Westrum et al. [16] have reported C_p measurements for temperatures to 312.68 K.

Arkhipov et al. [74] have done drop-calorimetry measurements from 350 to 1100 K. Extrapolations of the two sets of measurements appear to differ by 10 to 15 $J \cdot K^{-1} \cdot mol^{-1}$ in the range 300 to 400 K. Because the uncertainties are considerably larger in the C_p values from the drop-calorimetry study, the low-temperature heat capacity results from 200 to 312.68 K have been fitted to a function of the form $C_p = A + BT + C/T^2$ and high-temperature C_p values (to 423 K) have been obtained by extrapolation.

Belyaev et al. [75] have measured the heat capacity of Np_2O_5 from 350 to 750 K by drop calorimetry. This work appears to be more precise than the work on NpO_2 from the same research group. On conversion to a molar basis, the equation in reference 75 for C_p° (Np_2O_5) becomes $C_p^\circ = 99.2 + 98.6 \times 10^{-3}T$ $J \cdot K^{-1} \cdot mol^{-1}$ (T in K), and this equation has been used in the present work over the entire temperature range required.

The heat capacity of neptunium metal was taken from the assessment of Oetting et al. [29]. Heat capacities for $Np(HPO_4)_2(s)$, $Np(OH)_4(s)$, $NpO_2(OH)(am)$, $NpO_2(OH)_2(s)$ and $NaNpO_2CO_3 \cdot 3.5H_2O(s)$ were estimated to be 224 $J \cdot K^{-1} \cdot mol^{-1}$, 131 $J \cdot K^{-1} \cdot mol^{-1}$, 86 $J \cdot K^{-1} \cdot mol^{-1}$, 112 $J \cdot K^{-1} \cdot mol^{-1}$ and 269 $J \cdot K^{-1} \cdot mol^{-1}$, respectively, using Kopp's law as outlined by Sturtevant [76]. The value for $NpO_2(OH)_2(s)$ may be somewhat low since the heat capacity for the similar $UO_2(OH)_2(s)$ ranges from 141 to 146 $J \cdot K^{-1} \cdot mol^{-1}$ for temperatures between 25 and 150°C [3].

2.2.2   Effective Heat Capacities for Aqueous Species

The temperature dependence of the Gibbs energy and entropy of a species can be described if the heat capacity function C_p° is known. The evaluation of $\bar{C}_p^\circ|_{25}^{200}$ for the ligand species has been discussed previously [3] and similar methods have been used to obtain $\bar{C}_p^\circ|_{25}^{150}$ for use in this report. However, no values have been reported for C_p° of any aqueous species of neptunium.

Values are needed for both simple ions (e.g., Np^{3+}) and polyatomic species (e.g., NpO_2^{2+}). The most widely used method of estimating $\bar{C}_p^\circ$ for such species is the Criss-Cobble correspondence principle [10].

As discussed in a previous paper [3], the correspondence principle must be modified for use with ions that have an electronic degeneracy (Russell–Saunders total angular momentum quantum number $J \neq 0$). Assuming spin–orbit coupling effects are large compared with ligand field effects, and the ligand field effects are of the order of kT or smaller, the contribution of the electronic degeneracy to the entropy, $\bar{S}_e^\circ$, is equal to that of the corresponding free metal ion in the gas phase:

$$\bar{S}_e^\circ \approx R \ln (2J + 1). \tag{12}$$

Values of J were taken from Figgis [77] (Np^{3+}, Np^{4+}) and from McGlynn and Smith [78] (NpO_2^+, NpO_2^{2+}). $\bar{S}_e^\circ$ was subtracted from the room-temperature entropy. The residual entropy, $\bar{S}_{adj}^\circ(T) = S^\circ(T) - \bar{S}_e^\circ$, was estimated at 60, 100 and 150°C from the Criss–Cobble principle in the usual way [10]. These values were then put in a convenient analytical form by a least-squares curve fit to the expression

$$\bar{S}^\circ(T) = \bar{S}^\circ + \bar{C}_p^\circ\Big|_{25}^{150} \ln(T/298.15), \tag{13}$$

where $\bar{S}^\circ$ is the partial molal entropy at 25°C and $\bar{C}_p^\circ\big|_{25}^{150}$, the curve-fitted constant, is defined to be the mean partial molal heat capacity over the range 25 to 150°C. More complex expressions for the heat capacity function are unjustified in view of the large uncertainties in the room-temperature entropy data used here. The assumption that $\bar{C}_p^\circ$ is a constant between 25 and 150°C introduces an error generally much less than the precision of the extrapolation. We note that the values for $\bar{S}^\circ$ and $\bar{C}_p^\circ\big|_{25}^{150}$ listed here are conventional standard properties that should not be confused with the so-called "absolute" parameters referred to in Criss and Cobble's papers [10,79].

The validity of the Criss–Cobble method is most firmly established for simple anions and cations. Therefore it was used for Np^{3+}, Np^{4+}, NpO_2^+ and NpO_2^{2+}. For $NpO_2SO_4(aq)$, $NpO_2(CO_3)_2^{2-}$, NpO_2Cl^+ and $NpCl^{3+}$, the Gibbs energies at temperatures above 25°C were calculated by assuming that the equilibrium constants for the neptunium complexation reactions have the same

temperature dependence as the constants for the corresponding uranium reactions [41, 80-82]. For all other ionic neptunium species, $\bar{C}_p^\circ\big|_{25}^{150}$ values were calculated directly by the Criss-Cobble method using coefficients for the simple cations, anions, oxyanions, and acid oxyanions. The assumption that the coefficients for a simple species can be applied to metal complexes is often used [83-85], but it is clearly an oversimplification. For most of the neutral aqueous species considered, no high-temperature Gibbs energy data were available. Also, there is no good general method, comparable to the Criss-Cobble treatment for ions, for calculating such data. In such cases $C_p^\circ\big|_{25}^{150}$ has arbitrarily been assigned a value of zero in the equilibrium constant calculations.

3. CALCULATION OF THE BEHAVIOUR OF NEPTUNIUM IN WATER AND IN MODEL GROUNDWATERS

3.1 THERMODYNAMIC DATA AND METHODS OF CALCULATION OF THE BEHAVIOUR OF NEPTUNIUM

Table 1 gives thermochemical data for H_2O, relevant gases and solid neptunium compounds. Tables 2 and 3 show Gibbs energies and entropies at 25°C and the values for $\bar{C}_p^\circ\big|_{25}^{150}$, whether derived from the Criss-Cobble calculations or by analogy. It should be noted that $\bar{C}_p^\circ\big|_{25}^{150}$ differs somewhat from $\bar{C}_p^\circ\big|_{25}^{200}$ [3] for many of the species in Table 2.

Gibbs energies of reaction, $\Delta_r G^\circ(T)$, and equilibrium constants, $K(T)$, for reactions involving these species can be calculated from the data in Tables 1 to 3 using the following expressions [86,87]:

$$\Delta_r G^\circ(T) = \Delta_r G^\circ(298.15) + [\Delta_r C_p^\circ - \Delta_r S^\circ] (T - 298.15)$$

$$- T\Delta_r C_p^\circ \ln(T/298.15) \tag{14}$$

$$\log_{10} K(T) = -\Delta_r G^\circ(T)/(2.3026\ RT). \tag{15}$$

TABLE 1

THERMODYNAMIC PARAMETERS FOR WATER, GASES, AND SOLID NEPTUNIUM COMPOUNDS[a,b,c]

Species	$\Delta_f G^\circ$	S°	$C_p^\circ = A + 10^{-3} BT + 10^5 C/T^{-2}$		
			A	B/K	C/K^{-2}
$H_2O(l)$	−237.18	69.95	75.291	0	0
$H^+(aq)$	0	0	0	0	0
$OH^-(aq)$	−157.29	−10.84	2236.3	−4426	−954
$O_2(g)$	0	205.03	29.957	4.18	−1.67
$CO_2(g)$	−394.38	213.68	44.22	8.79	−8.62
$H_2(g)$	0	130.57	27.28	3.26	0.50
Np	0	50.46 ± 0.42	−4.054	82.55	8.058
NpO_2	−1021.8 ± 2.5	80.3 ± 0.4	56.392	53.737	−5.518
$Np(OH)_4(s)$	−1447 ± 20	(139 ± 25)	(131)	0	0
Np_2O_5	−2013 ± 14	163 ± 23	99.2	98.6	0
$NpO_2(OH)(am)$	−1128.0 ± 5.5	(101 ± 8)	(86)	0	0
$NpO_2(OH)_2(s)$	−1236 ± 12	118 ± 20	(112)	0	0
$Np(HPO_4)_2(s)$	(−2858 ± 14)	(200 ± 20)	(224)	0	0
$NaNpO_2CO_3 \cdot 3.5H_2O$	−2601 ± 10	(314 ± 50)	(269)	0	0
NpO_2 in UO_2[d]	−1043 ± 2.5	(151 ± 2)	(56.392)	(53.737)	(−5.518)

[a] Numbers in parentheses represent estimated values.
[b] Details of the selection of values for the gases and for $H_2O(l)$ and OH^- are given in reference 3.
[c] Units of $\Delta_f G^\circ$, S° and C_p° are $kJ.mol^{-1}$, $J.K^{-1}.mol^{-1}$ and $J.K^{-1}mol^{-1}$, respectively.
[d] NpO_2 (0.00020 mole fraction) in solid solution in UO_2.

TABLE 2

THERMODYNAMIC PARAMETERS FOR AQUEOUS LIGAND SPECIES[a,b]

Species	$\Delta_f G°$ (kJ.mol^{-1})	$\bar{S}°$ (J.K^{-1}.mol^{-1})	$\bar{C}_p° \mid^{150}_{25}$ (J.K^{-1}.mol^{-1})
H^+[b]	0	0	0
Na^+	−261.89	58.41	(36)
Cl^-	−131.29	56.74	(−117)
F^-	−281.75	−13.18	(−115)
$HF(aq)$	−299.93	93.62	(49)
CO_3^{2-}	−527.99	−54.62	−282
HCO_3^-	−586.95	92.49	−6
H_2CO_3	−623.20	188.3	267
PO_4^{3-}	−1018.8	−221.8	(−480)
HPO_4^{2-}	−1089.3	−33.47	(−285)
$H_2PO_4^-$	−1130.4	93.68	(−86)
H_3PO_4	−1142.6	163.30	(54)
SO_4^{2-}	−744.54	18.83	(−172)
HSO_4^-	−755.88	120.00	(24)

[a] Numbers in parentheses represent values from Criss-Cobble entropies

[b] Values for OH^-, which are defined by K_w (see reference 3), are listed in Table 1.

TABLE 3

THERMODYNAMIC PARAMETERS FOR AQUEOUS NEPTUNIUM SPECIES[a]

Species	$\Delta_f G°$ (kJ.mol^{-1})	$\bar{S}°$ (J.K^{-1}.mol^{-1})	$\bar{C}_p° \vert_{25}^{150}$ (J.K^{-1}.mol^{-1})
Np^{3+}	-517.1 ± 3.3	-179.1 ± 6.4	(-60)
Np^{4+}	-502.9 ± 7.5	-389 ± 21	(-60)
NpO_2^+	-915.0 ± 5.4	-21 ± 8	(92)
NpO_2^{2+}	-795.8 ± 5.4	-92 ± 8	(10)
$NpOH^{2+}$	-714.3 ± 3.7	(-75 ± 30)	(2)
$NpOH^{3+}$	-734 ± 9	(-167 ± 40)	(-66)
$Np(OH)_2^{2+}$	-961 ± 15	(-44 ± 80)	(-15)
$Np(OH)_3^+$	-1181 ± 20	(44 ± 110)	(55)
$Np(OH)_4$	-1397 ± 20	(75 ± 130)	$-$
$Np(OH)_5^-$	$-1607 \begin{smallmatrix}+40\\-20\end{smallmatrix}$	(96 ± 170)	(-67)
NpO_2OH	-1101 ± 5	(25 ± 60)	$-$
NpO_2OH^+	-1004 ± 5	(24 ± 50)	(64)
$(NpO_2)_2(OH)_2^{2+}$	-2030 ± 11	(-14 ± 50)	(-32)
$(NpO_2)_3(OH)_5^+$	-3474 ± 17	(116 ± 50)	(16)
NpF^{3+}	-834.3 ± 7.7	(-247 ± 50)	(-20)
NpF_2^{2+}	-1154.3 ± 8.1	(-100 ± 100)	(17)
NpO_2F	-1202 ± 6	(100 ± 100)	$-$
NpO_2F^+	-1103.8 ± 5.7	(-14 ± 80)	(86)
NpO_2F_2	-1403.8 ± 6.1	(40 ± 80)	$-$
$NpSO_4^{2+}$	-1279 ± 10	(-195 ± 50)	(71)
$Np(SO_4)_2$	-2048 ± 10	(-27 ± 70)	$-$
$NpO_2SO_4^-$	-1662 ± 8	(70 ± 50)	(-281)
NpO_2SO_4	-1559 ± 6	(57 ± 100)	359^b
$Np(CO_3)_5^{6-}$	(-3361 ± 14)	(160 ± 200)	(771)

TABLE 3 (concluded)

Species	$\Delta_f G°$ (kJ.mol^{-1})			$\bar{S}°$ (J.K^{-1}.mol^{-1})			$\bar{C}_p° \mid_{25}^{150}$ (J.K^{-1}.mol^{-1})
$NpO_2CO_3^-$	-1469	±	7	(200	± 200)		(-20)
$NpO_2(CO_3)_2^{3-}$	-2011	±	7	(110	± 200)		(149)
$NpO_2(CO_3)_3^{5-}$	-2547	±	7	(80	± 50)		(438)
$NpO_2(CO_3)_2^{2-}$	-1933	±	11	(170	± 130)		(-382)[b]
$NpO_2(CO_3)_3^{4-}$	(-2496	±	10)	(12	± 50)		(134)
$NpH_2PO_4^{2+}$	(-1661	±	10)	(-146	± 200)		(42)
$Np(H_2PO_4)_2^+$	(-2799	±	10)	(-180	± 200)		(182)
$Np(H_2PO_4)_3$	(-3941	±	20)	(-245	± 200)		—
$NpHPO_4^{2+}$	(-1666	±	20)	(-150	± 200)		(45)
$Np(HPO_4)_2$	(-2817	±	20)	(-120	± 200)		—
$Np(HPO_4)_3^{2-}$	(-3962	±	20)	(0	± 200)		(-228)
$Np(HPO_4)_4^{4-}$	(-5107	±	20)	(80	± 200)		(515)
$Np(HPO_4)_5^{6-}$	(-6246	±	20)	(160	± 200)		(1260)
$NpO_2HPO_4^-$	-2025	±	6	(180	± 200)		(266)
$NpO_2H_2PO_4$	-2049	±	6	(20	± 200)		—
NpO_2HPO_4	-1932	±	8	(10	± 200)		—
$NpO_2H_2PO_4^+$	-1940	±	8	(-50	± 200)		(106)
$NpCl^{3+}$	-636	±	9	(-260	± 150)		(273)[b]
$NpCl_2^{2+}$	-765	±	9	(40	± 200)		(-63)
NpO_2Cl	-1044	±	8	(80	± 200)		—
NpO_2Cl^+	-926	±	6	(0	± 150)		(432)[b]

[a] Numbers in parentheses represent estimated values.
[b] Heat capacities estimated from the temperature dependence of $\Delta_f G°$ of the species (based on data for the corresponding uranium species) — see text.

Equilibrium constants for a selection of key reactions at 25, 60, 100 and 150°C are given in Table 4. The effect of uncertainties in the room-temperature data on the equilibrium constants in Table 4 was estimated from

$$\sigma(\log_{10}K,T) = \frac{1}{2.3026\ RT}\ [\sigma(\Delta_r G°,298)^2 + (T - 298.15)^2\ \sigma(\Delta_r S°,298)^2]^{\frac{1}{2}} \quad (16)$$

This equation does not include a term reflecting the uncertainty in $\log_{10}K$ introduced by uncertainty in the heat capacities. If the use of the Criss-Cobble principle for the neptunium ionic species is valid, then the uncertainty in $\log_{10}K$ (25°C < T < 150°C) introduced in the estimation of $\Delta_r C°_p$ is generally much less than the error from the uncertainty in the entropy of reaction. If the Criss-Cobble principle cannot be applied, then there is also no method of estimating the errors in the heat capacities. For reactions involving neutral aqueous species for which $\bar{C}°_p$ has been arbitrarily taken as zero, $\sigma(\Delta_r C°_p)$ has been estimated as ± 350 $J.K^{-1}.mol^{-1}$. This introduces an additional uncertainty of ± 1 in $\log_{10}K$ at 150°C and lesser uncertainties at lower temperatures.

Methods of calculating the potential-pH diagrams and distribution diagrams have been outlined previously [88]. Note that although data in Tables 1 to 3 employ the convention that $\Delta_f G°(H^+) \equiv 0$ at all temperatures, the convention employed in the potential-pH diagrams in this report is that all potentials are referred to a standard hydrogen electrode at each temperature considered. This change in standard state greatly simplifies the comparison of the potential-pH diagrams at different temperatures. Also, the value of pH at temperatures above 25°C is the equilibrium pH at the temperature of interest, rather than the pH the solution would have at 25°C.

In a previous paper on the behaviour of uranium and plutonium [88], five different electrochemical couples were chosen as representative of the possible reducing (or oxidizing) conditions in groundwaters. These are shown in Figure 2 for 25°C. Lines A and E represent reactions that delineate the stability field of water. Below or above these lines, water is thermodynamically unstable (at a total pressure of 101 kPa). Line B represents the boundary between hematite and magnetite and, if the tempera-

TABLE 4

EQUILIBRIUM CONSTANTS FOR NEPTUNIUM

Reaction No.	Reaction	$\log_{10}K$			
		25°C	60°C	100°C	150°C
(A) Solid Transformations					
1	$Np + O_2 = NpO_2$	179.0 ± 0.4	159.2 ± 0.4	141.2 ± 0.4	123.5 ± 0.3
2	$NpO_2 + 2H_2O = Np(OH)_4(s)$	-8.6 ± 3.5	-8 ± 3	-8 ± 3	-8 ± 3
3	$4NpO_2 + O_2 = 2Np_2O_5$	-10.7 ± 5.3	-11 ± 5	-11 ± 4	-11 ± 4
4	$4NpO_2 + O_2 + 2H_2O = 4NpO_2(OH)(am)$	-8.7 ± 4.2	-9 ± 4	-10 ± 3	-10 ± 3
5	$2NpO_2 + O_2 + 2H_2O = 2NpO_2(OH)_2$	-8.1 ± 4.4	-9 ± 4	-9 ± 4	-10 ± 3
(B) Redox Reactions					
6	$4NpO_2^+ + 4H^+ + O_2 = 4NpO_2^{2+} + 2H_2O$	-0.4 ± 3.9	-2 ± 3	-4 ± 3	-6 ± 3
7	$4NpO_2^+ + 12H^+ = 4Np^{4+} + O_2 + 6H_2O$	-39.5 ± 6.1	-40 ± 6	-41 ± 5	-41 ± 5
8	$2NpO_2^+ + 4H^+ = 2Np^{3+} + O_2 + 2H_2O$	-56.3 ± 2.3	-50 ± 2	-45 ± 2	-40 ± 2
(C) Oxide Dissolution Reactions					
9	$NpO_2 + 4H^+ = Np^{4+} + 2H_2O$	-7.8 ± 1.4	-9 ± 1	-10 ± 1	-11 ± 1
10[a]	$NpO_2(in\ UO_2) + 4H^+ = Np^{4+} + 2H_2O$	-11.5 ± 1.4	-12 ± 1	-13 ± 1	-14 ± 1
11	$2NpO_2 + 4H^+ + O_2 = 2NpO_2^{2+} + 2H_2O$	3.9 ± 2.1	1 ± 2	-1 ± 2	-4 ± 2
12	$4NpO_2 + 4H^+ + O_2 = 4NpO_2^+ + 2H_2O$	8.3 ± 4.2	5 ± 4	2 ± 3	-1 ± 3
13	$4NpO_2 + 12H^+ = 4Np^{3+} + O_2 + 6H_2O$	-104.4 ± 3.0	-96 ± 3	-88 ± 2	-80 ± 2
14	$Np(OH)_4(s) + 4H^+ = Np^{4+} + 4H_2O$	0.8 ± 4.0	-1 ± 4	-2 ± 3	-3 ± 3
15	$Np_2O_5 + 2H^+ = 2NpO_2^+ + H_2O$	9.5 ± 2.6	8 ± 2	6 ± 2	5 ± 2
16	$NpO_2(OH)(am) + H^+ = NpO_2^+ + H_2O$	4.2 ± 0.2	3.5 ± 0.2	2.9 ± 0.2	2.4 ± 0.2
17	$NpO_2(OH)_2 + 2H^+ = NpO_2^{2+} + 2H_2O$	6.0 ± 2.0	5 ± 2	4 ± 2	3 ± 2
(D) Dissolution of Neptunium Compounds					
18	$Np(HPO_4)_2(s) = Np^{4+} + 2HPO_4^{2-}$	-30.9 ± 2.0	-32 ± 2	-33 ± 2	-34 ± 2
19	$2(NaNpO_2CO_3 \cdot 3.5H_2O) = 2Na^+ + 2NpO_2^+ + 2CO_3^{2-} + 7H_2O$	-23.2 ± 3.0	-22 ± 3	-21 ± 3	-20 ± 3

[a] 0.0002 mole fraction NpO_2 (see text)

TABLE 4 (continued)

Reaction No.	Reaction	$\log_{10}K$			
		25°C	60°C	100°C	150°C
(E) Hydrolysis Reactions					
20	$Np^{3+} + H_2O = NpOH^{2+} + H^+$	-7.0 ± 0.3	-6.1 ± 0.3	-5.3 ± 0.4	-4.5 ± 0.5
21	$Np^{4+} + H_2O = NpOH^{3+} + H^+$	-1.0 ± 1.0	-0.1 ± 0.9	0.7 ± 0.9	1.4 ± 0.9
22	$Np^{4+} + 2H_2O = Np(OH)_2^{2+} + 2H^+$	-2.8 ± 2.6	-1 ± 2	0 ± 2	1 ± 2
23	$Np^{4+} + 3H_2O = Np(OH)_3^+ + 3H^+$	-5.8 ± 3.5	-4 ± 3	-2 ± 3	-1 ± 3
24	$Np^{4+} + 4H_2O = Np(OH)_4(aq) + 4H^+$	-9.6 ± 3.5	-8 ± 3	-6 ± 3	-5 ± 3
25	$Np^{4+} + 5H_2O = Np(OH)_5^- + 5H^+$	$-14.3 \begin{smallmatrix}+3.5\\-7.0\end{smallmatrix}$	$-12 \begin{smallmatrix}+3\\-7\end{smallmatrix}$	$-11 \begin{smallmatrix}+3\\-6\end{smallmatrix}$	$-9 \begin{smallmatrix}+3\\-6\end{smallmatrix}$
26	$NpO_2^+ + H_2O = NpO_2OH(aq) + H^+$	-8.9 ± 0.1	-8.2 ± 0.4	-7.6 ± 0.9	-7.2 ± 1.4
27	$NpO_2^{2+} + H_2O = NpO_2OH^+ + H^+$	-5.2 ± 0.1	-4.4 ± 0.3	-3.7 ± 0.5	-3.0 ± 0.8
28	$2NpO_2^{2+} + 2H_2O = (NpO_2)_2(OH)_2^{2+} + 2H^+$	-6.4 ± 0.3	-5.6 ± 0.4	-5.0 ± 0.6	-4.6 ± 0.8
29	$3NpO_2^{2+} + 5H_2O = (NpO_2)_3(OH)_5^+ + 5H^+$	-17.5 ± 0.8	-15.5 ± 0.8	-14.0 ± 0.8	-12.8 ± 0.9
(F) Complexation Reactions					
30	$Np^{4+} + F^- = NpF^{3+}$	8.7 ± 0.3	8.7 ± 0.4	8.8 ± 0.6	9.0 ± 0.8
31	$Np^{4+} + 2F^- = NpF_2^{2+}$	15.4 ± 0.6	15.6 ± 0.8	16.0 ± 1.1	16.6 ± 1.6
32	$NpO_2^+ + F^- = NpO_2F$	1.0 ± 0.4	1.6 ± 0.6	2.2 ± 1.2	2.8 ± 1.8
33	$NpO_2^{2+} + F^- = NpO_2F^+$	4.6 ± 0.3	4.7 ± 0.5	4.3 ± 0.9	5.2 ± 1.3
34	$NpO_2^{2+} + 2F^- = NpO_2F_2$	7.8 ± 0.5	7.9 ± 0.6	8.1 ± 1.0	8.5 ± 1.6
35	$Np^{4+} + SO_4^{2-} = NpSO_4^{2+}$	5.5 ± 1.1	6.0 ± 1.0	6.6 ± 1.0	7.5 ± 1.1
36	$Np^{4+} + 2SO_4^{2-} = Np(SO_4)_2$	9.9 ± 1.1	10.7 ± 1.1	11.8 ± 1.2	13.1 ± 1.7
37	$NpO_2^+ + SO_4^{2-} = NpO_2SO_4^-$	0.4 ± 1.0	0.7 ± 0.9	0.9 ± 1.0	0.9 ± 1.0
38	$NpO_2^{2+} + SO_4^{2-} = NpO_2SO_4$	3.3 ± 0.5	3.8 ± 0.7	4.6 ± 1.1	5.8 ± 1.6
39	$Np^{4+} + 5CO_3^{2-} = Np(CO_3)_5^{6-}$	38.3 ± 2.0	39 ± 2	42 ± 3	46 ± 3
40	$NpO_2^+ + CO_3^{2-} = NpO_2CO_3^-$	4.6 ± 1.0	5.7 ± 1	7 ± 2	8 ± 3
41	$NpO_2^+ + 2CO_3^{2-} = NpO_2(CO_3)_2^{3-}$	7.0 ± 1.0	7.8 ± 1	9 ± 2	10 ± 3
42	$NpO_2^+ + 3CO_3^{2-} = NpO_2(CO_3)_3^{5-}$	8.5 ± 1.0	9.4 ± 1.0	10.9 ± 1.0	13.4 ± 1.1
43	$NpO_2^{2+} + 2CO_3^{2-} = NpO_2(CO_3)_2^{2-}$	14.0 ± 2.0	15 ± 2	16 ± 2	16 ± 2
44	$NpO_2^{2+} + 3CO_3^{2-} = NpO_2(CO_3)_3^{4-}$	20.4 ± 1.4	20 ± 1	20 ± 1	21 ± 1

TABLE 4 (concluded)

| Reaction No.	Reaction	$\log_{10}K$			
		25°C	60°C	100°C	150°C
45	$Np^{3+} + H_2PO_4^- = NpH_2PO_4^{2+}$	2.4 ± 1.8	2 ± 2	1 ± 3	1 ± 3
46	$Np^{3+} + 2H_2PO_4^- = Np(H_2PO_4)_2^+$	3.7 ± 1.8	2 ± 2	1 ± 3	1 ± 3
47	$Np^{3+} + 3H_2PO_4^- = Np(H_2PO_4)_3$	5.6 ± 3.5	3 ± 3	1 ± 4	0 ± 4
48	$Np^{4+} + HPO_4^{2-} = NpHPO_4^{2+}$	12.9 ± 3.5	13 ± 3	14 ± 4	14 ± 4
49	$Np^{4+} + 2HPO_4^{2-} = Np(HPO_4)_2(aq)$	23.7 ± 3.5	23 ± 3	23 ± 4	24 ± 4
50	$Np^{4+} + 3HPO_4^{2-} = Np(HPO_4)_3^{2-}$	33.4 ± 3.5	33 ± 3	33 ± 4	33 ± 4
51	$Np^{4+} + 4HPO_4^{2-} = Np(HPO_4)_4^{4-}$	43.2 ± 3.5	43 ± 3	43 ± 4	45 ± 4
52	$Np^{4+} + 5HPO_4^{2-} = Np(HPO_4)_5^{6-}$	52.0 ± 3.5	51 ± 3	52 ± 4	55 ± 4
53	$NpO_2^+ + H_2PO_4^- = NpO_2H_2PO_4$	0.6 ± 0.2	0.3 ± 1.1	0 ± 2	0 ± 3
54	$NpO_2^+ + HPO_4^{2-} = NpO_2HPO_4^-$	3.5 ± 0.5	4.5 ± 1.1	6 ± 2	7 ± 3
55	$NpO_2^{2+} + H_2PO_4^- = NpO_2H_2PO_4^+$	2.3 ± 1.0	1.9 ± 1.5	2 ± 2	1 ± 3
56	$NpO_2^{2+} + HPO_4^{2-} = NpO_2HPO_4$	8.2 ± 1.0	8.2 ± 1.5	8 ± 2	9 ± 3
57	$Np^{4+} + Cl^- = NpCl^{3+}$	0.2 ± 1.0	0.7 ± 1.2	1.5 ± 1.8	3 ± 2
58	$Np^{4+} + 2Cl^- = NpCl_2^{2+}$	-0.1 ± 1.0	1.7 ± 1.2	3.5 ± 1.8	5 ± 2
59	$NpO_2^+ + Cl^- = NpO_2Cl$	-0.4 ± 1.0	-0.1 ± 1.4	0 ± 2	0 ± 3
60	$NpO_2^{2+} + Cl^- = NpO_2Cl^+$	-0.2 ± 0.2	0.2 ± 1.1	1 ± 2	2 ± 3
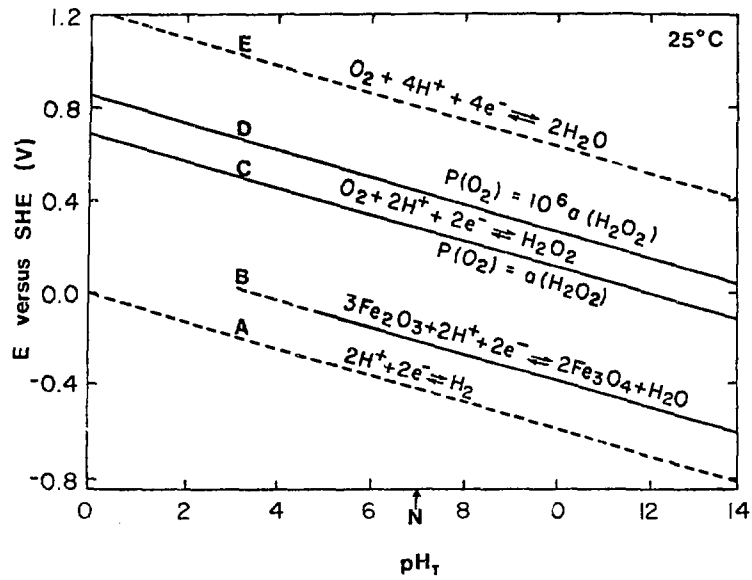
FIGURE 2: Potential Lines for Different Reduction Reactions as a Function of pH at 25°C
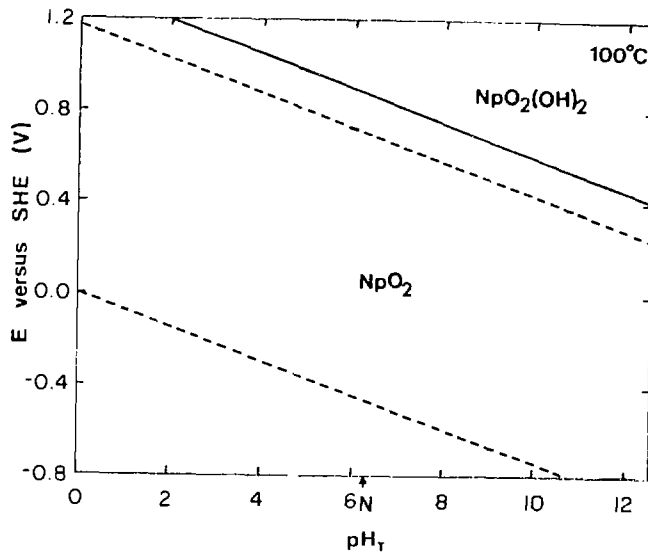

FIGURE 3: Potential-pH Diagrams for 100°C Showing Neptunium Solids Stable in Water

ture were sufficiently high for the reaction to be rapid, these minerals could together act as a buffer of potential to maintain fairly reducing conditions. Lines C and D represent the reduction of oxygen to peroxide at $P(O_2) = a(H_2O_2)$ and $P(O_2) = 10^6 a(H_2O_2)$. These reactions would occur at more oxidizing potentials. No assumption is made that these particular reduction reactions are actually occurring in a geological system. However, the potentials of the reactions have been chosen as representative of the different types of reducing conditions that may be found. Equations for these potentials as a function of temperature are given in Table 5.

The behaviour of neptunium was calculated for pure water and for two model "groundwaters" of differing ionic composition (see Table 6). The composition of groundwater No. 1 was chosen to be similar to that of deep groundwaters found in contact with granitic rocks and to synthetic ground- waters used in glass and fuel-leaching tests and in sorption experiments. The composition of groundwater No. 2 was chosen to be representative of granitic water containing higher concentrations of ions, and in particular containing maximum likely concentrations of the trace ions – fluoride and phosphate [89]. Concentrations of other ions are also quite high compared with many reported granitic groundwaters and this facilitated calculation of the effects of a general increase in the activities of potential complexing agents. This water also corresponds roughly to a groundwater found in one of the boreholes in the Lac du Bonnet batholith [90]. Only those ions that could form species for which data were available in the data base were considered in the selection of groundwater composition, although other ions may form complexes or compounds with neptunium. Therefore, concentrations of silica and of additional ions such as Ca^{2+}, which would undoubtedly occur in real groundwaters, are not given. The purpose of the calculations was to examine the gross effects of changing the concentrations of specific groundwater constituents, rather than to consider behaviour in a real groundwater. No attempt was made to maintain electroneutrality in this "open system". Calculations were not done for a brine groundwater (I = 1 to 2 mol·dm^{-3}) because activity corrections for most of the solution species are unavailable.

TABLE 5

POTENTIALS OF REDUCTION BUFFERS

The potentials of the reductions buffers may be expressed as

$$E = a + bpH.$$

The following reactions were used:

(1) $O_2 + 4H^+ + 4e^- \rightleftarrows 2H_2O$

(2) $O_2 + 2H^+ + 2e^- \rightleftarrows H_2O_2$ for $P(O_2) = 10^6 \, a(H_2O_2)$

(3) $O_2 + 2H^+ + 2e^- \rightleftarrows H_2O_2$ for $P(O_2) = a(H_2O_2)$

(4) $3Fe_2O_3 + 2H^+ + 2e^- \rightleftarrows 2Fe_3O_4 + H_2O$

(5) $2H^+ + 2e^- \rightleftarrows H_2$

Values for a and b are given below.

T (C°)	b	a for Reaction (1)	(2)	(3)	(4)	(5)
25	−0.0592	1.2291	0.8724	0.6949	0.2103	0.0000
60	−0.0661	1.1999	0.8579	0.6596	0.2049	0.0000
100	−0.0740	1.1671	0.8400	0.6178	0.1998	0.0000
150	−0.0890	1.1273	0.8158	0.5639	0.1940	0.0000

TABLE 6

IONIC COMPOSITION OF TWO ARTIFICIAL GROUNDWATERS

Ions	Ionic Activity (molal Scale)	
	Groundwater No. 1	Groundwater No. 2
Chloride	1.4×10^{-4}	0.10
Carbonate (total)	1.0×10^{-3}	1.0×10^{-2}
Fluoride (total)	1.0×10^{-5}	5.0×10^{-5}
Phosphate (total)	------	2.0×10^{-6}
Sodium	3.6×10^{-4}	0.10
Sulphate (total)	9.0×10^{-5}	1.0×10^{-2}

3.2   PREDICTED BEHAVIOUR OF NEPTUNIUM IN WATER AND MODEL GROUNDWATERS

3.2.1   Neptunium in Pure Water

        This is an artificial case to provide a basis for discussion of
the effects of other ions on neptunium solubility and speciation. It is
also important in determining how neptunium will behave during laboratory
experiments under conditions much simpler than those expected in a geologi-
cal environment.

        Within the stability field of water (total pressure 101 kPa), the
predominant solid is NpO_2 for all pH and all oxidation conditions (see Fig-
ure 3, page 32), and for the entire temperature range from 25 to 150°C. The
solution chemistry, as shown in the dissolved species diagrams (see
Figure 4), is dominated by Np(V) (NpO_2^+ and NpO_2OH) for oxidizing conditions
and by Np(IV) hydrolysis species for reducing conditions - especially at
high pH. Under acidic reducing conditions, Np^{3+} is also predicted to have a
small region of predominance within the stability field of water. Again
there is little difference in behaviour over the temperature range
considered here.

        Figure 5 shows how the solubility of neptunium at 100°C changes
with oxidation potential and pH. The predicted solubility under reducing
conditions is very low (10^{-9} to 10^{-15} mol.dm^{-3}), but it increases with
increasing pH. The solubility also increases as the solution becomes more
oxidizing, but only for acidic oxidizing conditions does the equilibrium
solubility of neptunium exceed 10^{-6} mol.dm^{-3}.

3.2.2   Neptunium in Groundwater No. 1

        As can be seen in the solubility contour diagram for 100°C, Fig-
ure 6, neptunium solubility does not increase substantially in groundwater
No. 1. The reason for this becomes apparent if the corresponding potential-
pH diagrams, Figures 7(a) to 7(c) (10^{-9} mol.dm^{-3} boundaries), are examined.
The only complex solution species that cuts significantly into the stability
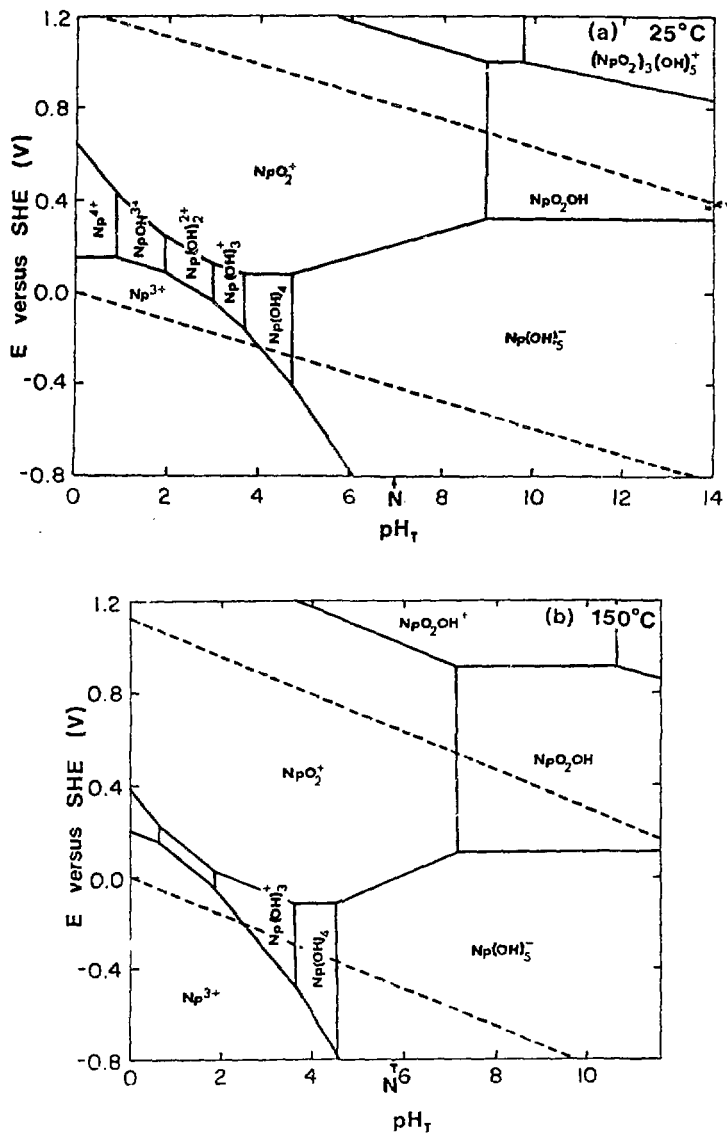field of NpO_2 is $NpO_2CO_3^-$. This species is important for oxidizing condi-

FIGURE 4: Dissolved Species for Neptunium in Pure Water (10^{-9} mol.dm^{-3} Boundaries). (a) 25°C; (b) 150°C
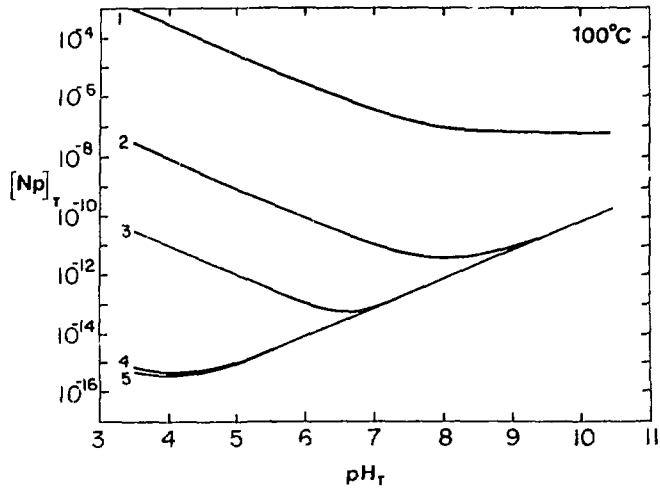
FIGURE 5: Total Neptunium Solubility in Water at 100°C as a Function of pH;
(1) $P(O_2)$ = 101 kPa;   (2) $P(O_2)$ = 10^6 $a(H_2O_2)$;
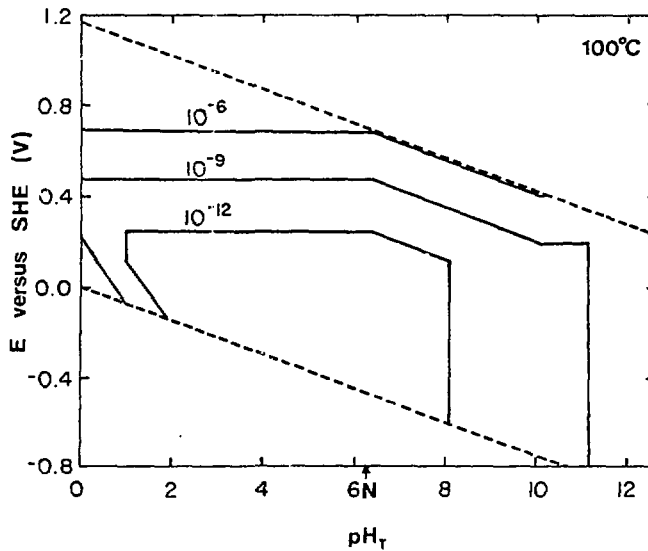(3) $P(O_2)$ = $a(H_2O_2)$;   (4) hematite/magnetite boundary;
(5) $P(H_2)$ = 101 kPa

FIGURE 6: Solubility Contours for Neptunium in Groundwater No. 1 at 100°C
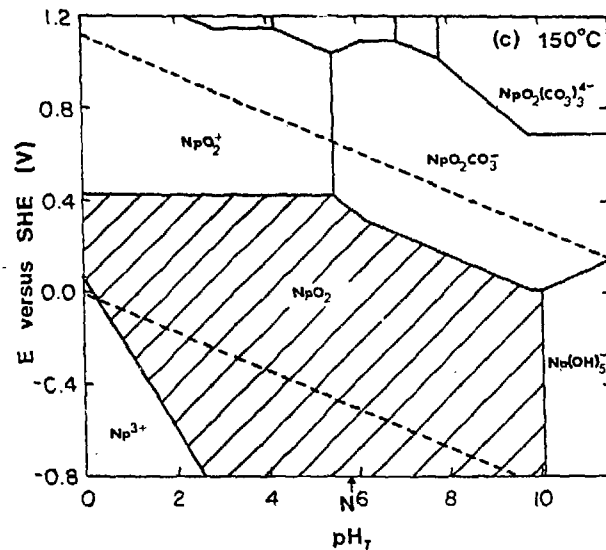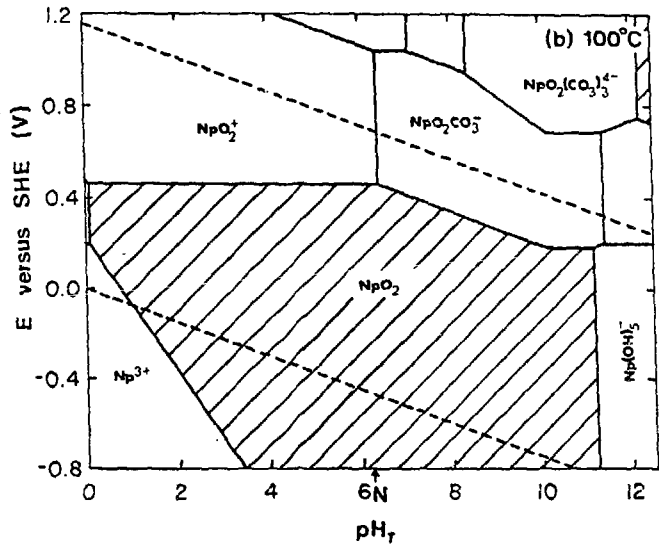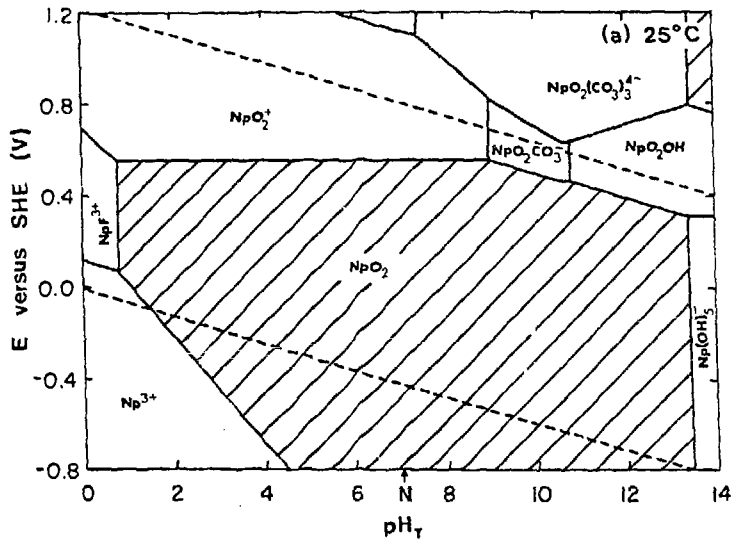as a Function of Potential and pH

FIGURE 7: Potential-pH Diagrams for Neptunium in Groundwater No. 1 at (a) 25°C, (b) 100°C, (c) 150°C. Boundaries are 10^{-9} mol.dm^{-3}

tions near neutral pH and for basic conditions. Its field of predominance increases with increasing temperature. NpF_3^+ also cuts very slightly into the NpO_2 region at low temperatures in very acidic reducing solutions. It is interesting that the field of stability for the Np(VI) species, $NpO_2(CO_3)_3^{4-}$, does not extend into the stability field for water within the temperature range considered here.

3.2.3   Neptunium in Groundwater No. 2

In groundwater No. 2 it is again apparent (see Figure 8) that carbonate complexation is a major process in increasing the solubility of neptunium. For oxidizing solutions (near the upper stability line for water), Np(V) carbonate species increase their range of stability at the expense of Np(VI) species as the temperature is increased. $Np(SO_4)_2$ ($NpCl_2^{2+}$ at 150°C) supplants NpF^{3+} as the major aqueous neptunium species for low pH and reducing conditions. Nevertheless, the overall behaviour of neptunium in groundwater No. 2 does not differ greatly from the behaviour predicted for pure water. Deep granitic groundwaters are expected to be reducing and have pH values between 4 and 10. Solubility contours for 25°C (see Figure 9(a)) indicate that neptunium solubility is still less than 10^{-12} mol.dm^{-3} over much of the potential-pH field important to nuclear fuel waste disposal. These solubility contours, however, depend on NpO_2 being the stable solid. If NpO_2 is present in solid solution in a UO_2 matrix (0.0002 mole fraction, i.e., CANDU fuel, 600 GJ.kg^{-1} burnup, 1000 years), the solubility is much lower (see Figure 9(b)). On the other hand, NpO_2 may not precipitate readily, even from fairly concentrated neptunium solutions, if the temperature is near 25°C. Under such conditions, $Np(OH)_4(s)$ may precipitate initially and then, only gradually, undergo dehydration. As can also be seen from Figure 9(b), $Np(OH)_4(s)$ is very soluble ($> 10^{-6}$ mol.dm^{-3}) over much of the stability field of water. This means that if neptunium is put in solution in the laboratory (or by breakdown of a waste form in groundwater), and if the temperature is reasonably low, then relatively high concentrations of neptunium might be maintained in solution for long periods of time, regardless of the pH or the oxidation conditions.
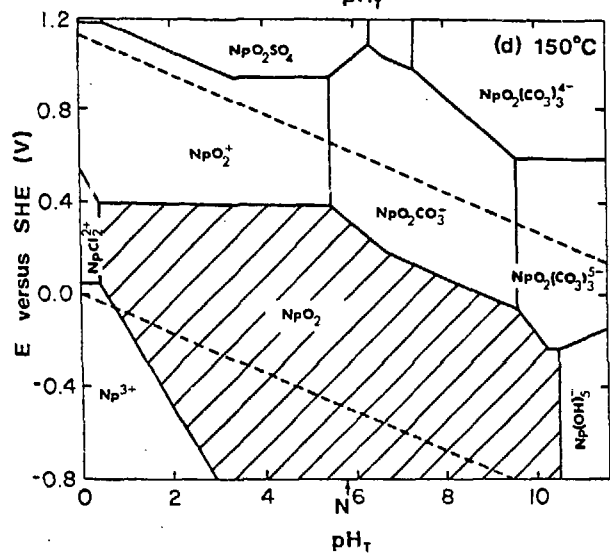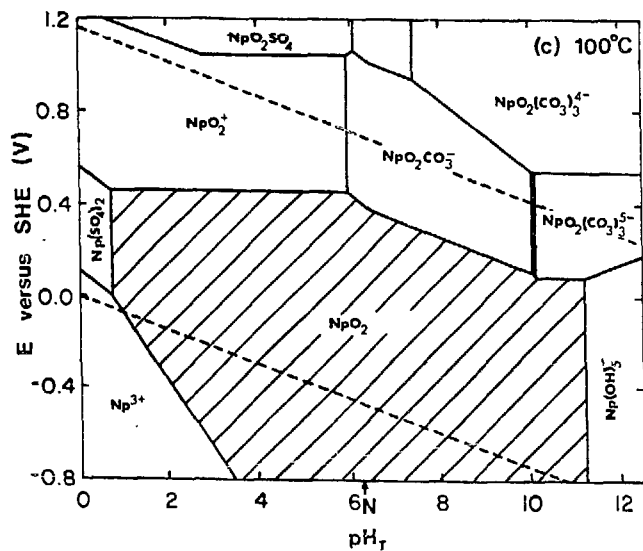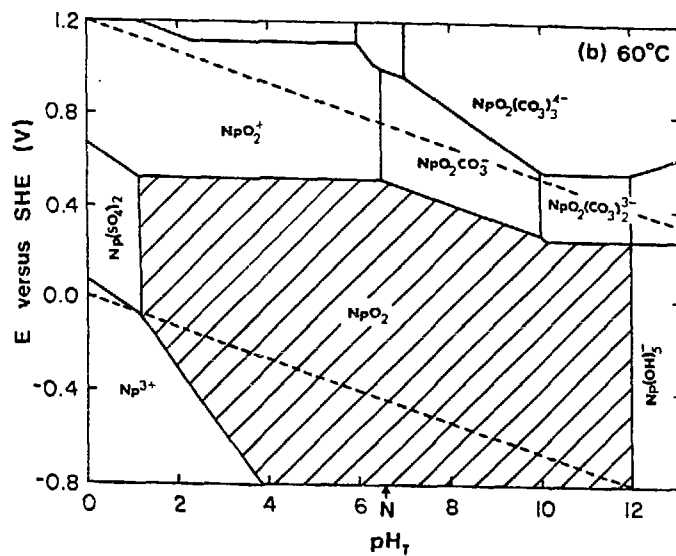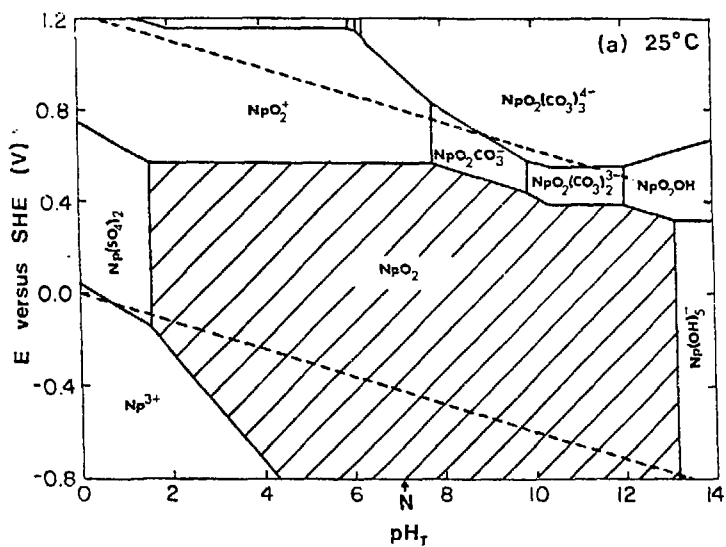
FIGURE 8: Potential-pH Diagrams for Neptunium in Groundwater No. 2 at (a) 25°C, (b) 60°C, (c) 100°C, (d) 150°C. Boundaries are 10^{-9} mol.dm^{-3}
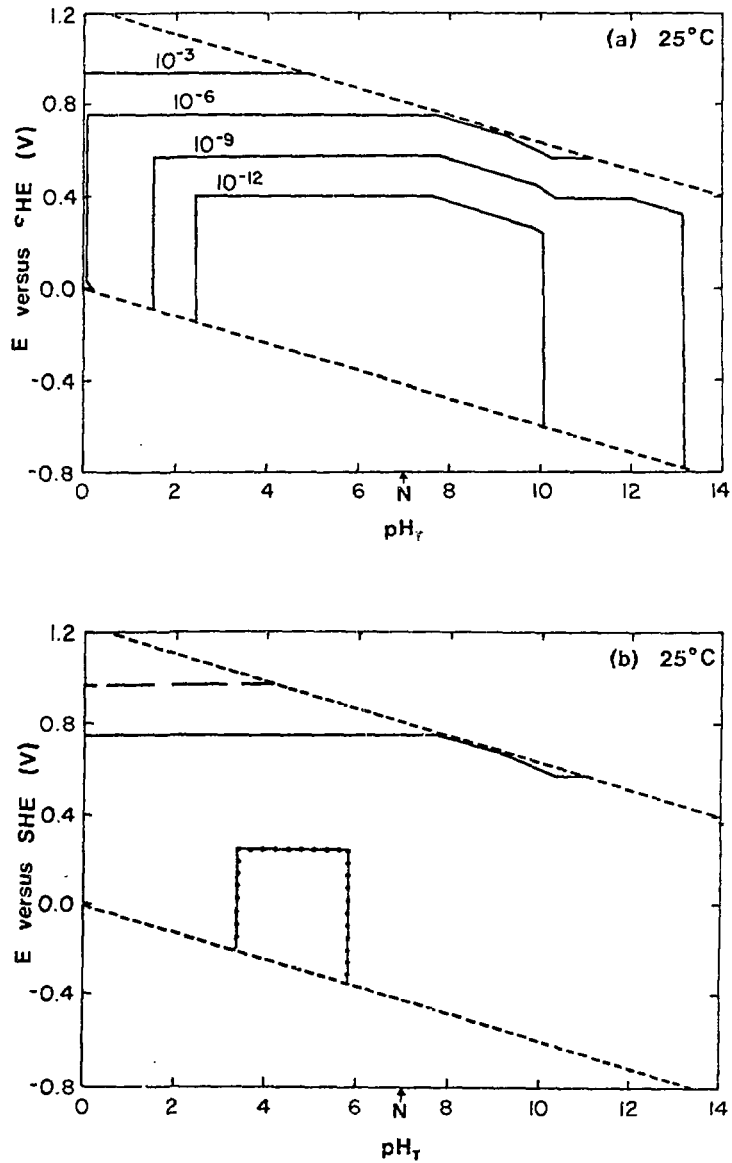
FIGURE 9:   Neptunium Solubility Contours at 25°C in Groundwater No. 2:

(a) Solid is NpO_2; (b) 10^{-6} mol.dm^{-3} Contours, ___ Solid
is NpO_2; ___ ___ Solid is NpO_2 in Solution in UO_2; ___ Solid
is $Np(OH)_4$

Solid $NaNpO_2CO_3 \cdot 3.5H_2O$ supplants NpO_2 as the stable solid at 25°C over a narrow range of pH near the upper stability boundary for water. This fairly soluble solid apparently becomes less important at higher temperatures.

Figure 10 shows the distribution of neptunium species at 100°C as a function of pH for both moderately oxidizing and moderately reducing conditions. This further emphasizes that hydrolysis species and carbonate complexes are of primary importance. The predominance of Np(IV) and Np(V) as the major oxidation states of neptunium is also apparent. Data on the U(IV) system in a recent paper by Ryan and Rai [40] indicate that the concentrations of $Np(OH)_5^-$ and $Np(OH)_4(aq)$ could be even lower than those shown (see Section 2.1.4).

Figure 11 shows the temperature dependence of neptunium solubility for the oxidizing and reducing conditions used in Figure 10. The solubility only increases with increasing temperature for oxidizing solutions that are neutral or basic. Under other conditions, the solubility of neptunium is essentially temperature independent in groundwater No. 2.

4. CONCLUSIONS CONCERNING THE DATA BASE

For the purpose of nuclear fuel waste management, the primary function of a thermodynamic data base for neptunium is to facilitate predictions of neptunium solubility as a function of the pH, temperature, ionic composition and oxidation potential of a selected groundwater. Figure 12(a) shows the uncertainties in the 10^{-9} mol.dm^{-3} solid/liquid boundaries of a potential-pH diagram for 25°C and pure water, while Figure 12(b) is the corresponding diagram for 150°C and groundwater No. 2. It is apparent that, particularly in basic solutions, more fundamental thermodynamic data are needed for neptunium species.
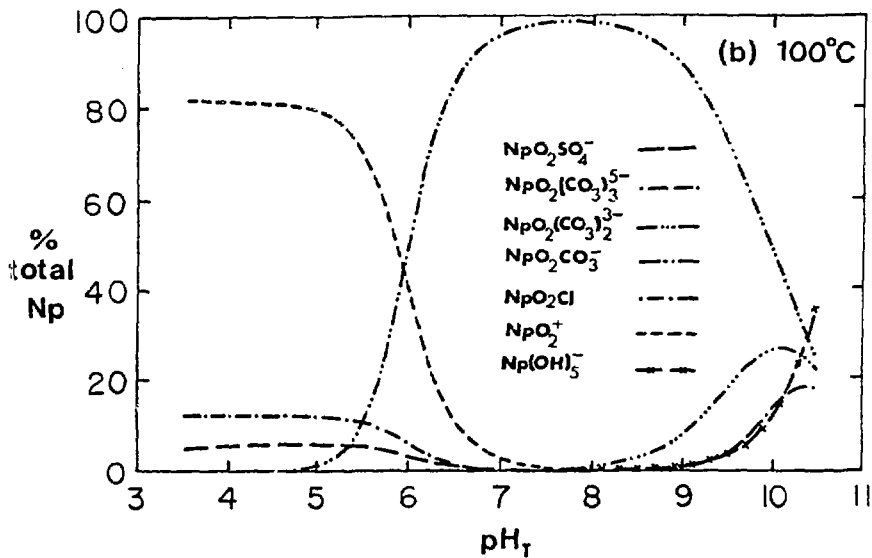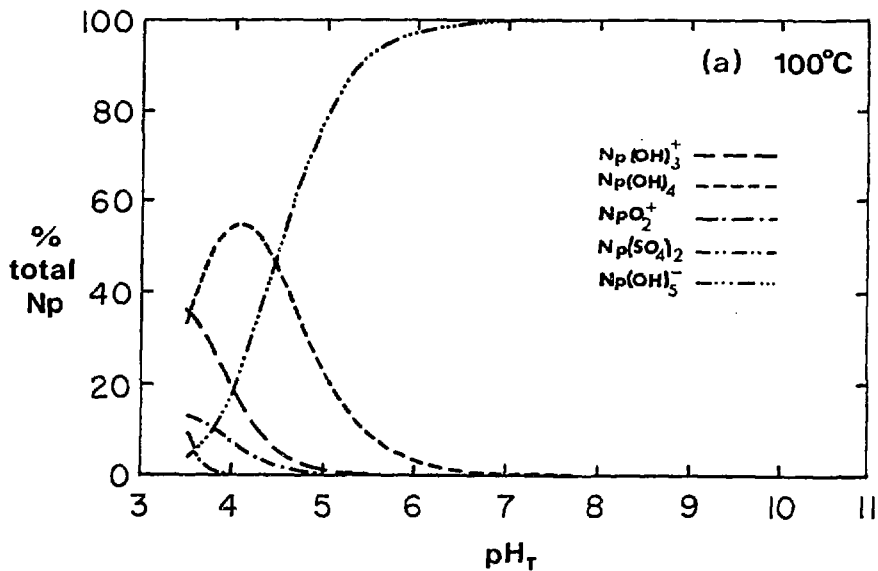
FIGURE 10: Neptunium Species Distributions for Groundwater No. 2 at 100°C:
(a) E = (0.200 − 0.074 pH)V; (b) E = (0.840 − 0.074 pH)V

FIGURE 11: Total Neptunium Solubility in Groundwater No. 2 as a Function
            of Temperature; —— Reducing Conditions, - - - Oxidizing
            Conditions (at Points on the Potential-pH Lines used in
            Figures 10(a) and 10(b), Respectively)

FIGURE 12: Uncertainties in Neptunium Solubility as a Function of Potential and pH, 10^{-9} mol.dm^{-3} Boundaries; (a) Water, 25°C; (b) Groundwater No. 2, 150°C

Perhaps the most important problem is the lack of information on the hydrolysis behaviour of Np(IV) in neutral and basic solutions. Measurements on this system are difficult an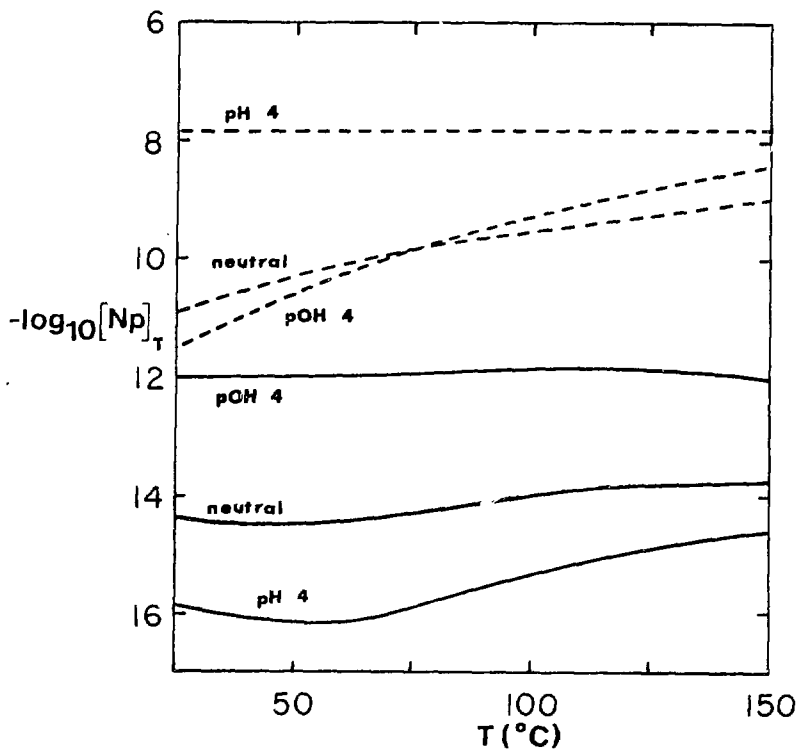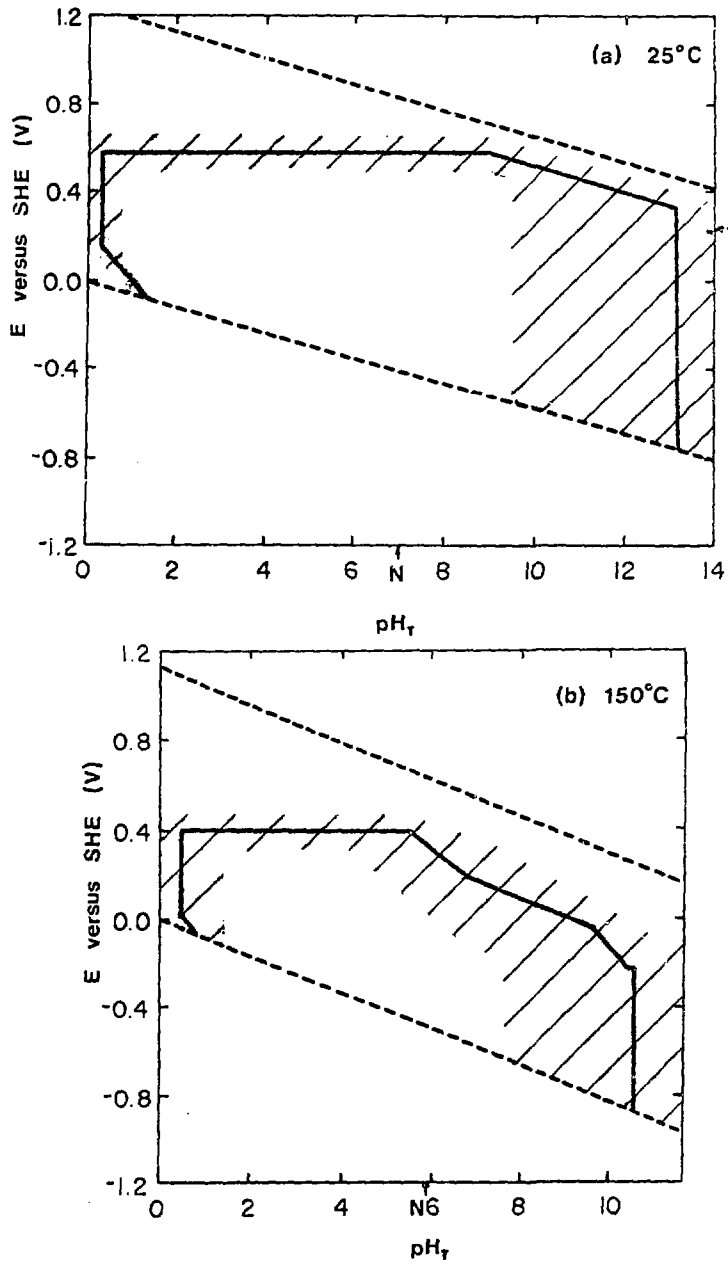d restricted both by the apparently low solubility of NpO_2 and by the ease of oxidation of Np(IV) in aqueous solution. Formation of strong carbonate complexes of Np(IV), Np(V) and Np(VI) may further complicate attempts to study the hydrolysed species. In addition, the data for Np^{4+} are markedly poorer than the data for the other simple neptunium ions.

The error limits shown in Figure 12 are based on the assumption that the Criss-Cobble treatment is suitable for dioxoneptunium (V,VI) ions and for complex neptunium ions. This has not been proven and heat capacity measurements are needed for NpO_2^+ and NpO_2^{2+} in particular. Also, a value of $C_p^\circ |_{25}^{150} = 0$, which is clearly incorrect, has been used for many important species (including $NpO_2OH(aq)$), and, again, experimental data must be obtained.

Except for some of the phosphate complexes, reasonable formation constants are available for neptunium complexes at 25°C. The temperature dependence of the formation constants of the important carbonate species needs further investigation. Solubility calculations for 100 to 150°C will be strongly affected if incorrect values are used for the entropies of species such as $NpO_2CO_3^-$ and $NpO_2(CO_3)_3^{4-}$.

Thermodynamic parameters are needed for many more of the complex neptunium solids. It is possible that formation of such compounds lowers the solubility of neptunium in oxidizing saline groundwaters. As discussed previously, NpO_2 does not precipitate readily at low temperatures despite its high stability. Therefore, complex neptunium solids may lower the effective neptunium solubility if the kinetics for their precipitation is rapid and if the complex solids are more stable than the metastable amorphous $Np(OH)_4$.

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