

# **The reliability of solubility data**

## **Results from a limited literature survey focusing on Ni, Pd and Np**

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## Abstract

The performance assessment (PA) of, e.g., repositories for spent nuclear waste needs data that relies on databases containing large amounts of chemical thermodynamic data. It is evident that the quality of such data should be good, in the sense that its uncertainties and origin, etc. should be well documented. The presence of erroneous data might make the outcome of the PA doubtful, in the worst case even partly worthless. However, the task of checking the quality of data is far from effortless and demands a considerable amount of time and money.

The objective of this work was to examine, within limited resources, the solubility data for three elements of interest, for example, in the safety analyses of repositories for nuclear waste. The elements studied were nickel, palladium, and neptunium. In order to delimit the topic, this report deals only with a small number of relevant species; the discussions of the solubilities of nickel, palladium and neptunium are mainly restricted to sulphides, oxide/hydroxide, and phosphates, respectively.

The report discusses some general difficulties associated with “data evaluation”, and presents the outcome of a minor literature survey on the solubility studies for nickel, palladium, and neptunium, respectively. The results indicate that in the case of palladium, few published data exist. This is however not alarming since palladium, being a member of the platinum group metals, is known to have considerable stability in the environment. In the cases of nickel and neptunium, it was found that there is a lack of proper solubility data. The report does not discuss whether this is serious or not, since this depends on the system studied and the conditions considered.

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# 1. Introduction

The performance assessment (PA) of e.g. repositories for spent nuclear waste needs data that relies on databases containing large amounts of chemical thermodynamic data, like  $\Delta G_f^\circ$ ,  $\Delta H_f^\circ$ , and  $\log K$  values. It is evident that the quality of such data should be good, in the sense that their uncertainties, origin, etc. should be well documented. The presence of erroneous data might in the worst case make the outcome of the PA worthless. However, the task of checking the quality of data in thermodynamic databases (TDBs) is far from easy and often presupposes large efforts in the form of international long-term projects.

The difficulties in checking the data quality usually emanate from the fact that little or no explicit information about the data quality is given in connection with TDBs. It may, for example, be difficult for users of TDBs to know whether the data has been estimated or based on measurements, and also to know the quality of the data (NEA 1996). This may not be a problem when regarding simple and, perhaps, well-known systems characterized by a relatively small number of chemical reactions. However, the problem becomes substantial when modelling the chemistry of complex systems like repositories for spent nuclear fuel. In practice, modellers may in this case not be able to check more than a fractional part of the data used and then simply leave the rest unchecked. In some cases modellers may use a TDB without any data checking at all. It may or may not be defensible to do so, depending on the system considered and the conditions chosen.

However, in the case of PAs of repositories for spent nuclear fuel rigorous data control is needed. In order to show both to the public and to the authorities that the quality of the modelled results is satisfactory, it is not enough to “rely” on the data in the databases or to be “convinced” that the data is good. Instead, it must be proved that sufficient efforts have been made in order to verify that the quality of the data is good enough to make safety assessments trustworthy.

In order to examine the reliability of data, which in this report is considered more or less synonymous with examining the quality of data, information has to be collected about

- (1) the underlying experiments,
- (2) the associated experimental uncertainties,
- (3) the mathematical methods used in order to calculate the above data from “raw” experimental data, and
- (4) the mathematical uncertainties associated with the calculations.

Therefore, the evaluation of the quality of thermodynamic data presupposes reviewing original publications (articles, reports and so on) that contain the data in question. However, this fundamental prerequisite is sometimes difficult or even impossible to fulfil, when, for example, chemical handbooks present "selected" data without any

referential notification. In such and similar situations one simply has to accept that a proper examination of the data quality is probably not possible.

Many TDBs contain data that has been made internally consistent, i.e. non-conflicting, by means of mathematical methods. Such methods and their possible effects on the quality of data are not discussed in this report.

The evaluation of data quality presupposes that the reviewers have experience in both practical and theoretical chemical work. Ideally, all necessary relevant data should be checked, but limited resources make such ambitions impossible. Instead, one must focus on solubility data for a few important elements.

The objective of this work was to examine, within limited resources, the solubility data for three categories of elements of interest, for example, in the safety analyses of repositories for spent nuclear waste. The categories were 1) elements from cladding and structural parts 2) fission and corrosion products, and 3) actinides and their daughters. The elements chosen from each category were nickel (Ni), palladium (Pd), and neptunium (Np), respectively.

Chapter 2 discusses some difficulties associated with “data evaluation”, while Chapters 3, 4 and 5 show the results of the survey of the solubility data for nickel, palladium, and neptunium, respectively. Chapter 6 provides a discussion and summary of the results.

## 2. Data and the evaluation of data quality

### 2.1 General

#### **The term "reliability"**

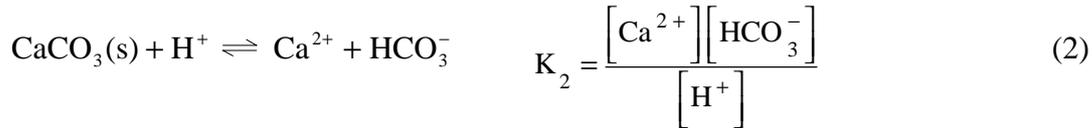
Although being a trivial statement, it should explicitly be stressed that the term "reliability" and its various derivatives are inevitably associated with a certain degree of subjectivity. Even in cases where experimental data is seemingly highly reliable, there is still a risk that the data is completely false. False data may emanate from incorrectly performed measurements, calculations, misprinting, conversion errors when transferring data electronically from one computer program to another, etc., or in rare cases, false data may arise quite simply from lying scientists. The impact of false data does not necessarily have to be very strong. If the data is important, it is normally verified by independent scientists in new experiments. If found irreproducible, the knowledge of false results is spread through the scientific community, and their future use rejected. This underlines the well-known fact that it is not sufficient to consult original publications when evaluating data quality, since important additional information (corrections, re-evaluations etc.) might have been published in subsequent literature. As a rule, it is thus necessary to cover all the subsequent literature to date when checking chemical data in order to ensure that no later corrections have been reported.

In contrast to mathematics, where achievements can be shown to be reliable or true by presenting written proof, published results in natural science can probably never be rid of at least some amount of uncertainty concerning their quality. Although this uncertainty cannot be completely eliminated, it should, however, be kept "as minimal as reasonably achievable". It is beyond the scope of this study to deal in detail with the philosophical question of how to know whether a statement like "the solubility constant for the compound A has the value of X at NPT" is reliable or not. Instead, we have chosen, although we are aware that this is not enough in the strictest sense, to use a pragmatic attitude: scientific data is reliable if it is reasonably well documented and seems to be consistent with general observations, etc.

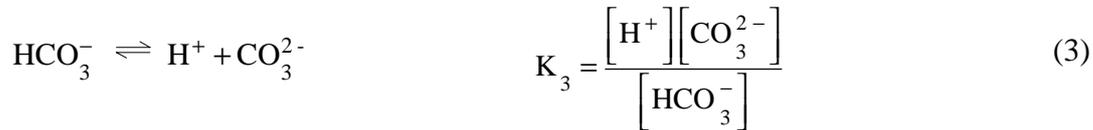
#### **Data format**

A critical evaluation of the quality of chemical data in a TDB is often a cumbersome and time-consuming process. There are several reasons for this. For example, a given TDB value does not necessarily emanate from one single original publication, but may have been taken from some standard table of chemical data, in which the data value in question represents a calculated average of some values selected from scientific literature. In order to determine the data quality in this case, it is necessary to consult the references on which the calculated average is based and also to consider whether the choice of selected values used is acceptable. Sometimes, however, this is not possible since the selection criteria used are not presented in sufficient detail.

Other problems associated with the evaluation of data quality stem from the fact that original experimental data may have been converted or corrected (with regard to data consistency, format, standard state, etc.) in order to fit into the tables. For example, the common dissolution reaction of, e.g. calcite,  $\text{CaCO}_3(\text{s})$ , is often described in the literature by the following reactions:



where  $K_{s0}$  is the solubility product of calcite, and  $K_2$  is the reaction constant for the reaction (2). In order to determine whether or not the reactions (1) and (2) correspond to the same solubility or not, a third reaction has to be considered:



Reactions (1) and (2) correspond to the same calcite solubility if  $K_{s0} = K_2 \cdot K_3$ . Chandratillake et al. (1988) gives another example, the formation of the species  $\text{UO}_2(\text{OH})^+$  in a redox reaction. In the PHREEQE format the formation is written



The same species formation in the MINEQL format is given by the following ligand replacement process



The  $\text{U}^{4+}$  is related to this process by the redox process



For this reason, Chandratillake et al. (1988) claims it is not possible to make a direct comparison of data for uranium species between the two formats, except in the case of  $\text{U}^{4+}$  complexes, which do not involve any redox processes in the PHREEQE format.

Thermodynamic data refers to a selected standard state, e.g. a temperature of 25 °C and solutions with zero ionic strength. However, for many reactions, measurements cannot be made accurately in dilute solutions from which the necessary extrapolation to the standard state would be trivial. Instead, precise chemical information can only be obtained in systems containing an inert electrolyte of relatively high concentration, thus ensuring that the activity factors are approximately constant throughout the

measurements. The details of procedures for temperature corrections and ionic strength corrections can be found in, e.g. Grenthe & Puigdomenech (1997).

### Solubility data

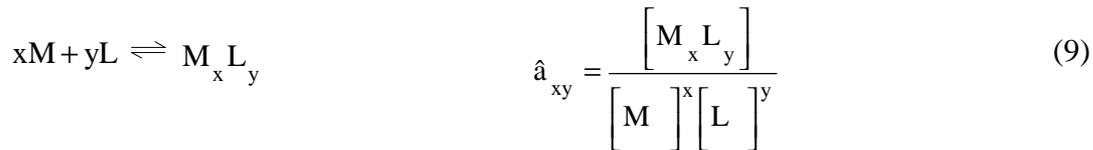
It is well known that the solubility, for example, of metals in aqueous environments, is generally associated with the dissolution or formation of solids and, often also with the formation of complex ions. The general dissolution in the absence of complexation is in simple cases described by the following reaction



where  $K_{s0}$  is the conventional solubility product, M is a metal ion with charge  $b+$ , and B is an anion of charge  $a-$ . For the reason of simplicity, the ionic charges are not noted in the following. Provided that no, or little, complexation occurs in a given system, the metal solubility can be calculated from

$$[M] = K_{s0} [B]^{b/a} \quad (8)$$

When the metal ion forms complexes  $M_x L_y$  with a ligand L, reactions like the following have to be considered



where  $\hat{\beta}_{xy}$  is the overall complex formation constant of the complex  $M_x L_y$ . Thus, in the case of complexation, the metal solubility is given by

$$[M] = K_{s0} [B]^{b/a} + \sum x \hat{\beta}_{xy} [M]^x [L]^y \quad (10)$$

The equation can easily be extended in order to cover more complex situations. The use of Eqn. 7 in stead of Eqn. 10 may or may not be serious, depending on the physico-chemical situation. This is demonstrated in Figure 1, where the solubility of nickel has been calculated in a simple closed system consisting of water in contact with excess amounts of NiO. In this case, the metal ion is  $Ni^{2+}$  and the ligand  $OH^-$ . The pH was assumed to be adjusted by adding NaOH or HCl and the temperature value chosen was 30 °C. At pH 8 - 9, the error introduced by ignoring complexation is insignificant. At higher pH values, however, this omission becomes serious, and leads to errors in the calculated solubility by several orders of magnitude.

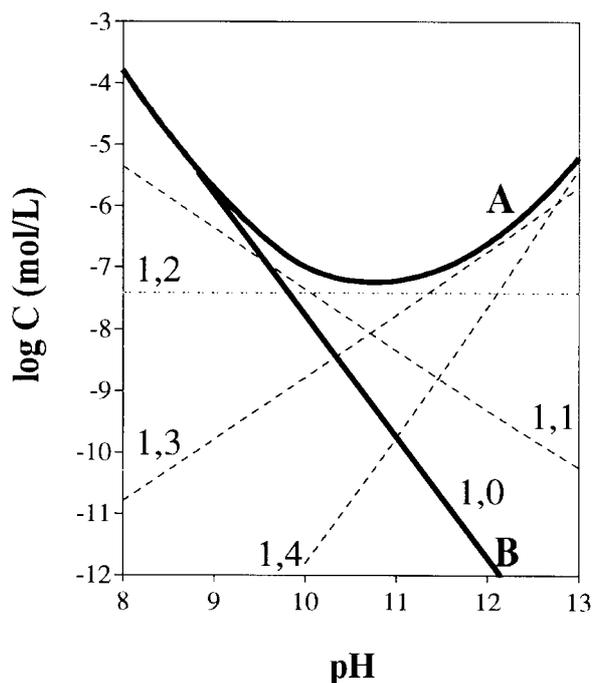


Figure 1. Calculated solubility of nickel when complexation is considered (curve A) and not considered (curve B). Species notation: 1,0 =  $\text{Ni}^{2+}$ , 1,1 =  $\text{Ni}(\text{OH})^+$ , 1,2 =  $\text{Ni}(\text{OH})_2^0$ , 1,3 =  $\text{Ni}(\text{OH})_3^{1-}$ , and 1,4 =  $\text{Ni}(\text{OH})_4^{2-}$ . The concentrations of the polynuclear species  $\text{Ni}_2\text{OH}^{3+}$  and  $\text{Ni}_4(\text{OH})_4^{4+}$  give negligible contributions to the nickel solubility in the pH interval considered and the corresponding graphs are therefore not shown.

The example clearly demonstrates the well-known fact that proper examination of the solubility data for a given element should not only involve checking the quality of the data associated with available relevant reactions found in, e.g. TDBs, but also focus on the question of whether all the necessary data is present. However, it is beyond the scope of this report to deal in detail with all aspects of the quality assurance of solubility data for Ni, Pd and Np. Instead, a few questions have been selected, which illustrate some of the aspects that need to be considered.

## 2.2 Selection criteria

There are at least two main strategies for presenting compiled data. Firstly, the data for a given system can be collected from various sources and presented as it is (non-critical compilation); or secondly, the data can be presented after some careful selection procedure (critical compilation), eventually combined with some correction procedure(s) or procedures for making the data internally consistent. The need for critical stability constants stems from the fact that the literature contains wide variations in, for example, the published constants for the same metal complex equilibrium, which indicates the presence of one or more errors in the ligand purity, in the experimental measurements, or in the calculations. Usually, the nature of these errors is not readily

apparent in the publication, and the reader is frequently faced with uncertainties concerning the correct values (Smith & Martell 1976).

An example of the former type of compilation is "Stability Constants" (Högfeldt 1982), which contains equilibrium constants of various types but does not include any attempt at critical evaluation of the quality of the data. An example of the latter type of compilation is "Critical Stability Constants" (Smith & Martell 1976), which presents a selection of "best" values at certain ionic strengths. Unfortunately, Smith & Martell (1976) do not give an exact description of the activities and associated decisions leading to the "best" values, and this lack of traceability makes the evaluation of their data somewhat difficult.

The general principles used in order to obtain the "best" values from the literature, may vary somewhat between one work and another, but the selection criteria used by Smith & Martell (1976) demonstrate reasonably well the underlying principles that can be applied in the evaluation of data quality. The choice of a "best" value is relatively trivial when many references give similar values, but where only a few scattered values exist, Smith & Martell (1976) recognized, that "more subtle methods were needed, to select the best value".

Selection criteria where a large amount of data is in close agreement:

- When several workers are in close agreement on a particular value, the average of their results is selected.
- Values showing considerable scatter are eliminated.

Selection criteria where little data is in poor agreement:

- Established trends among similar metal ions and among similar ligands are valuable in deciding between widely varying values. However, this type of guideline should be used cautiously, so as not to overlook occasionally unexpected real examples of specificity or anomalous behaviour.
- When there is poor agreement between published values and comparison with other metal ions and ligands does not suggest the best value, the result of more experienced research groups who have supplied reliable values for other ligands are selected.
- If constants reported by several workers for a given group of metal ions have similar values, but differ considerably in the absolute magnitudes of the constants, then a set of values from one worker near the median of all values reported is selected as the best constant.
- Values reported by only one investigator are included in the table unless there is some reason to doubt their validity. It is recognized that some of these values may be

erroneous, and that such errors will not be detected until the work is repeated by other investigators, or until more data become available for analogous ligands or other closely related metal ions.

Criteria for disqualification of published data:

- Papers deficient in specifying experimental conditions (e.g., temperature, ionic strength, and nature of supporting electrolyte) or defining the equilibrium quotients reported are not employed.
- Values involving unusual metal ions are disregarded if there are serious questions about the form of their complexes.

It is beyond the scope of this report to deal in detail with the intricate topic of finding the "best" values for a certain chemical reaction or to determine the quality of some chemical data. The above, which is a shortened and slightly modified excerpt from Smith & Martell (1976), may serve as a suitable demonstration of some of the guidelines that have to be considered in such cases.

## 2.3 Modelled data

The criteria in Section 2.2 were written at a time when published data emanated mostly from laboratory experiments. The evaluation of the results from such studies is relatively straightforward. Today, computer modelling is extensively used when evaluating the behaviour of hazardous material under complex environmental conditions to calculate, for instance, the solubility of radionuclides in complex systems like groundwater in, e.g. the vicinity of a repository for nuclear waste or interpreting experimental results. Proper interpretation of the elemental behaviour at thermodynamic equilibrium is a prerequisite for understanding the system behaviour. Hence, it is essential to have knowledge of the relative stabilities of the compounds and complexes that may form under the considered conditions. The computer codes for speciation-solubility calculations provide the computed results based on chemical thermodynamic data. Such data in scientific literature, mainly equilibrium constants and redox potentials in aqueous solutions, has in many cases been contradictory, especially in actinide chemistry.

In order to improve the quality of thermodynamic data, the Radioactive Waste Management Committee (RWMC) of the OECD Nuclear Energy Agency has undertaken the development of the NEA Thermochemical Data Base. This is an internationally acknowledged, internally consistent high-quality thermochemical database for application in the safety assessment of radioactive waste disposal. In principle, a thermodynamic database is internally consistent only if the combined set of standard state and excess thermodynamic data is mutually consistent, which has quite rarely been achieved. (Wolery 1992). To accomplish such a database, a critical and comprehensive review of all the available literature is required. Presently, reviewed data

for the NEA-TDB has been published for two actinides, U (Grenthe et al. 1992) and Am (Silva et al. 1995) and in the near future reviewed data on Np, Pu and Tc will be completed. The main source for the selection of recommended data is the experimental measurements published in scientific literature and the data selected is provided with uncertainties representing a 95 % confidence level. As no unique way of assigning uncertainties exists, the assignments given are to a large extent based on the subjective choice by the reviewers, supported by their scientific and technical experience in the corresponding area (Silva et al. 1995).

It has been stated that “the quality of thermodynamic models cannot be better than the quality of the data they are based on” (Silva et al. 1995). It also has to be recognized that no present geochemical modelling code can cover all of the possible physical and chemical phenomena that may potentially be required. The evaluation of the quality of the modelled data follows guidelines similar to those mentioned earlier. This means that the modelled results have to be examined with regard to the underlying assumptions concerning, among other things, redox-conditions, choice of solubility-limiting solid, assumed complexation reactions, and the options used in the computer model (concerning the handling of charge-balancing, the choice of equation for calculating activity coefficients, etc.). Furthermore, incomplete documentation of the underlying assumptions sometimes renders the reported results more or less useless.

The evaluation of modelled results also requires consideration of how the problems of bad data or the lack of important information in the database have been handled. Some examples are the bad data and erroneous values of reaction constants or the inclusion of values for reactions that are not relevant in the system modelled. The consequence of using irrelevant data is demonstrated in an example reported by Grauer (1997). Four working groups were given the task of modelling the nickel concentration in a given type of natural water. The groups chose different solubility-limiting phases for nickel -  $\text{NiFe}_2\text{O}_4$ ,  $\text{Ni}(\text{OH})_2$  and  $\text{NiO}$  - none of which exists in nature under the natural conditions modelled. As a result, the calculated nickel solubility differed several orders of magnitude from the natural value (calculated nickel concentrations:  $2.7 \cdot 10^{-2}$  -  $3.0 \cdot 10^{-14}$  M, natural nickel concentration:  $5 \cdot 10^{-9}$  M). One reason for the unrealistic result is that databases mostly contain only pure phases, while natural compounds are mostly mixed phases. In the case of modelling dissolved radionuclides at trace concentrations, it is not sufficient to consider only the formation of pure precipitates; also co-precipitation has to be considered. Recently, co-precipitation approaches have been applied (Bruno et al. 1997) in order to calculate more realistic solubility limits for certain radionuclides, but this type of modelling is still in its infancy. Other possible explanations for the poor agreement between measured and calculated results in the above example are found in the well-known fact that modelling is mostly performed assuming systems at chemical equilibrium; kinetics and the formation of metastable mixed phases are not considered.

Another difficulty with databases is the lack of important information. According to Grenthe & Puigdomenech (1997), “the poorest solution is to include only information that is available in the databases - a much better solution is to use chemical theories to predict reasonable estimates of the quantities needed, and then to find out how sensitive,

e.g. a mineral solubility or a total element concentration is to variations in the unknown model parameters."

Finally, it should be emphasized that modelled data only give rough estimates of, for example, radionuclide solubilities. This is stated by Grauer (1997) in the following way: "Owing to the formation (of metastable) mixed phases, it is scarcely possible to predict the composition of the solution and the remaining solid in a precipitation experiment with  $n$  cations and  $m$  ligands in quite different initial concentrations. It will perhaps be possible to predict the behaviour of the main constituents with some accuracy or at least as an order of magnitude. But the behaviour of the trace elements can at best be estimated or even only guessed."

The uncertainty of modelled data is also pointed out by Arthur & Apted (1996): "Chemical models of near-field evolution combined with thermodynamic models of radionuclide speciation-solubility behavior can be used to assimilate site characterization data into the performance assessment process, and to deal with uncertainties that are inherent in both site properties and in concepts of near-field chemistry. It must be recognized, however, that it is not possible to specify radionuclide solubilities precisely given the complex chemical environments and long timescales involved in disposal technologies for nuclear waste."

The above gives some general aspects that have to be considered in evaluating the quality of chemical data, both experimental and modelled. The reader is referred to the cited literature and references therein for further information on this matter.

## 2.4 Measured data

As pointed out above, experimental measurements are the basis for the thermodynamic data. The experiments, on which the data in the databases of today is based on, may date back to the first half of this century and even earlier when instrumentation and analysis methods were less developed. For instance, new techniques in speciation measurements give valuable tools in assessing many results measured. The new possibilities in instrumentation and measurement techniques have given rise to repeating measurements as well as for conducting new ones in order to ascertain questionable and evaluated values. The experimental data reported in scientific literature may also be inaccurate in the sense that all the details needed to evaluate the appropriate conducting of the experiments and obtained results are not presented leaving room for speculation.

Piepponen (1991) has pointed out that the quality of analytical results depends on how close they are to the correct values, and that this is an analytical paradox; the result of an unknown sample cannot usually be compared with the correct value because the correct value is not known. The only way of confirming the result is to verify the analytical method. The quality assurance measures at a chemical laboratory include many steps, e.g. the use of certified reference materials, recovery tests, inter-laboratory tests, and many kinds of calibrations. The amount of work put into quality assurance varies greatly

between different laboratories, depending on the type of analytical work. Human errors should also be taken into consideration, because man-made errors are common. A further discussion of the criteria for analytical reliability is found in Piepponen (1991).

A detailed discussion on how to conduct complete and thermodynamically meaningful solubility studies, which can be found, e.g. in Nitsche et al. (1993), is not given here; we only outline the main points. Ideally, solubility should be approached from both over- and undersaturation, and a complete solubility study should provide detailed knowledge of the nature and chemical composition of the solubility-controlling solid, the concentration of the components in solution and the identity and electrical charge of the species in the solution phase. Further, in order to be thermodynamically meaningful, it should be shown that equilibrium conditions\* have been attained, accurate solution concentrations determined, a well-defined solid phase attained and identified, and knowledge of the speciation/oxidation state of the soluble species at equilibrium is known. Confirmation of the oxidation state of the species is especially important when elements exhibiting several oxidation states are in question.

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\* Sometimes "equilibrium" may not be a sufficient requirement, but must be replaced by the stronger "dynamic equilibrium". Calculations of, e.g., saturation indices, presuppose that the assumed underlying dissolution reactions are associated with dynamic equilibrium conditions. If this condition is not met, as in the case for solids having one-way dissolution reactions, then the chemical interpretation of the saturation index may occasionally be a matter of debate. Further discussions on this matter are found in Wanner (1991).

### 3. The solubility of nickel

A critical evaluation of the solubility of nickel is beyond the scope of this report. The focus is on some solubility data for nickel sulphide, which has long been cited in the literature. A broader discussion on nickel solubility can be found in, e.g., Carlsson (1998).

The +2 oxidation state of nickel is by far the most important one in aquatic environments. In reducing, sulphidic groundwaters it is reasonable to assume *a priori* that the nickel solubility is limited by the formation of discrete nickel sulphide minerals or by the co-precipitation of nickel with sulphide minerals of dominant dissolved elements, e.g. iron. The latter type of data is not discussed here, since co-precipitation data is normally not found in TDBs.

#### 3.1 Nickel sulphides

In general, proper calculations of solubility limits presuppose that the solubility constant of the solubility-limiting solid is known. However, in the case of NiS, the published solubility constants may differ by ten orders of magnitude from each other (Thoenen 1999 and refs. therein). Interest is focused on the solubility products of the following nickel sulphides:  $\alpha$ -NiS,  $\beta$ -NiS, and  $\gamma$ -NiS. These compounds and their associated solubility constants are still found in the literature and databases (e.g. Dyrssen & Kremling 1990, Berner 1995, IUPAC 1997), although their origin dates from the early years of this century (see below).

The solubility products for  $\alpha$ -NiS,  $\beta$ -NiS, and  $\gamma$ -NiS can be found in recent handbooks. Table 1 shows the  $pK_{s0}$ -values ( $pK_{s0} = -\log K_{s0}$ ) given by Kotrlý & Š•cha (1985). Kotrlý & Š•cha (1985) state that these values have been taken from another source (Smith & Martell 1976) in which it is stated that the values correspond to zero ionic strength and a temperature of 25 °C.

Table 1. Solubility products at 25 °C of three nickel sulphides, according to Smith & Martell (1976) and Kotrlý & Š•cha (1985).

Mineral	$pK_{s0}$	$K_{s0}$
$\alpha$ -NiS	19.4	$10^{-19.4}$
$\beta$ -NiS	24.9	$10^{-24.9}$
$\gamma$ -NiS	26.6	$10^{-26.6}$

Smith & Martell (1976) present  $\log K_{s0}$  values for specified conditions of temperature and ionic strength. Smith & Martell (1976) claim that their values are those considered the most reliable of the ones available. In some cases, the symbol  $\pm 0.00$  is used to indicate that there are one or more values that agree exactly with the stated value for the

number of significant figures given. Values of questionable validity are enclosed within parenthesis. Such values are included when the evidence available is not strong enough to exclude them on the basis of the criteria presented in Chapter 2. The  $\log K_{s0}$  values in Smith & Martell (1976) are given for the more commonly reported ionic strengths; 0, 0.1, 0.5, 1.0, 2.0, 3.0, and 4.0 M. Smith & Martell claim that "zero ionic strength is perhaps more important from a theoretical point of view, but several assumptions are involved in extrapolating from the measured values. The Davies equation is often used to calculate constants to zero from low-ionic measurements". Smith & Martell (1976) do not discuss ionic strength corrections any further. The temperature of 25 °C is given preference in Smith & Martell (1976) because of its widespread use in equilibrium measurements and in reporting other physical properties. When available, enthalpy changes were used to calculate  $\log K_{s0}$  at 25 °C when only the measurements at other temperatures were available.

For the values in Table 1, it is not possible to tell immediately whether Smith & Martell (1976) present exact original data, adjusted ("corrected") original data, or data that represents an average of data (possibly adjusted) from what Smith & Martell (1976) considered to be a reliable set of papers and reports, etc. In some cases, Smith & Martell (1976) list what they classify as "more reliable references" directly after the ions for which the values are reported. The term "other references" is used for those references reporting questionable values, values at conditions considerably different from those used in the tables, or values not included in the tables because of questionable knowledge about their complexes. Smith & Martell (1976) state that these additional references are cited to inform the reader of the extent of the literature search made in arriving at the selected values.

Smith & Martell (1976) do not give any reference for the three nickel sulphides, and consequently they indicate that the corresponding solubility constants are not of the best possible quality. In order for the reader to find the original source(s) for the three solubility constants, it is necessary to examine all the "other references" listed, see Table 2. Such a task is simple but time-consuming, especially since no titles of the cited works are given (in which case some references might be ruled out immediately from the information contained in their titles). After some research, the authors of this report found that one and only one of the references contains solubility data for  $\alpha$ -NiS,  $\beta$ -NiS, and  $\gamma$ -NiS. The work in question is Thiel & Gessner (1914): *Über Nickelsulfid und Kobaltsulfid. 1. Die scheinbare Anomalie im Verhalten des Nickelsulfids gegen Säure.*

Table 2. List of "other references" in Smith & Martell (1976). See text for explanation.

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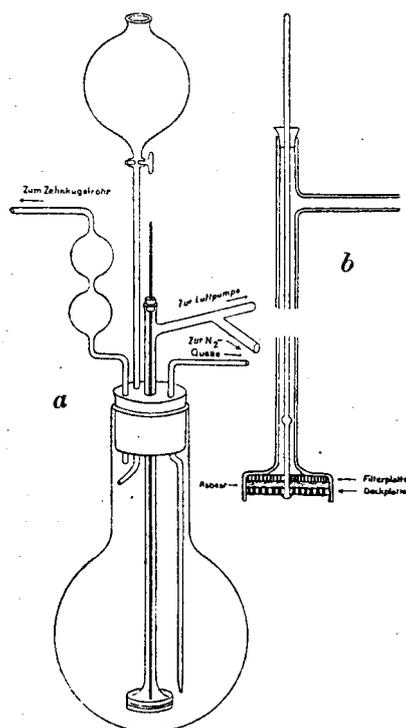


Figure 2. Equipment used in studies on the solubility of nickel sulphide (Thiel & Gessner 1914).

The main objective of the study by Thiel & Gessner (1914) was to determine the big differences observed in solubility between various NiS precipitates in dilute acids. The experimental studies included the production and purification of nickel sulphides in a closed vessel under nitrogen atmosphere. The nickel sulphides were mainly made by mixing cobalt-free nickel chloride with freshly prepared sodium sulphide. Thiel and Gessner (1914) stress that fresh sodium sulphide should be used in order to avoid the conversion of sulphide to polysulphide.

A large series of measurements was performed under varying conditions, in which nickel sulphide was precipitated, washed and finally analyzed with regard to solubility. The experiments were mainly carried out using the equipment shown in Figure 2. The nitrogen gas used was made oxygen-free by using alkaline pyrogallol solution and glowing copper. The precipitates were prepared at different temperatures by mixing, for example, nickel chloride with either sodium sulphide (mostly), ammonium sulphide, or a mixture of acetic acid and H<sub>2</sub>S water. After some hours, the precipitates were subsequently washed, mostly using warm, oxygen-free water. The main analyses of the nickel sulphides consisted of extraction procedures using various acids. Based on the solubility, Thiel & Gessner could distinguish between three different types of nickel sulphide by making a two-step extraction. The extraction of the most easily dissolved nickel sulphide was made with cold 2 N HCl containing H<sub>2</sub>S, while the intermediately soluble sulphide was made using boiling HCl. The remainder, after the two extractions, was the least soluble nickel sulphide. Thiel & Gessner named the sulphides  $\alpha$ -NiS (most soluble),  $\beta$ -NiS, and  $\gamma$ -NiS (least soluble), respectively.

The analyses of the nickel precipitates included the determination of the atomic weight ratio S:Ni. For all the sulphides it was found that S:Ni = 1. Briefly, the determination of the nickel content was made with electrolysis, while the sulphide content was determined after oxidation with bromine and precipitation with barium chloride. Thiel & Gessner (1914) discuss the possibility that the most soluble precipitate ( $\alpha$ -NiS) is a hydrate, but they conclude that this is not probable. Appendix A, which shows the original discussion on this matter, serves as an example of the thorough discussions given in the original reference. Microscope studies of the three sulphides indicated that  $\alpha$ -NiS is an amorphous substance, while  $\beta$ -NiS, and  $\gamma$ -NiS are crystalline substances with metallic lustre.

Thiel & Gessner (1914) estimate the solubilities of the three nickel sulphides, but they stress that it is not possible to achieve a high accuracy: "Es kommt hier gar nicht darauf an, eine recht gro• e Genauigkeit der Löslichkeitsbestimmung zu erzielen, sondern nur darauf, einen Anhalt für die Grö• enordnung der Löslichkeit der drei Formen zu gewinnen. Wir kommen daher mit einer grö• eren Schätzung aus; mehr ist auch bei der zum Teil noch recht erheblichen Unsicherheit der Grundlage vorläufig nicht möglich."

Thiel & Gessner (1914) calculated the solubility products for the three nickel sulphides by using the following expression from Bruner & Zadawski (1910):

$$K_{s0} \left( = \left[ \text{Ni}^{2+} \right] \left[ \text{S}^{2-} \right] \right) = \frac{\left[ \text{H}^+ \right] \left[ \text{CO}_3^{2-} \right]}{\left[ \text{HCO}_3^- \right]} \quad (11)$$

where  $k' = 1.092 \cdot 10^{-22}$ . Thiel & Gessner (1914) inserted the approximation  $k' \approx 10^{-22}$  and equilibrium concentrations, representative for their experiments, for  $\text{H}^+$ ,  $\text{H}_2\text{S}$  and  $\text{Ni}^{2+}$ . Furthermore, it was assumed that the dissociation of  $\text{NiCl}_2$  is about 0.3. Thus, an estimate of the solubility constant for  $\alpha$ -NiS was obtained:

$$K_{s0} = 0.03 \cdot 0.1 \cdot 10^{-4} \cdot 10^{-22} = 3 \cdot 10^{-21} \quad (12)$$

Similar calculations were used for determining the solubility constants for the two other sulphides, see Table 3.

Part of the experiments were performed at temperatures between 0 and 20 °C. Thiel & Gessner (1914) could not, however, find any temperature effect within this interval. In the case of the calculated solubility constants, no corresponding temperature is given.

Table 3. Solubility products reported by Thiel & Gessner (1914).

Mineral	$\text{PK}_{\text{s0}}$	$\text{K}_{\text{s0}}$
$\alpha$ -NiS	20.5	$3 \cdot 10^{-21}$
$\beta$ -NiS	26.0	$10^{-26}$
$\gamma$ -NiS	27.7	$2 \cdot 10^{-28}$

### 3.2 Discussion

The solubility constants for the nickel sulphides  $\alpha$ -NiS,  $\beta$ -NiS, and  $\gamma$ -NiS found in Kotrlý & Šticha (1985) emanate from Smith & Martell (1976), who based their data on an original study by Thiel & Gessner (1914). Smith & Martell (1976) slightly modified the original data without explicitly describing how the modification was done. However, this is often a less serious problem; most modellers and chemists will probably be content with the general descriptions of the methods used by Smith & Martell (1976).

A more serious problem arises when examining the work by Thiel & Gessner (1914). Their paper is a detailed presentation of an extensive work seemingly performed with proper care. However, the analytical tools available for the experiments at the time (electrolysis, microscopy, wet chemical analysis, etc.) did not allow for any detailed examination of the structure of the three nickel sulphides. X-ray diffraction techniques for studying crystal structures were not available. (The first X-ray diffraction experiments were performed by the German physicist von Laue in 1912 and the powder method of X-ray diffraction were devised independently by Debye and Scherrer in 1916, and in 1917 by Hall in the United States (Cullity 1967 and refs. therein)).

The solubility constants for  $\alpha$ -NiS,  $\beta$ -NiS, and  $\gamma$ -NiS, see Table 3, can be compared with the solubility constants for another nickel sulphide, millerite NiS. According to, e.g., the EQ3/6 database data0.com, the millerite dissolution at 25 °C is given by



while the formation of the  $\text{HS}^-$  at 25 °C is given by



Thus, according to the principles outlined in Chapter 2, the solubility constant for millerite at 25 °C is about  $10^{-20.97}$ , which is close to the value  $3 \cdot 10^{-21}$ , the solubility constant for  $\alpha$ -NiS. The relatively good agreement between the two solubility constants may be coincidental, and does not necessarily indicate that millerite and  $\alpha$ -NiS are identical.

Thus, the nature of the nickel compounds analyzed by Thiel & Gessner (1914) are not known in great detail, and therefore their calculated solubility constants can, in the best case, only be associated with some more or less unknown nickel sulphides. It is therefore recommended that the solubility constants for  $\alpha$ -NiS,  $\beta$ -NiS, and  $\gamma$ -NiS be used with great care.

## 4. The solubility of palladium

### 4.1 Palladium solids

Palladium and palladium compounds appear to have been sparsely investigated. Published studies focus mainly on some aqueous halogen and hydroxide complexes, as well as on a few solids, like sulphides, oxides and hydroxides. The most important oxidation state is +2, which is found in solids like  $\text{Pd}(\text{OH})_2$  and  $\text{PdO}$ . The +4 oxidation state is found in, for example,  $\text{PdO}_2$  and the complex chloride  $\text{K}_2\text{PdCl}_6$ .

Palladium, as well as the other platinum group metals (Ru, Rh, Pd, Os, Ir, and Pt), exhibit considerable stability in the environment. This is demonstrated by Brookins (1988) in the Eh-pH diagram for the Pd-O-H-S system, where the native palladium is associated with a large stability field, limited by a  $\text{Pd}(\text{OH})_2$  field at more oxidizing conditions and a  $\text{PdS}$  field at more reducing conditions, Figure 3. The phase  $\text{PdO}$  is not shown in the diagram since it is metastable with regard to  $\text{Pd}(\text{OH})_2$  under normal conditions.

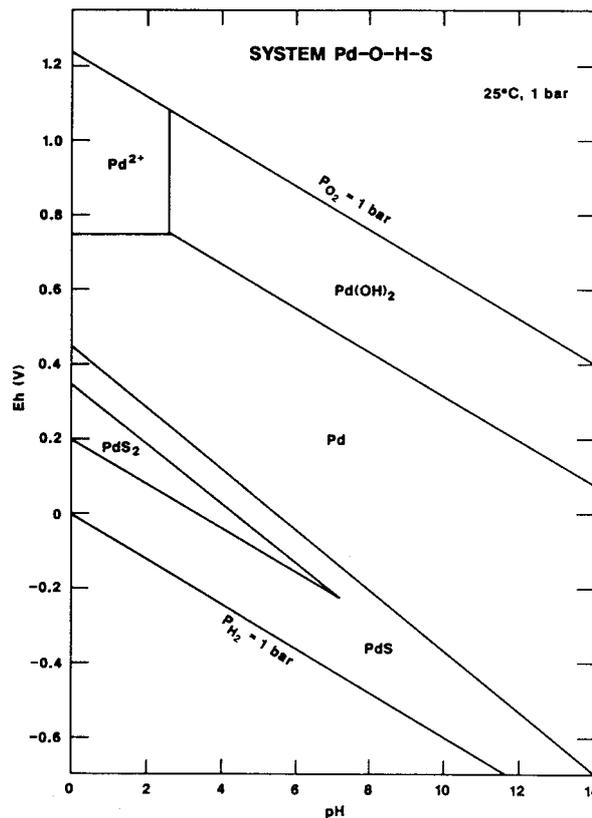


Figure 3. Eh-pH diagram for part of the system Pd-OH-S. Assumed activities for dissolved species are:  $\text{Pd} = 10^{-8}$ ,  $\text{S} = 10^{-3} \text{ M}$  (Brookins 1988).

Recent reports dealing with radionuclide solubilities in the context of repositories for spent nuclear waste suggest that the solubility of palladium be determined by some of the above palladium compounds. Bruno et al (1997) determined solubility limits for a number of radionuclides. In the case of palladium, they claim that PdO is the solubility-limiting solid in the groundwaters considered and for the pH and pe limits chosen (pH 5 to 10, and pe -5 to 5). Berner (1995) describes radionuclide solubility limits for a bentonite porewater under reducing conditions (pH = 9.0, Eh = -400 mV, I = 0.08 M, T = 50 °C). In choosing a solubility-limiting solid for palladium, Berner (1995) suggests that the realistic choice is Pd<sup>0</sup>, while conservative alternatives are PdO or Pd(OH)<sub>2</sub>.

## 4.2 Palladium oxide

The palladium oxide PdO appears in the EQ3/6 database data0.com in the following dissociation reaction



for which the reaction constants are given in the temperature interval of 0 to 300 °C. Two references are given in connection with the formula. The first one describes a software package used for extrapolating chemical data (Johnson et al. 1992). The second reference is a recent paper (Sassani & Shock 1990) that contains experimental data on, among other things, standard molal thermodynamic properties (values on  $\Delta G_f^0$ ,  $\Delta H_f^0$ , and  $S^0$ ) for PdO. These values are taken from Latimer (1952), who indicates that the  $\Delta G_f^0$  value is taken from the US Bureau of Standards (1949), while the value of  $\Delta H_f^0$  and  $S^0$  seems to have been calculated by Latimer. The  $S^0$  value is said to be an estimate. Latimer (1952) does not provide any further information about the data for PdO, which probably means that the calculation and the estimation were made by Latimer.

In the case of the  $\Delta G_f^0$  value, the reader can only know that it has selected by the US Bureau of Standards (1949). No reference or any further information concerning the chemical data was given in this context. At this point, we considered it unreasonable to go any further in tracking the origin of the chemical data for PdO. Our conclusion is that the available information concerning these values does not allow for a closer examination of the associated uncertainties. In the light of our efforts, we agree completely with the following statement by NEA (1996): "The quality of data within a database is often not clearly apparent to the user. The suppliers of databases should be encouraged to grade the quality of the data and the assessment for the substances included in their databases."

Solubility modelling inevitably involves certain assumptions concerning the physico-chemical conditions, and in this case the question of possible complex formation is crucial. Palladium forms a great amount of complexes with most ligands, and the element tends to complex strongly with the so-called soft ligands, e.g. amines (Baes & Mesmer 1976). The predominance area diagram in Figure 4 demonstrates the complexation of Pd<sup>2+</sup> in dilute Pd(II)solutions containing chloride ions. The diagram

shows the dominant species at pH values between 0 and 7 and total chloride concentrations between  $10^{-6}$  and 1 mol/L. It is seen that the strong  $\text{Pd}(\text{OH})_2(\text{aq})$  complex plays a dominant role and that its formation is favoured by increasing pH. At pH 6, for example, a chloride concentration above 0.1 mol/L is needed in order for  $\text{PdCl}_4^{2-}$  to dominate over  $\text{Pd}(\text{OH})_2(\text{aq})$ .

### 4.3 Discussion

Databases mostly contain a large number of complex-forming reactions for various elements. However, the known amount of data for palladium complex formation is relatively sparse and restricted to a few reactions, mainly involving chloride or hydroxyl ions. Lack of data may, or may not, be a serious limitation, depending on the system and conditions considered. In the case of palladium, we feel that the scarcity of data may be a more serious problem than the question of the quality of (a small number of) the data.

The general problem of lacking data has been discussed in, e.g., Grenthe & Puigdomenech (1997) who answer the question "What to do when important information is missing?" in the following way (excerpt from a longer treatise):

"The poorest solution is to include only information that is available in the databases – a much better solution is to use chemical theories to predict reasonable estimates of the quantities needed, and then to find out how sensitive the model result (e.g. a mineral solubility, or a total element concentration) is to variations in the unknown model parameters. If these parameters turn out to be important for the modelling it may be necessary to determine them experimentally."

Thus, the major problem associated with palladium chemistry seems to be the lack of data rather than uncertainties in the data. Proper solubility calculations for palladium therefore presupposes, to a greater extent than for most other elements, careful considerations of possible missing information with regard to solid formation and complexing reactions.

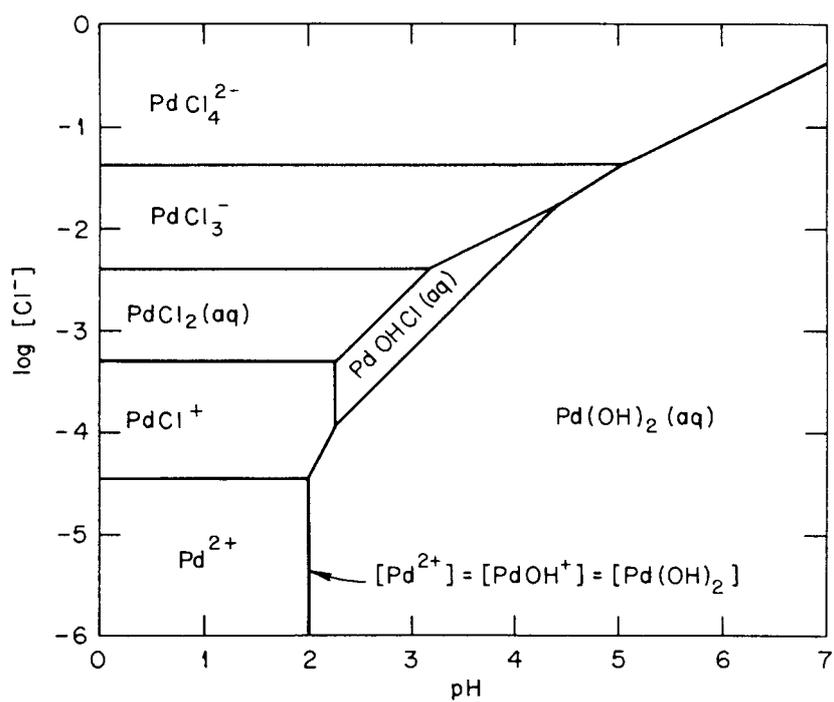


Figure 4. Predominance diagram for the  $\text{Pd}^{2+}$ - $\text{OH}^-$ - $\text{Cl}^-$  species at 25 °C in 1 M perchlorate (Baes & Mesmer 1976).

## 5. The solubility of neptunium

Neptunium, which exhibits well-characterized oxidation states from III to VII, covers a wide range of chemical behaviour. All the oxidation states are exhibited in aqueous solutions. However, in this context only one oxidation state is considered, the IV state, which is important in anoxic conditions, as in deep bedrock groundwater.

Solubility, which is the issue here, depends on the limiting solid phase but different complexation agents present can, depending on their amounts, have significant effects. Based on qualitative observations, Np(IV) forms various stable complex ions, e.g. with fluoride, sulphate, phosphate, oxalate, acetate (Katz et al. 1986). However, only phosphate is discussed here, because a recent solubility evaluation (Vuorinen et al. 1998) indicated fairly high stability of the Np(IV) phosphate complex ( $\text{Np}(\text{HPO}_4)_5^{6-}$ ) in modelling, resulting in rather high solubility. As has already been pointed out, when experimental data in complex chemical conditions, e.g. in deep groundwater is lacking, an option for assessing, e.g. solubilities in such conditions and evaluating the sensitivity of solubilities to important parameter variations, is modelling. In the Finnish programme for safe disposal of spent fuel, modelling has been performed with the hydrogeochemical modelling code EQ3/6 (Wolery 1992) with its accompanying thermodynamic data files. One of the data files often used is Data0.com.R2 (generated by GEMBOCHS.V2-JEWEL.SRC.R3 02-Aug-1995). Hence, in this context the thermodynamic data that is included in the Data0.com.R2 data file for Np, Appendix B (extracted Np data) is of interest. All the data in the data file on Np originates from one reference (Lemire 1984), which according to the author “presents a critical review of thermodynamic data available in the literature for neptunium oxide, hydroxide, phosphate, fluoride, sulphate, carbonate and chloride equilibria.”

### 5.1 Neptunium(IV) phosphate complexes

In the EQ3/6 data0.com database, five aqueous monohydrogenphosphate species for Np(IV) are included,  $\text{NpHPO}_4^{2+}$ ,  $\text{Np}(\text{HPO}_4)_2(\text{aq})$ ,  $\text{Np}(\text{HPO}_4)_3^{2-}$ ,  $\text{Np}(\text{HPO}_4)_4^{4-}$ , and  $\text{Np}(\text{HPO}_4)_5^{6-}$ , which have equilibrium constant values for the dissociation reaction given as  $\log K$  ranging from -12.9 to -52.00. In the reference (Lemire 1984) in question, the values of the formation constants of the Np(IV) monohydrogenphosphate complexes ( $I = 0$ ) are assumed equal to the experimental values ( $I \sim 2$ ) for the corresponding Pu(IV) phosphate species, which were obtained from the work by Denotkina et al. (1960a). The calculated values of Gibb's standard free energies of formation ( $\Delta_f G^0$ ) at 25 °C and the estimated entropy values ( $S^0$ ) of the Np phosphate species given in Lemire (1984) and those calculated by Denotkina et al. (1960a) for the corresponding Pu species are presented in Table 4.

Table 4. Gibb's free energy values ( $\Delta_f G^0$ ), entropies ( $\overline{S^0}$ ) and  $\log K_{[25^\circ\text{C}, 1.0132 \text{ bar}]}$  for the Np(IV) phosphate species (Lemire 1984) and the calculated values of the overall concentration instability constants ( $K_{n_j}$ ,  $j = 1 \dots 5$ ) for the corresponding Pu complex species (Denotkina et al. 1960a).

Complex species [Np(HPO <sub>4</sub> ) <sub>j</sub> ] <sup>4-2j</sup>	$\Delta_f G^0$ kJ/mol	$\overline{S^0}$ J/K·mol	$\log K_{[25^\circ\text{C}, 1.0132 \text{ bar}]}$ for $\text{Np}^{4+} + j\text{HPO}_4^{2-} = [\text{Np}(\text{HPO}_4)_j]^{4-2j}$	$K_{n_j}$ for [Pu(HPO <sub>4</sub> ) <sub>j</sub> ] <sup>4-2j</sup>
<b>j=1, NpHPO<sub>4</sub><sup>2+</sup></b>	-1 666± 20	-150 ± 200	-12.9± 3.5	1.2·10 <sup>-13</sup>
<b>j=2, Np(HPO<sub>4</sub>)<sub>2</sub>(aq)</b>	-2 817± 20	-120 ± 200	-23.7± 3.5	1.8·10 <sup>-24</sup>
<b>j=3, Np(HPO<sub>4</sub>)<sub>3</sub><sup>2-</sup></b>	-3 962± 20	0 ± 200	-33.4± 3.5	3.7·10 <sup>-34</sup>
<b>j=4, Np(HPO<sub>4</sub>)<sub>4</sub><sup>4-</sup></b>	-5 107± 20	80 ± 200	-43.2± 3.5	6·10 <sup>-44</sup>
<b>j=5, Np(HPO<sub>4</sub>)<sub>5</sub><sup>6-</sup></b>	-6 246 ± 20	160 ± 200	-52.0± 3.5	9·10 <sup>-53</sup>

Lemire, when adapting the values of Pu for Np did not make any attempt to “correct” the experimental Gibb's free energy values of Denotkina et al. (1960a) to  $I = 0$ , but instead assumed large uncertainties ( $\pm 20$  kJ/mol) for the calculated values. The entropy values of Np were estimated using Cobble's method (Cobble 1953) in which the partial molal entropies of aqueous complex ions are correlated as a function of the ratio of their charge to interatomic distance. The method gives a possibility to estimate the heats of formation for many complex ions for which only free-energy data at one temperature is available.

The Pu data of Denotkina et al. (1960a) that Lemire used is based on the measured solubility of gelatinous Pu(HPO<sub>4</sub>)<sub>2</sub>·xH<sub>2</sub>O in phosphoric acid solutions of different concentrations (0.012–2 M) in the presence of 2 M HNO<sub>3</sub> (at 25 °C ± 0.5 °C). The Pu(IV) content was determined radiometrically, but there is no statement on checking the oxidation state of the measured Pu. The solubility was studied only from undersaturation. The gelatinous Pu(IV)-hydrogen phosphate precipitate used in the solubility study was prepared according to a procedure which was only briefly described, and instead reference was made to an earlier study by Denotkina et al. (1960b) on the description of the composition and preparation of the Pu(IV) phosphate solid. In the earlier study, which is also a rather concise presentation of the experimental part of the work performed, the solid Pu(IV) phosphate was prepared by precipitation with 0.4 M phosphoric acid from 1–2 M Pu(IV)-nitrate solution to yield a product with a metal:ligand ratio = 1:2, as determined by chemical analysis. Denotkina et al. (1960b) states that the composition of the Pu(IV) phosphate formed is influenced by the concentration of the wash liquid (HNO<sub>3</sub> in this case) and by the number of washings referring to an other work by King (1949). The work by King, also on the solubility of Pu(IV) phosphate and phosphate complexes, is a rather thorough study approaching the solubility from both under- and oversaturation, finding evidence of the equilibrium reached, analysing the oxidation states and determining the composition of the solid phase (x-ray diffraction), but just for one batch though. Some discrepancies were found between several runs on solubility.

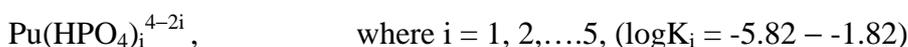
- Values of solubility obtained with a given solid were quite reproducible, but samples run under identical conditions except for the solid used did not agree as well as those run with the same solid (= same batch). It was also noted that the discrepancies were greater in the samples run at lower phosphoric acid concentration. The possible presence of colloidal Pu(IV) was not known.

King's (1949) presentation is quite detailed and also includes a discussion and a comparison of the crystalline solid  $\text{Pu}_2\text{H}(\text{PO}_4)_3 \cdot x\text{H}_2\text{O}$ . The gelatinous Pu(IV)-phosphate solid is converted to the crystalline substance as it is heated with its mother liquor. The crystalline form was found to be isomorphous (referring to private communication) with other phosphates of tetrapositive metals (Zr, Ce, Th and U).

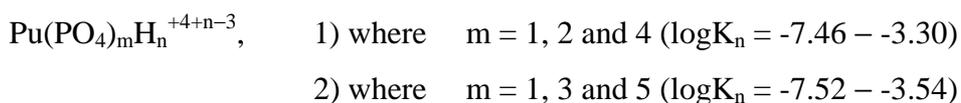
The conditions in King's (1949) solubility study (temperature  $25 \pm 0.07$  °C, concentrations of  $\text{HNO}_3$  0.35 M, 0.832 M and 2.08 M, and concentration of  $\text{H}_2\text{PO}_4$  varying from 0 M to 1.20 M) are almost identical to those in Denotkina et al. (1960a). Both references represent the solubility of gelatinous  $\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}$  with a general dissolution formula



where  $m = 0, 1, 2, \dots$  and  $n = 0, 1, 2, \dots, 3m$  (given in King 1949). However, the interpretation of the solubility data in terms of Pu(IV) phosphate complexes formed, is somewhat different; Denotkina et al. (1960a) proposed formation of five Pu-hydrogen phosphate complexes



whereas, King (1949) explained the solubility by two sets of possible phosphate complexes formed,



stating that “unique values of the equilibrium constants for the reactions involving the various complex species have not been obtained, however. It has been shown that different sets of assumed species lead to good agreement between the experimentally determined solubilities and those calculated on the basis of the equilibrium constants for reactions in which these take part. Uncertainties in the activity coefficients of hydrogen ion and the complex phosphates of plutonium(IV) make it quite difficult to establish the exact number of hydrogen ions present in the various species.”

The intention in this case was not to review the literature extensively but to trace back from the references given in the EQ3/6 database. However, a later compilation of the thermodynamic data of actinide elements (Fuger et al. 1992) was available, stating that the text gives a critical evaluation of published data found in the literature up to early 1989. Thus, the Np(IV) phosphate data was checked and all other monohydrogen phosphate species but  $\text{Np}(\text{HPO}_4)_5^{6-}$  are presented referring to the data of Moskvina et al.

(1967) dealing with Th(IV) and U(IV) complexes in phosphate solutions and Denotkina et al. (1960a) presenting Pu(IV) phosphate complexes. The values for the four Np phosphato-complexes appearing in Fuger et al. (1992), are those found in Moskvina et al. (1967) as determined by extrapolation. The values differ slightly from those chosen by Lemire (1984), but are within the given uncertainty limit though, except that one complex is completely missing. Table 5 presents the values that appear in Fuger et al. (1992) and those of Lemire (1984).

Table 5.  $\log K_{[25^\circ\text{C}, 1.0132\text{bar}]}$  for the Np(IV) phosphate species (Lemire 1984) and the overall stability constants ( $\beta_j$ ) for the Np phosphato-complexes (Moskvina et al. 1967).

Complex species	$\log K_{[25^\circ\text{C}, 1.0132\text{bar}]}$ for $\text{Np}^{4+} + j\text{HPO}_4^{2-} = [\text{Np}(\text{HPO}_4)_j]^{4-2j}$	$\log \beta_j$ for $[\text{Np}(\text{HPO}_4)_j]^{4-2j}$
j=1, $\text{NpHPO}_4^{2+}$	-12.9 ± 3.5	12.4
j=2, $\text{Np}(\text{HPO}_4)_2(\text{aq})$	-23.7 ± 3.5	23.1
j=3, $\text{Np}(\text{HPO}_4)_3^{2-}$	-33.4 ± 3.5	32.0
j=4, $\text{Np}(\text{HPO}_4)_4^{4-}$	-43.2 ± 3.5	41.0
j=5, $\text{Np}(\text{HPO}_4)_5^{6-}$	-52.0 ± 3.5	–

Fuger et al. (1992) do not recommend the stability constants of the complexes  $\text{U}(\text{HPO}_4)_n^{(4-2n)}$  and the assumed complex-forming ligand ( $\text{HPO}_4^{2-}$ ) did not seem probable in the case of Th(IV) when considering the experimental conditions, and the data on Np(IV) estimated based on the U(IV) complexes, and Pu(IV) complexes were not verified by experiment. Hence, Fuger et al. (1992) have not included any data for Np(IV) phosphato-complexes in their table of the summary of recommended values.

## 5.2 Discussion

Neptunium has been of lesser interest than uranium and plutonium, and accordingly far fewer experimental studies and data on Np appear in older scientific literature, and in the case of Np(IV) phosphates, no experimental data was found up to 1989 (Fuger et al. 1992). Surveying the more recent literature on Np was beyond the scope in this study, but especially in the case of Np(IV) the impression is that, even up to today, very little if any data has been published on Np(IV) phosphates.

As has been pointed out previously (4.3) it is important in modelling to have some data rather than completely disregard the data even if the data is estimated based on chemical theories, which is the case for Np(IV) phosphates. However, the quality of the data or the uncertainty assumed by Lemire (1984) for the calculated free energy values does not appear in the Data0.com.R2 file in association with the species at issue. Thus, for the user there is no way of knowing if the specific data is estimated, because the data file says (Appendix B), e.g. in the case of  $\text{Np}(\text{HPO}_4)_5^{6-}$ , “reported logK data used”, giving

the reference reaction for Np species. In the code manual (Wolery 1992) it is stated though, that “the user must select which of the five data files is most appropriate to a given problem. Each data file corresponds to a general formalism for treating the activity coefficients of the aqueous species and contains the relevant activity coefficient data as well as standard state thermodynamic data. The Data0.com.R2 file is the largest one and draws on many data sources. Some of the data is estimated, based on correlations or extrapolations (as to higher temperature), and is not tied to experimental measurements. The Data0.com.R2 file thus represents a melange of data, which by its nature offers less assurance of internal consistency, but offers the only means presently available for modelling aqueous solutions with a high degree of compositional complexity.”

It is clear that, when in modelling questionable results are obtained, the origin of the data used should be checked and its quality evaluated for the specific case. If the data proves to be crucial in the modelled system and is of questionable quality it should be experimentally verified.

## 6. Results and discussion

The performance assessment of the repositories for spent nuclear fuel depends, among other things, on thermodynamic data. The reliability of this data requires that the quality of the data be known. The data quality must satisfy the demands formulated by the authorities with regard to the uncertainties associated with the values given and with regard to the documentation of experimental methods, etc. The acceptance or rejection of data is, of course, coupled to the type of chemical system considered. For example, the contribution from complexation reactions to the observed nickel solubility was almost 100 % at high pH values but zero at close to neutral pH (see Chapter 2). In such a case, high uncertainties in given reaction constants are probably more easily accepted when modelling the nickel solubility in neutral waters compared to alkaline ones.

It was found during this work that even a limited quality checking of chemical data in the literature and in thermodynamic databases demands considerable resources with regard to time and money, which are consumed in searching, ordering, (sometimes) translating, and assessing the publications. The cost-efficiency of the work can be improved using computer-based literature searching, but this possibility is restricted to the literature from recent decades. (The number of years covered depends on the database used.)

The assessment of chemical data presupposes consulting both the original publications (i.e. the paper etc. where the data were first published), and all the subsequent literature. The original publications, since these are mostly the only place in literature containing all relevant information, and the subsequent literature since it is necessary to try to eliminate the possibility of missing possible re-evaluation or corrections of the original data. One benefit from consulting the sources of data is that the use of erroneous or absurd data can be avoided. Grauer (1997) points out that perhaps mythical numbers ("an expert opinion, once referenced, becomes fact despite evidence to the contrary") can never be completely avoided in databases, but their frequency can be reduced by simply consulting the relevant texts. Illustrative examples of mythical and absurd data in chemical literature are found in Grauer (1997).

The source of data is sometimes difficult to find because the literature does not always refer directly to the original publications, but to references within references. In unfortunate cases, the chain of references that needs to be consulted to find an original publication of given data is quite long, which tends to extend the literature search over a relatively long time span. Occasionally, the lack of proper bibliographic data for cited references adds an extra obstacle in the search for the origin of data (see Chapter 4). The sometimes necessary ordering of references from abroad may take days or even weeks of waiting, which tends to hamper the speed of the work. Minor documents are transferred electronically, but mostly books and other large documents have to be handled using older, manual techniques.

Looking for the origin of data may be more or less difficult. In simple cases, the origin consists of a single document that presents the results from, e.g. a chemical experiment.

In more complicated situations, however, the origin of a given number in the literature might have been obtained by collecting and treating data in some way, e.g., by calculating an average of a number of selected data from various sources. Then, finding the source of such data does not mean that the literature search is over; instead, all the references used in calculating the data have to be examined. When no bibliographic information is given about the references used, one simply has to reject or accept the data as it is.

The above roughly indicates the type and amount of work that is needed in the proper checking of the reliability of data. This study has encompassed the three elements, nickel, palladium and neptunium. It was seen that the literature, when quoting chemical data, far too seldom refers to the original works. Instead, the often-substantial effort in finding the source rests upon the reader. It was also seen that important information is sometimes missing in references that do not represent the original paper of the data in question, and also, that this information is sometimes missing even in the source publication.

When several original publications give highly scattered data for a certain reaction, it may be necessary to repeat older studies with today's technique. This was found, for example, by Mattigod et al. (1997) who collected published solubility data for  $\text{Ni}(\text{OH})_2$  and recognized that the solubility product for this compound, collected from fourteen references, varies up to seven orders of magnitude. It was also seen that the documentation in many cases lacked important information about the experimental procedures. Based on the results from the literature search, a new solubility experiment was made (Mattigod et al. 1997), resulting in better solubility data with regard to both accuracy and documentation.

This literature study demonstrates insufficiencies in some of the data necessary for solubility studies in, e.g., the performance assessment of repositories for nuclear waste. The shortcomings concern the quality of data, poor documentation, or both. In the case of nickel, the interest was focused on solubility data for three forms of nickel sulphide ( $\alpha$ -,  $\beta$ -, and  $\gamma$ -NiS). The identification of these compounds was made using cumbersome wet chemical analytical methods, at a time when XRD analytical tools were not yet at hand. The researchers, Thiel & Gessner (1914), report calculated solubilities that they stress are only estimated values. Thus, since there is a considerable uncertainty associated with both the identity of  $\alpha$ -,  $\beta$ -, and  $\gamma$ -NiS, and with their respective solubility values, we suggest that new solubility studies of nickel sulphide using today's methods are made. A similar statement has been made by, e.g., Grauer (1997): "A critical examination of sulfide solubilities would probably be a worthwhile exercise." The need for more experiments on nickel solubility has also been stressed in a recent article on the use of solubility limits for radioactive waste disposal (Thoenen 1999): "It is obvious from these findings that at the present stage of knowledge, solubility limitation of dissolved Ni by sulfide minerals cannot be relied upon in safety assessment. Detailed solubility experiments on NiS are required to determine its solubility product constant and the complexation constants of the relevant Ni sulfide complexes. In addition, more experiments on the coprecipitation of Ni with authigenic Fe sulfide minerals are needed.

Only with these data at hand can realistic solubility limits for Ni be established in sulfidic environments".

For palladium the problem is not so much the quality of the data, as the amount of data, which is relatively small. The databases mostly contain only a few palladium solids and aqueous species. However, being a metal of the platinum group, palladium exhibits considerable stability in the environment. The quality of the solubility data for Pd seems to be sufficient for the solids of interest ( $\text{Pd}(\text{OH})_2$  and  $\text{PdS}$ ) in the performance assessment of repositories for nuclear waste. However, we feel that the determination of data for complex formation reactions with, for example, organic species, would possibly add valuable complementary information to the solubility chemistry of palladium.

For neptunium, which exhibits several oxidation states and forms complexes with several ligands, only data on the phosphate complexes of Np(IV) were the issue in this work. Phosphate is an important ligand present in the groundwater environment and may thus effect solubilities. As computed solubilities at a lower pH ( $\approx 7$ ) of natural groundwater indicated strong complexation of Np(IV) by phosphate leading to rather high solubility, the origin of the Np data in the database used was of interest. The phosphate data on Np(IV) proved to be estimated data based on experiments conducted for Pu(IV) phosphate at rather high ionic strength (2 M). Instead of "correcting" the values to  $I=0$ , large uncertainties (for  $\log K \pm 3.5$ ) were assumed in the reference in question. However, in the database the original values for Pu(IV) phosphates at high ionic strength are incorporated, and without checking the origin of the data, one does not have any clue of the magnitude of uncertainty connected with the data. Knowledge of the overall quality of the database is given though, which in this case (EQ3/6 Data0.com.R2) means the inclusion of a melange of data, measured values as well as estimated ones, the objective having been to compile a database able to solve the models of complex systems. The large uncertainty should thus also be considered in the modelling exercises, at least with the span values of  $\log K$ . The best solution for having good data would, of course, be the replacement of the estimated values with measured ones. As Np has been of lesser interest than U, Pu and Th, such measurements may still await being conducted.

Consequently, this limited work clearly indicates the importance of knowledge concerning the quality of solubility data in thermodynamic databases and the data used in the performance assessment of the repositories for spent nuclear fuel. We will not speculate on how serious the lack of such knowledge may be; it will depend on the system and on the physico-chemical conditions considered. Where co-precipitation of trace elements occurs, there may be little need for exact values of solubility constants for pure phases. However, in order to minimize the uncertainties associated with performance assessments, the quality of data should in some cases be improved, for example by repeating former experiments in better controlled conditions, using today's techniques, or by studying reactions that have not yet been included in the thermodynamic databases.

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## Appendix A: Thiel & Gessner: Die Hydratfrage

The following text shows the complete discussion by Thiel & Gessner (1914) in order to conclude that the easily dissolved precipitate I (denoted "Anteil I by Thiel & Gessner) was a nickel sulphide and not a hydrate.

### Die Hydratfrage.

Die Frage, ob das leichtlösliche Nickelsulfid (Anteil I) ein Hydrat ist, besitzt beträchtliches Interesse. Einmal begegnet man ja häufig der Anschauung, daß anscheinend amorphe Fällungen, insbesondere bei Sulfiden, Hydrate sind, und andererseits würde der Nachweis, daß etwas Derartiges gerade in unserem Falle vorläge, der Sachlage ein besonderes Gepräge geben, man kann sagen: den Fall wesentlich vereinfachen. Denn er wäre dann nicht weiter wunderbar, daß Hydrat und Anhydrid, wenn sie sehr verschiedene Löslichkeiten besitzen, sich auch gegen Säure verschiedenen verhalten.

Nun hat es Glixelli (1907) sehr wahrscheinlich gemacht, daß keine der beiden Zinksulfidformen ein Hydrat ist, daß das in diesen Niederschlägen vorgefundene Wasser vielmehr nur adsorbiert ist. Bei näherer Überlegung finden wir, daß die Annahme eines Hydrats auch beim Nickelsulfid wenig Wahrscheinlichkeit besitzt. Denn wenn Anteil I ein Hydrat wäre (für II und III ist das nach dem Ergebnis der analytischen Untersuchung ja ausgeschlossen), so müßte seine gesättigte Lösung für Anhydrid außerordentlich stark sein. Der Bodenkörper wäre daher in Gegenwart des Anhydrids instabil und müßte sich in Berührung mit diesem mit meßbarer Geschwindigkeit in wasserfreie Substanz umwandeln. Nun lassen ja allerdings die Beobachtungen an lange aufbewahrten Präparaten den Schluß zu, daß allmählich eine Verminderung mit einer Langsamkeit, die kaum einer einfachen Anhydrierung angemessen scheinen kann. Es ist unwahrscheinlich, daß I das zu einer der beiden Formen II oder III gehörige Hydrat darstellt.

Dazu kommen einige experimentelle Befunde. Die Tabelle 13 enthält einen Versuch mit einem Präparat, das nach dem Auswaschen noch längere Zeit mit Alkohol gekocht wurde. Es geschah das in der Erwartung, daß im Falle des Vorhandenseins eines hydratischen Sulfids als Anteil I nach dieser Behandlung Anhydrierung eingetreten sein würde. Wie das Ergebnis zeigt, ist nachher aber noch recht reinlich Anteil I vorhanden. Letzterer kann also kaum Hydrat sein.

Noch beweiskräftiger sind aber die Resultate von Versuchen, bei denen frischbereitete Präparate durch Erhitzen entwässert wurden.

Da sich herausgestellt hatte, daß Waschen mit Alkohol und Äther in der Kälte den Anteil I nicht verschwinden läßt, wurden in dieser Weise von anhaftendem Wasser befreite Substanzen unter möglichstem Ausschluss von Luft (Arbeiten in einer Atmosphäre von Kohlendioxid) in Porzellanschiffchen übergeführt und im Stickstoffstrom durch anfangs gelindes, dann stärkeres Erhitzen von den darin enthaltenen flüchtigen Bestandteilen getrennt. Der Gehalt an den letzteren war z.T.

äußerst gering, stand jedenfalls zu dem Gehalt der Präparate an dem Anteil I in gar keiner gesetzmässigen Beziehung und zeigte auch ganz unregelmässige Schankungen, so daß von einer Wiedergabe der erhaltenen Werte Abstand genommen werden soll.

Entscheidend war vor allen Dingen aber die Feststellung, daß der z.T. sogar recht kräftig gegläute Rückstand immer noch erhebliche, wenn auch dem Anschein nach bedeutend geringere Mengen insofern vorhanden, als die Auflösung dieses Anteils hier viel langsamer vonstatten ging. Das ist aber angesichts der zweifellos eingetretenen Oberflächenverkleinerung (Dichterwerden des Präparats) seine Leichtlöslichkeit nicht der etwaigen Hydratnatur verdankt.

Kurz erwähnt sei noch, daß auch versucht wurde, das etwa vorhandene Hydratwasser von adsorbiertem Wasser nach der Methode der Beimischung eines dritten Stoffes zu trennen. Diese Methode versagte jedoch, da der dritte Stoff sehr starke Adsorption am Präparat erlitt.

Die vorliegenden Beobachtungen gestatten also, die Hydratfrage in verneinendem Sinne zu beantworten. Mithin hat auch der Anteil I eine Zusammensetzung, die der Formel  $\text{NiS}$  entspricht, d.h. er enthält außer Nickel und Schwefel kein Element in chemischer Bindung.

Tabelle 13.

Präparat Nr. 11 (aus Nickelchlorid im Überschuß mit primärem Natriumsulfid k a l t gefällt, dann mit A l k o h o l gekocht).

Fällung: Nickelchlorid, mit H<sub>2</sub>S-Wasser gemischt, wurde durch allmähliches Zutropfenlassen verdünnter Natronlauge (8 Millimole in 50 ccm) gefällt. Gesamtvolumen 175 ccm. Nickelüberschuß ca. 10 mg.

Weiterbehandlung: Nach dem Waschen mit Wasser im Stickstoffstrome mit 100 ccm Alkohol 2 Stunden lang gekocht.

Auszug Nr.	Ccm Lösungsmittel	Dauer d. Extraktion in Stunden	Gelöstes in g	Nickel in %	Anteile
1. Extraktion.					
1	150	½	0.1171	37.2	37.2 5 I
2	150	½	0.0065	2.1	
3	100	½	0.0057	1.8	
2. Extraktion					
4	100	¾	0.0901	28.6	39.3 % II
5	100	¾	0.0121	3.8	
6	100	¾	0.0059	1.9	
7	100	¾	0.003	1.1	
		Rückstand	0.0741	23.5	23.5 % III (+II)
		Summe	0.3148	100.0	

**Source of data:** Np Thermodynamic data is extracted from *DATA0.com* one of the accompanying data bases of the computer programme EQ3/6 (version 7.2b) owned by the University of California. The Np data in the data base stems from Lemire 1984.

## Appendix B: Np data EQ3/6 version 7.2b

Data0.com.R2

CII: GEMBOCHS.V2-EQ8-DATA0.COM.R2 THERMODYNAMIC DATABASE  
generated by GEMBOCHS.V2-JEWEL.SRC.R3 02-aug-1995 16:45:06

**Np 237.04800 g/mol**

### BASIS SPECIES

**Np<sup>4+</sup>** EQ3/6, com, alt revised = 13-dec-1993

<i>[reported delG0f used]</i>	<i>extrapolation algorithm: 64cri/cob</i>
<i>ref-state data</i>	<i>[source: 84lem ]</i>
delG0f = -502.900 kj/mol	[reported]
delH0f = N/A	
S0PrTr = -389.000 j/(mol*K)	[reported]
Selec = 4.576 j/(mol*K)	[source: 72kes]

### AUXILIARY BASIS SPECIES

**Np<sup>4+</sup>** EQ3/6, com, alt revised = 13-dec-1993

**Np<sup>3+</sup> + H<sup>+</sup> + 0.25 O<sub>2</sub>(g) = 0.5 H<sub>2</sub>O + Np<sup>4+</sup>**

logK grid [0-25-60-100C @1.0132bar;	150-200-250-300C @Psat-H2O]:
20.5526 18.2885 15.7242 13.9807	12.2870 10.9708 9.9219 9.0687

<i>[reported delG0f used]</i>	<i>extrapolation algorithm: 64cri/cob</i>
<i>ref-state data</i>	<i>[source: 84lem ]</i>
delG0f = -517.100 kj/mol	[reported]
delH0f = N/A	
S0PrTr = -179.100 j/(mol*K)	[reported]
Selec = 4.366 j/(mol*K)	[source: 72kes]

**NpO<sub>2</sub><sup>+</sup>** EQ3/6, com, alt revised = 13-dec-1993

**NpO<sub>2</sub><sup>+</sup> + 3 H<sup>+</sup> = 0.25 O<sub>2</sub>(g) + Np<sup>4+</sup> + 1.5 H<sub>2</sub>O**

logK grid [0-25-60-100C @1.0132bar;	150-200-250-300C @Psat-H2O]:
-10.6025 -9.8683 -8.9258 -6.9757	-4.9679 -3.3058 -1.8980 -0.6837

<i>[reported delG0f used]</i>	<i>extrapolation algorithm: 64cri/cob</i>
<i>ref-state data</i>	<i>[source: 84lem]</i>
delG0f = -915.000 kj/mol	[reported]
delH0f = N/A	
S0PrTr = -21.000 j/(mol*K)	[reported]
Selec = 4.366 j/(mol*K)	[source: 72kes]

---

**NpO<sub>2</sub><sup>2+</sup>** EQ3/6, com, alt revised = 13-dec-1993



logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:  
-10.7503 -9.7615 -8.5494 -6.5581 -4.5317 -2.8745 -1.4862 -0.3009

[reported delGOf used] extrapolation algorithm: 64cri/cob  
ref-state data [source: 84lem]  
delGOf = -795.800 kJ/mol [reported]  
delHOf = N/A  
SOPrTr = -92.000 J/(mol\*K) [reported]  
Selec = 3.561 J/(mol\*K) [source: 72kes]

---

**AQUEOUS SPECIES**

**(NpO<sub>2</sub>)<sub>2</sub>(OH)<sub>2</sub><sup>2+</sup>** EQ3/6 = com revised = 06-dec-1993



logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:  
500.0000 6.4000 5.6000 5.0000 4.6000 500.0000 500.0000 500.0000

[reported logK data used]  
reference reaction: (NpO<sub>2</sub>)<sub>2</sub>(OH)<sub>2</sub><sup>2+</sup> + 2H<sub>2</sub>O = 2NpO<sub>2</sub><sup>2+</sup> + 2H<sup>+</sup>  
ref-state data:  
logK = -6.400 [source: 84lem]  
delGOf = -485.046 kcal/mol [calculated]  
delHOf = -537.092 kcal/mol [calculated]  
SOPrTr = -3.346 cal/(mol\*K) [calculated]  
Selec = 1.702 cal/(mol\*K) [source: 72kes]

---

**(NpO<sub>2</sub>)<sub>3</sub>(OH)<sub>5</sub><sup>+</sup>** EQ3/6 = com revised = 06-dec-1993



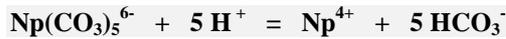
logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:  
500.0000 17.5000 15.5000 14.0000 12.8000 500.0000 500.0000 500.0000

[reported logK data used]  
reference reaction: (NpO<sub>2</sub>)<sub>3</sub>(OH)<sub>5</sub><sup>+</sup> + 5H<sup>+</sup> = 3NpO<sub>2</sub><sup>2+</sup> + 5H<sub>2</sub>O  
ref-state data:  
logK = -17.500 [source: 84lem]  
delGOf = -830.167 kcal/mol [calculated]  
delHOf = -931.717 kcal/mol [calculated]  
SOPrTr = 27.725 cal/(mol\*K) [calculated]  
Selec = 2.553 cal/(mol\*K) [source: 72kes]

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$\text{Np}(\text{CO}_3)_5^{6-}$  EQ3/6 = com revised = 14-dec-1993



logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:  
13.4933 13.3440 13.1227 14.3578 15.4439 16.0737 16.1891 15.5291

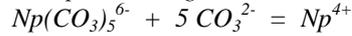
[reported logK data used]

reference reaction:

ref-state data:

logK = 38.300 [source: 84lem]  
delG0f = -803.402 kcal/mol [calculated]  
delH0f = -935.220 kcal/mol [calculated]  
S0PrTr = 38.241 cal/(mol\*K) [calculated]  
Selec = 1.094 cal/(mol\*K) [source: 72kes]

extrapolation algorithm: 64cri/cob



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$\text{Np}(\text{H}_2\text{PO}_4)_2^+$  EQ3/6 = com revised = 07-dec-1993



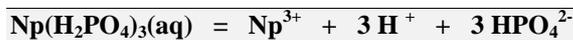
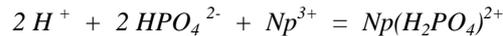
logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:  
500.0000 -3.7000 -2.0000 -1.0000 -1.0000 500.0000 500.0000 500.0000

[reported logK data used]

reference reaction:

ref-state data:

logK = 3.700 [source: 84lem]  
delG0f = -649.258 kcal/mol [calculated]  
delH0f = -743.981 kcal/mol [calculated]  
S0PrTr = -43.021 cal/(mol\*K) [calculated]  
Selec = 1.043 cal/(mol\*K) [source: 72kes]



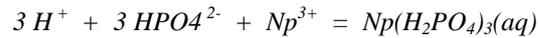
logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:  
500.0000 -5.6000 -3.0000 -1.0000 0.0000 500.0000 500.0000 500.0000

[reported logK data used]

reference reaction:

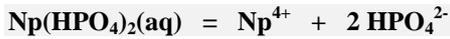
Ref-state data:

logK = 5.600 [source: 84lem]  
delG0f = -912.160 kcal/mol [calculated]  
delH0f = -1057.649 kcal/mol [calculated]  
S0PrTr = -58.556 cal/(mol\*K) [calculated]  
Selec = 1.043 cal/(mol\*K) [source: 72kes]



---

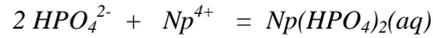
**Np(HPO<sub>4</sub>)<sub>2</sub>(aq)** EQ3/6 = com revised = 31-jul-1995



logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:  
500.0000 -23.7000 -23.0000 -23.0000 -24.0000 500.0000 500.0000 500.0000

[reported logK data used]

reference reaction:



ref-state data:

logK = 23.700 q [source: 84lem]  
delG0f = -673.149 kcal/mol [calculated]  
delH0f = -758.940 kcal/mol [calculated]  
S0PrTr = -28.681 cal/(mol\*K) [calculated]  
Selec = 1.094 cal/(mol\*K) [source: 72kes]

---

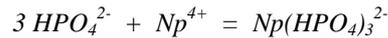
**Np(HPO<sub>4</sub>)<sub>3</sub><sup>2-</sup>** EQ3/6 = com revised = 06-dec-1993



logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:  
500.0000 -33.4000 -33.0000 -33.0000 -33.0000 500.0000 500.0000 500.0000

[reported logK data used]

reference reaction:



ref-state data:

logK = 33.400 [source: 84lem]  
delG0f = -946.692 kcal/mol [calculated]  
delH0f = -1070.066 kcal/mol [calculated]  
S0PrTr = 0.000 cal/(mol\*K) [calculated]  
Selec = 1.094 cal/(mol\*K) [source: 72kes]

---

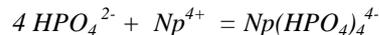
**Np(HPO<sub>4</sub>)<sub>4</sub><sup>4-</sup>** EQ3/6 = com revised = 06-dec-1993



logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:  
500.0000 -43.2000 -43.0000 -43.0000 -45.0000 500.0000 500.0000 500.0000

[reported logK data used]

reference reaction:



ref-state data:

logK = 43.200 [source: 84lem]  
delG0f = -1220.371 kcal/mol [calculated]  
delH0f = -1384.180 kcal/mol [calculated]  
S0PrTr = 19.120 cal/(mol\*K) [calculated]  
Selec = 1.094 cal/(mol\*K) [source: 72kes]

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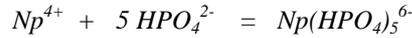
**Np(HPO<sub>4</sub>)<sub>5</sub><sup>6-</sup>** EQ3/6 = com revised = 23-nov-1988



logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:  
500.0000 -52.0000 -51.0000 -52.0000 -55.0000 500.0000 500.0000 500.0000

[reported logK data used]

reference reaction:



ref-state data:

logK = 52.000 [source: 84lem]  
delG0f = -1492.687 kcal/mol [calculated]  
delH0f = -1696.929 kcal/mol [calculated]  
S0PrTr = 38.241 cal/(mol\*K) [calculated]  
Selec = 1.094 cal/(mol\*K) [source: 72kes]

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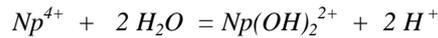
**Np(OH)<sub>2</sub><sup>2+</sup>** EQ3/6 = com revised = 07-dec-1993



logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:  
500.0000 2.8000 1.0000 0.0000 -1.0000 500.0000 500.0000 500.0000

[reported logK data used]

reference reaction:

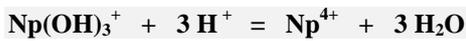


ref-state data:

logK = -2.800 [source: 84lem]  
delG0f = -229.752 kcal/mol [calculated]  
delH0f = -251.102 kcal/mol [calculated]  
S0PrTr = -10.516 cal/(mol\*K) [calculated]  
Selec = 1.094 cal/(mol\*K) [source: 72kes]

---

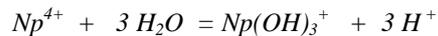
**Np(OH)<sub>3</sub><sup>+</sup>** EQ3/6 = com revised = 07-dec-1993



logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:  
500.0000 5.8000 4.0000 2.0000 1.0000 500.0000 500.0000 500.0000

[reported logK data used]

reference reaction:



ref-state data:

logK = -5.800 [source: 84lem]  
delG0f = -282.346 kcal/mol [calculated]  
delH0f = -314.048 kcal/mol [calculated]  
S0PrTr = 10.516 cal/(mol\*K) [calculated]  
Selec = 1.094 cal/(mol\*K) [source: 72kes]

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**Np(OH)<sub>4</sub>(aq)** EQ3/6 = com revised = 07-dec-1993



logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:  
500.0000 9.6000 8.0000 6.0000 5.0000 500.0000 500.0000 500.0000

[reported logK data used]

reference reaction:



ref-state data:

logK = -9.600 [source: 84lem]  
delG0f = -333.850 kcal/mol [calculated]  
delH0f = -379.964 kcal/mol [calculated]  
S0PrTr = 17.925 cal/(mol\*K) [calculated]  
Selec = 1.094 cal/(mol\*K) [source: 72kes]

---

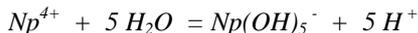
**Np(OH)<sub>5</sub><sup>-</sup>** EQ3/6 = com revised = 07-dec-1993



logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:  
500.0000 14.3000 12.0000 11.0000 9.0000 500.0000 500.0000 500.0000

[reported logK data used]

reference reaction:

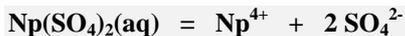


ref-state data:

logK = -14.300 [source: 84lem]  
delG0f = -384.126 kcal/mol [calculated]  
delH0f = -445.365 kcal/mol [calculated]  
S0PrTr = 22.945 cal/(mol\*K) [calculated]  
Selec = 1.094 cal/(mol\*K) [source: 72kes]

---

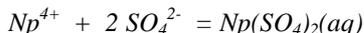
**Np(SO<sub>4</sub>)<sub>2</sub>(aq)** EQ3/6 = com revised = 21-jul-1986



logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:  
500.0000 -9.9000 -10.7000 -11.8000 -13.1000 500.0000 500.0000 500.0000

[reported logK data used]

reference reaction:



ref-state data:

logK = 9.900 [source: 84lem]  
delG0f = -489.562 kcal/mol [calculated]  
delH0f = -558.126 kcal/mol [calculated]  
S0PrTr = -6.453 cal/(mol\*K) [calculated]  
Selec = 1.094 cal/(mol\*K) [source: 72kes]

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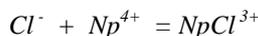
**NpCl<sup>3+</sup>** EQ3/6 = com revised = 08-dec-1993



logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:  
500.0000 -0.2000 -0.7000 -1.5000 -3.0000 500.0000 500.0000 500.0000

[reported logK data used]

reference reaction:



ref-state data:

logK = 0.200 [source: 84lem]  
delG0f = -151.848 kcal/mol [calculated]  
delH0f = -167.951 kcal/mol [calculated]  
S0PrTr = -62.141 cal/(mol\*K) [calculated]  
Selec = 1.094 cal/(mol\*K) [source: 72kes]

---

**NpCl<sub>2</sub><sup>2+</sup>** EQ3/6 = com revised = 23-nov-1988



logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:  
500.0000 0.1000 -1.7000 -3.5000 -5.0000 500.0000 500.0000 500.0000

[reported logK data used]

reference reaction:



ref-state data:

logK = -0.100 [source: 84lem]  
delG0f = -182.818 kcal/mol [calculated]  
delH0f = -190.147 kcal/mol [calculated]  
S0PrTr = 9.560 cal/(mol\*K) [calculated]  
Selec = 1.094 cal/(mol\*K) [source: 72kes]

---

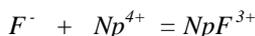
**NpF<sup>3+</sup>** EQ3/6 = com revised = 23-nov-1988



logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:  
500.0000 -8.7000 -8.7000 -8.8000 -9.0000 500.0000 500.0000 500.0000

[reported logK data used]

reference reaction:



ref-state data:

logK = 8.700 [source: 84lem]  
delG0f = -199.405 kcal/mol [calculated]  
delH0f = -213.859 kcal/mol [calculated]  
S0PrTr = -59.034 cal/(mol\*K) [calculated]  
Selec = 1.094 cal/(mol\*K) [source: 72kes]

---

<b>NpF<sub>2</sub><sup>2+</sup></b>	EQ3/6 = com	revised = 23-nov-1988
<b>NpF<sub>2</sub><sup>2+</sup> = Np<sup>4+</sup> + 2 F<sup>-</sup></b>		
logK grid [0-25-60-100C @1.0132bar; 500.0000 -15.4000 -15.6000 -16.0000		150-200-250-300C @Psat-H2O]: -16.6000 500.0000 500.0000 500.0000
<i>[reported logK data used]</i>		
<i>reference reaction:</i>		$Np^{4+} + 2 F^{-} = NpF_2^{2+}$
<i>ref-state data:</i>		
logK = 15.400		[source: 84lem]
delG0f = -275.885 kcal/mol		[calculated]
delH0f = -291.746 kcal/mol		[calculated]
S0PrTr = -23.901 cal/(mol*K)		[calculated]
Selec = 1.094 cal/(mol*K)		[source: 72kes]
<b>NpH<sub>2</sub>PO<sub>4</sub><sup>2+</sup></b>	EQ3/6 = com	revised = 07-dec-1993
<b>NpH<sub>2</sub>PO<sub>4</sub><sup>2+</sup> = H<sup>+</sup> + HPO<sub>4</sub><sup>2-</sup> + Np<sup>3+</sup></b>		
logK grid [0-25-60-100C @1.0132bar; 500.0000 -2.4000 -2.0000 -1.0000		150-200-250-300C @Psat-H2O]: -1.0000 500.0000 500.0000 500.0000
<i>[reported logK data used]</i>		
<i>reference reaction:</i>		$H^{+} + HPO_4^{2-} + Np^{3+} = NpH_2PO_4^{2+}$
<i>ref-state data:</i>		
logK = 2.400		[source: 84lem]
delG0f = -387.174 kcal/mol		[calculated]
delH0f = -433.340 kcal/mol		[calculated]
S0PrTr = -34.895 cal/(mol*K)		[calculated]
Selec = 1.043 cal/(mol*K)		[source: 72kes]
<b>NpHPO<sub>4</sub><sup>2+</sup></b>	EQ3/6 = com	revised = 23-nov-1988
<b>NpHPO<sub>4</sub><sup>2+</sup> = HPO<sub>4</sub><sup>2-</sup> + Np<sup>4+</sup></b>		
logK grid [0-25-60-100C @1.0132bar; 500.0000 -12.9000 -13.0000 -14.0000		150-200-250-300C @Psat-H2O]: -14.0000 500.0000 500.0000 500.0000
<i>[reported logK data used]</i>		
<i>reference reaction:</i>		$HPO_4^{2-} + Np^{4+} = NpHPO_4^{2+}$
<i>ref-state data:</i>		
logK = 12.900		[source: 84lem]
delG0f = -398.105 kcal/mol		[calculated]
delH0f = -439.899 kcal/mol		[calculated]
S0PrTr = -35.851 cal/(mol*K)		[calculated]
Selec = 1.094 cal/(mol*K)		[source: 72kes]

$\text{NpO}_2(\text{CO}_3)_2^{2-}$	EQ3/6 = com	revised = 14-dec-1993
$\text{NpO}_2(\text{CO}_3)_2^{2-} + 2 \text{H}^+ = \text{NpO}_2^{2+} + 2 \text{HCO}_3^-$		
logK grid [0-25-60-100C @1.0132bar;		150-200-250-300C @Psat-H2O]:
6.9409 6.6576 6.3162 6.6959		7.0177 7.1809 7.1552 6.8319
<i>[reported logK data used]</i>		<i>extrapolation algorithm: 64cri/cob</i>
<i>reference reaction:</i>		$\text{NpO}_2(\text{CO}_3)_2^{2-} = 2 \text{CO}_3^{2-} + \text{NpO}_2^{2+}$
<i>ref-state data:</i>		
logK = 14.000		[source: 84lem]
delG0f = -461.682 kcal/mol		[calculated]
delH0f = -521.770 kcal/mol		[calculated]
S0PrTr = 40.631 cal/(mol*K)		[calculated]
Selec = 0.851 cal/(mol*K)		[source: 72kes]
$\text{NpO}_2(\text{CO}_3)_2^{3-}$	EQ3/6 = com	revised = 13-dec-1993
$\text{NpO}_2(\text{CO}_3)_2^{3-} + 2 \text{H}^+ = \text{NpO}_2^+ + 2 \text{HCO}_3^-$		
logK grid [0-25-60-100C @1.0132bar;		150-200-250-300C @Psat-H2O]:
14.2637 13.6576 12.9336 12.6039		12.2277 11.8402 11.3693 10.6783
<i>[reported logK data used]</i>		<i>extrapolation algorithm: 64cri/cob</i>
<i>reference reaction:</i>		$\text{NpO}_2(\text{CO}_3)_2^{3-} = 2 \text{CO}_3^{2-} + \text{NpO}_2^+$
<i>ref-state data:</i>		
logK = 7.000		[source: 84lem]
delG0f = -480.622 kcal/mol		[calculated]
delH0f = -549.642 kcal/mol		[calculated]
S0PrTr = 26.291 cal/(mol*K)		[calculated]
Selec = 1.043 cal/(mol*K)		[source: 72kes]
$\text{NpO}_2(\text{CO}_3)_3^{5-}$	EQ3/6 = com	revised = 13-dec-1993
$\text{NpO}_2(\text{CO}_3)_3^{5-} + 3 \text{H}^+ = \text{NpO}_2^+ + 3 \text{HCO}_3^-$		
logK grid [0-25-60-100C @1.0132bar;		150-200-250-300C @Psat-H2O]:
23.3470 22.4864 21.4475 20.7335		19.9532 19.2017 18.3575 17.2074
<i>[reported logK data used]</i>		<i>extrapolation algorithm: 64cri/cob</i>
<i>reference reaction:</i>		$\text{NpO}_2(\text{CO}_3)_3^{5-} = 3 \text{CO}_3^{2-} + \text{NpO}_2^+$
<i>ref-state data:</i>		
logK = 8.500		[source: 84lem]
delG0f = -608.859 kcal/mol		[calculated]
delH0f = -711.667 kcal/mol		[calculated]
S0PrTr = 19.120 cal/(mol*K)		[calculated]
Selec = 1.043 cal/(mol*K)		[source: 72kes]

<b>NpO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub><sup>4-</sup></b>	EQ3/6 = com	revised = 13-dec-1993
<b>NpO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub><sup>4-</sup> + 3 H<sup>+</sup> = NpO<sub>2</sub><sup>2+</sup> + 3 HCO<sub>3</sub><sup>-</sup></b>		
logK grid [0-25-60-100C @1.0132bar; 10.3656 10.5864 10.7896 11.2180		150-200-250-300C @Psat-H2O]: 11.5621 11.6974 11.5704 11.0124
<i>[reported logK data used]</i>		<i>extrapolation algorithm: 64cri/cob</i>
<i>reference reaction:</i>		<i>3 CO<sub>3</sub><sup>2-</sup> + NpO<sub>2</sub><sup>2+</sup> = NpO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub><sup>4-</sup></i>
<i>ref-state data:</i>		
logK = 20.400		[source: 84lem]
delG0f = -596.604 kcal/mol		[calculated]
delH0f = -699.601 kcal/mol		[calculated]
S0PrTr = 2.868 cal/(mol*K)		[calculated]
Selec = 0.851 cal/(mol*K)		[source: 72kes]
<b>NpO<sub>2</sub>CO<sub>3</sub><sup>-</sup></b>	EQ3/6 = com	revised = 13-dec-1993
<b>NpO<sub>2</sub>CO<sub>3</sub><sup>-</sup> + H<sup>+</sup> = HCO<sub>3</sub><sup>-</sup> + NpO<sub>2</sub><sup>+</sup></b>		
logK grid [0-25-60-100C @1.0132bar; 6.3082 5.7288 5.0636 5.0492		150-200-250-300C @Psat-H2O]: 5.0091 4.9321 4.7910 4.5235
<i>[reported logK data used]</i>		<i>extrapolation algorithm: 64cri/cob</i>
<i>reference reaction:</i>		<i>CO<sub>3</sub><sup>2-</sup> + NpO<sub>2</sub><sup>+</sup> = NpO<sub>2</sub>CO<sub>3</sub><sup>-</sup></i>
<i>ref-state data:</i>		
logK = 4.600		[source: 84lem]
delG0f = -351.157 kcal/mol		[calculated]
delH0f = -382.113 kcal/mol		[calculated]
S0PrTr = 47.801 cal/(mol*K)		[calculated]
Selec = 1.043 cal/(mol*K)		[source: 72kes]
<b>NpO<sub>2</sub>Cl(aq)</b>	EQ3/6 = com	revised = 21-jul-1986
<b>NpO<sub>2</sub>Cl(aq) = Cl<sup>-</sup> + NpO<sub>2</sub><sup>+</sup></b>		
logK grid [0-25-60-100C @1.0132bar; 500.0000 0.4000 0.1000 0.0000		150-200-250-300C @Psat-H2O]: 0.0000 500.0000 500.0000 500.0000
<i>[reported logK data used]</i>		
<i>reference reaction:</i>		<i>Cl<sup>-</sup> + NpO<sub>2</sub><sup>+</sup> = NpO<sub>2</sub>Cl(aq)</i>
<i>ref-state data:</i>		
logK = -0.400		[source: 84lem]
delG0f = -249.524 kcal/mol		[calculated]
delH0f = -269.986 kcal/mol		[calculated]
S0PrTr = 19.120 cal/(mol*K)		[calculated]
Selec = 1.043 cal/(mol*K)		[source: 72kes]

<b>NpO<sub>2</sub>Cl<sup>+</sup></b>	EQ3/6 = com	revised = 23-nov-1988
<b>NpO<sub>2</sub>Cl<sup>+</sup> = Cl<sup>-</sup> + NpO<sub>2</sub><sup>2+</sup></b>		
logK grid [0-25-60-100C @1.0132bar; 500.0000 0.2000 -0.2000 -1.0000		150-200-250-300C @Psat-H2O]: -2.0000 500.0000 500.0000 500.0000
<i>[reported logK data used]</i>		
reference reaction:		$Cl^- + NpO_2^{2+} = NpO_2Cl^+$
ref-state data:		
logK = -0.200		[source: 84lem]
delG0f = -221.307 kcal/mol		[calculated]
delH0f = -242.814 kcal/mol		[calculated]
S0PrTr = 0.000 cal/(mol*K)		[calculated]
Selec = 0.851 cal/(mol*K)		[source: 72kes]
<b>NpO<sub>2</sub>F(aq)</b>	EQ3/6 = com	revised = 21-jul-1986
<b>NpO<sub>2</sub>F(aq) = F<sup>-</sup> + NpO<sub>2</sub><sup>+</sup></b>		
logK grid [0-25-60-100C @1.0132bar; 500.0000 -1.0000 -1.6000 -2.2000		150-200-250-300C @Psat-H2O]: -2.8000 500.0000 500.0000 500.0000
<i>[reported logK data used]</i>		
reference reaction:		$F^- + NpO_2^+ = NpO_2F(aq)$
ref-state data:		
logK = 1.000		[source: 84lem]
delG0f = -287.394 kcal/mol		[calculated]
delH0f = -305.709 kcal/mol		[calculated]
S0PrTr = 23.901 cal/(mol*K)		[calculated]
Selec = 1.043 cal/(mol*K)		[source: 72kes]
<b>NpO<sub>2</sub>F<sup>+</sup></b>	EQ3/6 = com	revised = 23-nov-1988
<b>NpO<sub>2</sub>F<sup>+</sup> + F<sup>-</sup> = NpO<sub>2</sub><sup>2+</sup></b>		
logK grid [0-25-60-100C @1.0132bar; 500.0000 -4.6000 -4.7000 -4.8000		150-200-250-300C @Psat-H2O]: -5.2000 500.0000 500.0000 500.0000
<i>[reported logK data used]</i>		
reference reaction:		$NpO_2^{2+} + F^- = NpO_2F^+$
ref-state data:		
logK = 4.600		[source: 84lem]
delG0f = -263.816 kcal/mol		[calculated]
delH0f = -285.598 kcal/mol		[calculated]
S0PrTr = -3.346 cal/(mol*K)		[calculated]
Selec = 0.851 cal/(mol*K)		[source: 72kes]

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**NpO<sub>2</sub>F<sub>2</sub>(aq)** EQ3/6 = com revised = 21-jul-1986



logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:  
500.0000 -7.8000 -7.9000 -8.1000 -8.5000 500.0000 500.0000 500.0000

[reported logK data used]

reference reaction:



ref-state data:

logK = 7.800 [source: 84lem]  
delGof = -335.522 kcal/mol [calculated]  
delHof = -365.337 kcal/mol [calculated]  
SOPrTr = 9.560 cal/(mol\*K) [calculated]  
Selec = 0.851 cal/(mol\*K) [source: 72kes]

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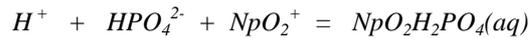
**NpO<sub>2</sub>H<sub>2</sub>PO<sub>4</sub>(aq)** EQ3/6 = com revised = 08-dec-1993



logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:  
500.0000 -0.6000 -0.3000 0.0000 0.0000 500.0000 500.0000 500.0000

[reported logK data used]

reference reaction:

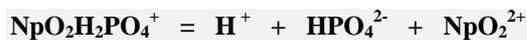


ref-state data:

logK = 0.600 [source: 84lem]  
delGof = -479.819 kcal/mol [calculated]  
delHof = -538.087 kcal/mol [calculated]  
SOPrTr = 4.780 cal/(mol\*K) [calculated]  
Selec = 1.043 cal/(mol\*K) [source: 72kes]

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**NpO<sub>2</sub>H<sub>2</sub>PO<sub>4</sub><sup>+</sup>** EQ3/6 = com revised = 08-dec-1993



logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:  
500.0000 -2.3000 -1.9000 -2.0000 -1.0000 500.0000 500.0000 500.0000

[reported logK data used]

reference reaction:



ref-state data:

logK = 2.300 [source: 84lem]  
delGof = -453.649 kcal/mol [calculated]  
delHof = -512.249 kcal/mol [calculated]  
SOPrTr = -11.950 cal/(mol\*K) [calculated]  
Selec = 0.851 cal/(mol\*K) [source: 72kes]

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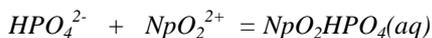
**NpO<sub>2</sub>HPO<sub>4</sub>(aq)** EQ3/6 = com revised = 21-jul-1986



logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:  
500.0000 -8.2000 -8.2000 -8.0000 -9.0000 500.0000 500.0000 500.0000

[reported logK data used]

reference reaction:



ref-state data:

logK = 8.200 [source: 84lem]  
delGof = -461.698 kcal/mol [calculated]  
delHof = -516.022 kcal/mol [calculated]  
SOPrTr = 2.390 cal/(mol\*K) [calculated]  
Selec = 0.851 cal/(mol\*K) [source: 72kes]

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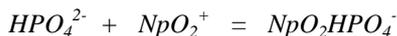
**NpO<sub>2</sub>HPO<sub>4</sub><sup>-</sup>** EQ3/6 = com revised = 23-nov-1988



logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:  
500.0000 -3.5000 -4.5000 -6.0000 -7.0000 500.0000 500.0000 500.0000

[reported logK data used]

reference reaction:



ref-state data:

logK = 3.500 [source: 84lem]  
delGof = -483.775 kcal/mol [calculated]  
delHof = -530.642 kcal/mol [calculated]  
SOPrTr = 43.021 cal/(mol\*K) [calculated]  
Selec = 1.043 cal/(mol\*K) [source: 72kes]

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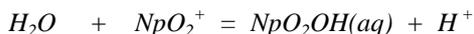
**NpO<sub>2</sub>OH(aq)** EQ3/6 = com revised = 08-dec-1993



logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:  
500.0000 8.9000 8.2000 7.6000 7.2000 500.0000 500.0000 500.0000

[reported logK data used]

reference reaction:



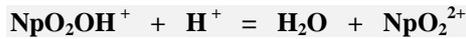
ref-state data:

logK = -8.900 [source: 84lem]  
delGof = -263.236 kcal/mol [calculated]  
delHof = -291.635 kcal/mol [calculated]  
SOPrTr = 5.975 cal/(mol\*K) [calculated]  
Selec = 1.043 cal/(mol\*K) [source: 72kes]

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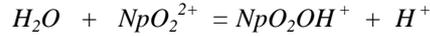
**NpO<sub>2</sub>OH<sup>+</sup>** EQ3/6 = com revised = 08-dec-1993



logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:  
500.0000 5.2000 4.4000 3.7000 3.0000 500.0000 500.0000 500.0000

[reported logK data used]

reference reaction:

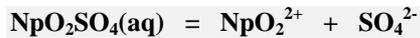


ref-state data:

logK = -5.200 [source: 84lem]  
delG0f = -239.794 kcal/mol [calculated]  
delH0f = -263.608 kcal/mol [calculated]  
S0PrTr = 5.736 cal/(mol\*K) [calculated]  
Selec = 0.851 cal/(mol\*K) [source: 72kes]

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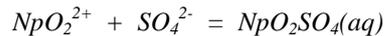
**NpO<sub>2</sub>SO<sub>4</sub>(aq)** EQ3/6 = com revised = 03-apr-1990



logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:  
500.0000 -3.3000 -3.8000 -4.6000 -5.8000 500.0000 500.0000 500.0000

[reported logK data used]

reference reaction:



ref-state data:

logK = 3.300 [source: 84lem]  
delG0f = -372.633 kcal/mol [calculated]  
delH0f = -418.308 kcal/mol [calculated]  
S0PrTr = 13.623 cal/(mol\*K) [calculated]  
Selec = 0.851 cal/(mol\*K) [source: 72kes]

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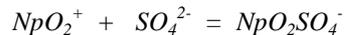
**NpO<sub>2</sub>SO<sub>4</sub><sup>-</sup>** EQ3/6 = com revised = 23-nov-1988



logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:  
500.0000 -0.4000 -0.7000 -0.9000 -0.9000 500.0000 500.0000 500.0000

[reported logK data used]

reference reaction:



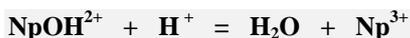
ref-state data:

logK = 0.400 [source: 84lem]  
delG0f = -397.166 kcal/mol [calculated]  
delH0f = -446.571 kcal/mol [calculated]  
S0PrTr = 16.730 cal/(mol\*K) [calculated]  
Selec = 1.043 cal/(mol\*K) [source: 72kes]

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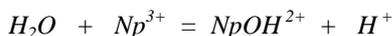
**NpOH<sup>2+</sup>** EQ3/6 = com revised = 08-dec-1993



logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:  
500.0000 7.0000 6.1000 5.3000 4.5000 500.0000 500.0000 500.0000

[reported logK data used]

reference reaction:

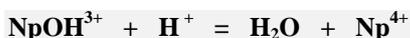


ref-state data:

logK = -7.000 [source: 84lem]  
delG0f = -170.728 kcal/mol [calculated]  
delH0f = -182.322 kcal/mol [calculated]  
S0PrTr = -17.925 cal/(mol\*K) [calculated]  
Selec = 1.043 cal/(mol\*K) [source: 72kes]

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**NpOH<sup>3+</sup>** EQ3/6 = com revised = 13-dec-1993



logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:  
500.0000 1.0000 0.1000 -0.7000 -1.4000 500.0000 500.0000 500.0000

[reported logK data used]

reference reaction:



ref-state data:

logK = -1.000 [source: 84lem]  
delG0f = -175.519 kcal/mol [calculated]  
delH0f = -189.013 kcal/mol [calculated]  
S0PrTr = -39.914 cal/(mol\*K) [calculated]  
Selec = 1.094 cal/(mol\*K) [source: 72kes]

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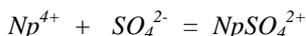
**NpSO<sub>4</sub><sup>2+</sup>** EQ3/6 = com revised = 23-nov-1988



logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:  
500.0000 -5.5000 -6.0000 -6.6000 -7.5000 500.0000 500.0000 500.0000

[reported logK data used]

reference reaction:



ref-state data:

logK = 5.500 [source: 84lem]  
delG0f = -305.629 kcal/mol [calculated]  
delH0f = -345.331 kcal/mol [calculated]  
S0PrTr = -46.606 cal/(mol\*K) [calculated]  
Selec = 1.094 cal/(mol\*K) [source: 72kes]

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**SOLIDS**

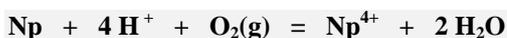
**NaNpO<sub>2</sub>CO<sub>3</sub> 3.5 H<sub>2</sub>O** EQ3/6 = com, alt revised = 18-jul-1986



logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:  
 -1.7626 -1.2342 -0.6258 0.0511 0.7461 1.3125 1.7706 2.0931

*[reported delG0f used]* *extrapolation algorithm: Cp integration*  
*ref-state data* *[source: 84lem]*  
 delG0f = -2601.000 kj/mol [reported]  
 delH0f = N/A  
 S0PrTr = 314.000 j/(mol\*K) [reported]  
 Cp coefficients [source: 84lem units: jou]  
 T 0 = 0.26900000E+03

**Neptunium Np** EQ3/6 = com, alt revised = 03-apr-1990



logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:  
 188.3425 171.2094 151.6216 134.9131 118.5343 105.6731 95.3141 86.7974

*[reported delG0f used]* *extrapolation algorithm: Cp integration*  
*alternate name = Neptunium*  
*ref-state data* *[source: 84lem]*  
 delG0f = 0.000 kj/mol [reported]  
 delG0f = 0.000 kj/mol [calculated]  
 delH0f = 0.000 kj/mol [reported]  
 S0PrTr = 50.460 j/(mol\*K) [reported]  
 Cp coefficients [source: 84lem units: jou]  
 T 0 = -0.40540000E+01  
 T 1 = 0.82550000E-01  
 T -2 = 0.80580000E+06  
 Tlimit = 279.85C

**Np(HPO<sub>4</sub>)<sub>2</sub>** EQ3/6 = com, alt revised = 18-jul-1986



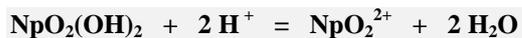
logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:  
 -31.8028 -30.9786 -30.3873 -29.1176 -28.3396 -28.2286 -28.6998 -29.8797

*[reported delG0f used]* *extrapolation algorithm: Cp integration*  
*ref-state data* *[source: 84lem]*  
 delG0f = -2858.000 kj/mol [reported]  
 delH0f = N/A  
 S0PrTr = 200.000 j/(mol\*K) [reported]  
 Cp coefficients [source: 84lem units: jou]  
 T 0 = 0.22400000E+03

<b>Np(OH)<sub>4</sub></b>	EQ3/6 = com, alt	revised = 23-nov-1988
<b>Np(OH)<sub>4</sub> + 4 H<sup>+</sup> = Np<sup>4+</sup> + 4 H<sub>2</sub>O</b>		
logK grid [0-25-60-100C @1.0132bar; 1.1454 0.8103 0.5562 1.5527		150-200-250-300C @Psat-H2O]: 2.6812 3.7209 4.7177 5.7128
<i>[reported delG0f used]</i>		<i>extrapolation algorithm: Cp integration</i>
<i>ref-state data</i>		<i>[source: 84lem]</i>
delG0f = -1447.000 kJ/mol		[reported]
delH0f = N/A		
S0PrTr = 139.000 j/(mol*K)		[reported]
Cp coefficients		[source: 84lem units: jou]
T 0 = 0.13100000E+03		
<b>Np<sub>2</sub>O<sub>5</sub></b>	EQ3/6 = com, alt	revised = 17-may-1990
<b>Np<sub>2</sub>O<sub>5</sub> + 2 H<sup>+</sup> = H<sub>2</sub>O + 2 NpO<sub>2</sub><sup>+</sup></b>		
logK grid [0-25-60-100C @1.0132bar; 500.0000 9.5000 8.0000 6.0000		150-200-250-300C @Psat-H2O]: 5.0000 500.0000 500.0000 500.0000
<i>[reported logK data used]</i>		
<i>ref-state data</i>		<i>[source: 84lem]</i>
<i>reference reaction:</i>		<i>Np<sub>2</sub>O<sub>5</sub> + 2 H<sup>+</sup> = H<sub>2</sub>O + 2 NpO<sub>2</sub><sup>+</sup></i>
<i>ref-state data:</i>		
logK = 9.500		[source: 84lem ]
delG0f = -2012.955 kcal/mol		[calculated]
delH0f = -2147.361 kcal/mol		[calculated]
S0PrTr = 163.000 cal/(mol*K)		[calculated]
Cp coefficients		[source: 84lem units: jou]
T 0 = 0.99200000E+02		
T 1 = 0.98600000E-01		
Tlimit = 476.85C		
<b>NpO<sub>2</sub></b>	EQ3/6 = com, alt	revised = 17-may-1990
<b>NpO<sub>2</sub> + 4 H<sup>+</sup> = Np<sup>4+</sup> + 2 H<sub>2</sub>O</b>		
logK grid [0-25-60-100C @1.0132bar; -7.8855 -7.8026 -7.6243 -6.2888		150-200-250-300C @Psat-H2O]: -4.9163 -3.7834 -2.8267 -2.0032
<i>[reported delG0f used]</i>		<i>extrapolation algorithm: Cp integration</i>
<i>ref-state data</i>		<i>[source: 84lem]</i>
delG0f = -1021.800 kJ/mol		[reported]
delH0f = N/A		
S0PrTr = 80.300 j/(mol*K)		[reported]
Cp coefficients		[source: 84lem units: jou]
T 0 = 0.56392000E+02		
T 1 = 0.53737000E-01		
T -2 = -0.55180000E+06		
Tlimit = 149.85C		

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**NpO<sub>2</sub>(OH)<sub>2</sub>** EQ3/6 = com, alt revised = 18-jul-1986



logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:  
6.6243 5.9851 5.2822 4.9583 4.6907 4.5435 4.5113 4.6004

*[reported delG0f used]* *extrapolation algorithm: Cp integration*  
*ref-state data* *[source: 84lem]*  
delG0f = -1236.000 kj/mol [reported]  
delH0f = N/A  
S0PrTr = 118.000 j/(mol\*K) [reported]  
Cp coefficients [source: 84lem units: jou]  
T 0 = 0.11200000E+03

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**NpO<sub>2</sub>OH(am)** EQ3/6 = com, alt revised = 13-dec-1993



logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:  
4.7783 4.2364 3.6121 3.1432 2.6965 2.3761 2.1779 2.1090

*[reported delG0f used]* *extrapolation algorithm: Cp integration*  
*ref-state data* *[source: 84lem]*  
delG0f = -1128.000 kj/mol [reported]  
delH0f = N/A  
S0PrTr = 101.000 j/(mol\*K) [reported]  
Cp coefficients [source: 84lem units: jou]  
T 0 = 0.86000000E+02

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