Thermodynamic database for actinide aqueous inorganic complexes

E.I. Sergeyeva, O.A. Devina and I.L. Khodakovsky
Vernadsky Institute of Geochemistry and Analytical Chemistry of Russian Academy of Sciences, Moscow (Russian Federation)

Abstract

All available published results of experimental investigations of the solubility, hydrolysis, and complex formation processes occurring in aqueous actinide-bearing systems were collected and analyzed within the framework of the "DiaNIK" database. The results of critical evaluations of the data published before early 1989 were adopted from Fuger *et al.* (J. Fuger, I.L. Khodakovsky, E.I. Sergeyeva, V.A. Medvedev and J.D. Navratil, in V.A. Medvedev, M.H. Rand and E.F. Westrum, Jr., (eds.), *The Chemical Thermodynamics of Actinide Elements and Compounds*, Part 12, *The Actinide Aqueous Inorganic Complexes*, International Atomic Energy Agency, Vienna, 1992). The most reliable experimental values of the equilibrium constants were selected and the values of corresponding thermodynamic constants recommended. In many cases thermodynamic equilibrium constants are not recommended owing to the lack of experimental data or discrepancies between the data available. Probable sources of discrepancies between the experimental data, obtained by various researchers, and the results of thermodynamic calculations are analyzed using examples. The necessity of further studies of the solubility of actinide compounds and refinement of the values of standard entropy of UO_2^{2+}, U^{4+}, and Th^{4+} aqueous ions is substantiated.

1. Introduction

Long-term predictions of the radiological consequences of nuclear reactor accidents and of radionuclide behavior under conditions of nuclear waste disposal require reliable thermodynamic data for the actinide compounds. In connection with this, a thermodynamic database for actinide inorganic species has been initiated within the framework of the "DiaNIK" computer system (Expert Version 3.2) at Vernadsky Institute.

There are comprehensive lists of thermodynamic reference books and databases for actinides and actinide compounds in the IAEA volume, *The Chemical Thermodynamics of Actinide Elements and Compounds*, Part 12 [1], and in the abstract presented (for condensed and gaseous states of those) by Gurvich to the *Actinides-93* international conference [2].

In this study, all sources of data (including computer databases) for the actinide aqueous species available to the authors [1, 3–9] were examined and compared (Table 1).

As can be seen in Table 1 the most recent and comprehensive data source for the actinide aqueous inorganic complexes is Part 12 of the IAEA reference book [1]. The volume is based on a literature survey terminated in early 1989. However, a considerable body of new experimental data has appeared since that time. In some instances these data have cast some doubt on previous data. This might necessitate revising the rec-

ommended data in specific cases. In this connection a start has been made on developing a new database for the actinide aqueous inorganic complexes. In the present paper we describe the database.

2. Previous works

2.1. Available literature data

The reference books and computer databases listed in Table 1 vary from each other not only in the date of preparation, but also in the amount of information and in its completeness. Some of these data sources include thermodynamic data for only one of the actinides (for example Pu [8] and U [9]) and others include data for only gaseous and solid actinide compounds [10, 11]. Among those which include data for actinide aqueous species, the most recent, aside from ref. 1, are the following. The computer program "SOLMINEQ 88" for geochemical modeling of water–rock interactions [7] has a revised thermodynamic database including data for some actinides (inorganic and organic aqueous species and minerals). The database incorporates physical parameters of aqueous species and equilibrium constants of dissociation, dissolution and redox reactions at nine temperatures from 0 to 350 °C. Reference 10, "Thermodynamic data for reactor materials and fission products", includes critically assessed thermodynamic data for actinide elements (only for Am, Pu, U) and

TABLE 1. Thermodynamic reference books and databases for actinide aqueous species

Year	Number of species	Number of references	Authors (Actinides)	Reference
1971	36	37	Naumov et al. (Th, U)	3
1976	30	193	Fuger and Oetting (Ac, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No)	4
1981	355	–	Wagman et al. (Ac, Th, Pa, U)	5
1982	472		Khodakovsky et al. (Ac, Th, Pa, U, Np, Pu Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md)	6
1988	44	16	Kharaka et al. (U)	7
1991	40	51	Puigdomenech and Bruno (Pu)	8
1992	292	860	Grenthe et al. (U)	9
1992	506	865	Fuger et al. (Ac, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md)	1
1993	145	500	Sergeyeva et al. (Ac, Th, Pa, U, Np, Pu, Am)	Our database

for some of their solid and gaseous compounds. The selection of recommended values is fully substantiated and updated.

In the former USSR an effort was made by the Akademia Nauk (Academy of Sciences) to produce a consistent set of thermodynamic tables of various chemical systems including the actinides [6]. The volumes contain data for solid and gaseous actinide compounds and for actinide aqueous species. However, some of the recommended values are now out of date and need to be revised.

The plutonium database of Puigdomenech and Bruno [8] includes data for aqueous and solid hydroxides, carbonates and phosphates. The authors state that their database is essentially that of Lemire and Tremaine [12], with changes introduced by Lemire and Garisto [13] and modifications by the authors themselves. The database of Puigdomenech and Bruno [8] consists of thermodynamic quantities (Gibbs free energies of formation, standard enthalpies of formation, standard entropies, heat capacities, etc.) and equilibrium constants as a function of temperature. The database includes estimated values for some Pu species (*e.g.* for $PuCO_3^+$).

In connection with the needs for nuclear production arising in the former USSR, in the late 1940s and 1950s a start was made in the study of the chemistry of actinides. The investigations headed by A.D. Gel'man were carried out at the Institute of Physical Chemistry of USSR Academy of Sciences. The results of these studies are summarized in later monographs [14, 15].

Preceded in Russia by the studies of R.P. Rafal'sky [19], the first attempts at Vernadsky Institute to obtain thermodynamic data characterizing the aqueous uranium system at elevated temperature were made about 30 years ago at the Laboratory of Uranium Geochemistry, headed successively by V.V. Scherbina, A.I. Tugarinov and G.B. Naumov. The pioneer investigators of this problem at the Laboratory were G.B. Naumov and O.F. Mironova (1960–1965) [20, 21]. Later the studies were continued in the Laboratory of Thermodynamics of Natural Processes, headed by I.L. Khodakovsky.

Starting in 1965, experimental work was in progress at the laboratories to determine the thermodynamic constants for uranium and thorium equilibria and compounds in a certain temperature range. Solubility measurements were performed for $UO_2(OH)_2(cr)$ and $UO_2CO_3(cr)$ at 298–473 K by Naumov and coworkers [20–23], for $ThO_2(cr)$* at 390–323 K by Zhidikova and Khodakovsky [24], and for $UO_2(cr)$ at 573–873 K by Khodakovsky et al. in cooperation with Red'kin and Ivanov (Institute of Experimental Mineralogy, Russian Academy of Sciences) and Omel'yanenko (Institute of Geology, Ore Deposits, Petrography, Mineralogy and Geochemistry, Russian Academy of Sciences) [25]. The data were used to calculate equilibrium constants for a number of reactions which occur in the systems UO_3–H_2O, ThO_2–H_2O, $UO_3(cr)$–$CO_2(g)$–$H_2O(l)$, and $UO_2(cr)$–$H_2O(ag)$–$HCl(ag)$ in the temperature range studied. The thermodynamic parameters ($\Delta_f H^0_{298.15}$, $\Delta_f G^0_{298.15}$, and $S^0_{298.15}$) of the species formed in the

2.2. Studies at Vernadsky Institute

At Vernadsky Institute studies (of U, Pu, Pa and some other actinides) were performed under the supervision of A.P. Vinogradov and P.N. Paley [16, 17]. Later the investigations at Vernadsky Institute were headed by B.F. Myasoedov [18].

---

*There were misprints in ref. 24. The values of equilibrium constants for the reactions $ThO_2(cr) + H^+(ao) + H_2O(l) = Th(OH)_3^+(ao)$ (1), $ThO_2(cr) + 2H_2O(l) = Th(OH)_4^0(ao)$ (2), and $Th(OH)_3^+(ao) + H_2O(l) = Th(OH)_4(ao) + H^+(ao)$ (3), should be negative as follows: lg $K_1^0 = -3.30 \pm 0.07$, lg $K_2^0 = -6.66 \pm 0.06$, lg $K_3^0 = -3.36$.

systems were calculated where this was possible. Thermodynamic properties of the uranyl ion in aqueous solution at elevated temperatures were determined by Devina and Khodakovsky in collaboration with Medvedev and Efimov (Institute for High Temperatures, Russian Academy of Sciences) [26] making use of calorimetric measurements of solution enthalpy at 288–318 K. Based on the calorimetric results and literature data, the values of $\Delta_f H^0$, C_p^0, S^0 and $\Delta_f G^0$, for the aqueous uranyl ion have been calculated in the range 298–573 K.

The system UO_3–H_2O–CO_2 was also studied using spectrophotometric and calorimetric methods [27–29]. The enthalpy of formation of $UO_2(CO_3)_3^{4-}$(ao) and the dependence on temperature of its stability constant (in the range 298–473 K) were determined by Devina and Khodakovsky (in collaboration with Efimov and Medvedev) from their measurements of dissolution enthalpy [27]. The third stepwise formation constant of $UO_2(CO_3)_3^{4-}$(ao) was measured spectrophotometrically in the range 298–353 K by Sergeyeva and Khodakovsky (in collaboration with Zotov (Institute of Geology, Ore Deposits, Petrography, Mineralogy and Geochemistry, Russian Academy of Sciences)) [30]. The low temperature heat capacities of UO_2CO_3(cr) and α-$UO_2(OH)_2$(cr) were measured by Gurevich, Sergeyeva and Khodakovsky (in collaboration with Gorbunov and Gavrichev (Kurnakov Institute of General and Inorganic Chemistry of Russian Academy of Sciences)) [28, 29]. In addition to these experimental studies, expert work on collecting, analyzing and evaluating thermodynamic data existing in the literature was initiated at the laboratory. All the results of this experimental and expert work were summarized in the report "Thermochemistry" (1976) [31], and incorporated into refs. 1, 3 and 6 as well. These studies were also used as the basis for the actinide thermodynamic database within the framework of DiaNIK.

3. Database description

3.1. Literature data

An attempt was made to cover the complete actinide equilibrium constant literature up to early 1993, but no guarantee can be made that every single published work has been recorded. The actinide thermodynamic database includes all the data of ref. 1 on the actinide hydrolysis constants and stability constants of the actinide aqueous inorganic complexes, supplemented, revised and modified taking into account experimental data published since early 1989.

Only experimental results are used in the database; estimates as well as recalculated data are ignored. Equilibrium constants are considered as a function of ionic strength and temperature.

All available published results of experimental studies of the solubility, hydrolysis and complex formation processes occurring in aqueous actinide-bearing systems were collected and analyzed. The results obtained by various methods were compared. The most reliable experimental values of the equilibrium (dissolution, hydrolysis and complex formation) constants were selected.

3.2. Selection criteria

Selection criteria for recommended values coincide with those used in ref. 1 and were the following:

reliability of the experimental method for determination of the concentration of reactants in systems;

achievement of a real equilibrium, especially when the solubilities were measured;

accuracy of the experimental measurements and full description of details of the experimental technique in the publications;

all the equilibria in the system taken into account;

method of calculation of the equilibrium constants;

reliability of all additional values used in calculations;

accuracy of the recalculation of stoichiometric constants to zero ionic strength.

In addition, where there is numerical agreement among a sufficient number of independent studies, this is used as a criterion for data selection.

3.3. Methods of calculation of thermodynamic equilibrium constants

Based on the selected data, consistent values of corresponding thermodynamic constants were calculated and recommended for reactions with aqueous actinide-bearing species at 298 K.

To determine the thermodynamic equilibrium constants one extrapolates to infinite dilution the stoichiometric constants measured in solutions with definite ionic strength. These estimates are based on the use of extended Debye–Huckel equations of various forms. The methods preferred in the DiaNIK database are in form of either the Guggenheim equation or the Vasil'ev, Harned and Pitzer approaches. These methods are used when constants are measured at several values of ionic strength. The recommended constants presented in the database were calculated using the Guggenheim equation. If the equilibrium constant is measured at a single value of ionic strength, the Davies equation is used for the extrapolation. The difference in the values obtained by extrapolation using the Guggenheim equation and Vasil'ev's, Harned's and Pitzer's equations was taken into account when the uncertainties of the recommended values were estimated.

These estimates are demonstrated in Table 2, where the results of our calculations of thermodynamic equilibrium constants of hydrolysis and complex formation

TABLE 2. Extrapolation to $I=0$ of the experimental data for the reactions

Reaction (with references from which the data are taken for calculations)	lg K^0	Method of extrapolation
$UO_2^{2+} + Cl^-$	0.16 ± 0.03	1
$= UO_2Cl^+$ [12–15]	0.27 ± 0.03	2
	0.21 ± 0.03	3
	0.32 ± 0.03	4
Selected value	0.27 ± 0.15	
	0.17 ± 0.02	5
$UO_2^{2+} + HF$	1.84 ± 0.05	1
$= UO_2F^+ + H^+$ [13, 16, 17]	1.88 ± 0.05	2
	1.86 ± 0.05	3
	1.90 ± 0.05	4
Selected value	1.88 ± 0.06	
	1.84 ± 0.06	5
$3UO_2^{2+} + 5H_2O(l)$	-15.58 ± 0.04	1
$= (UO_2)_3(OH)_5^+ + 5H^+$ [18–31]	-15.44 ± 0.04	2
	-15.52 ± 0.04	3
	-15.37 ± 0.04	4
Selected value	-15.44 ± 0.21	
	-15.55 ± 0.12	5
$NpO_2^+ + CO_3^{2-}$	4.63 ± 0.15	1
$= NpO_2CO_3^-$ [10, 32–35]	4.70 ± 0.15	2
	4.66 ± 0.15	3
	4.72 ± 0.15	4
Selected value	4.70 ± 0.19	
	4.69 ± 0.13	5a

1–4, our estimates, using 1 Vasil'ev's, 2 Guggenheim's, 3 Harned's, 4 Pitzer's equations; 5, estimate using the specific ion interaction theory [11] of ref. 9, and 5a of ref. 10.

of uranium and neptunium are compared with those of Grenthe et al. [9] (for UO_2^{2+}(ao)) and Nitsche and Standifer [32] (for NpO_2^+(ao)).

As may be seen in Table 2, the divergence between the results of various extrapolations are sometimes rather large, which certainly should be considered when estimating the uncertainties of the selected equilibrium constants.

3.4. The database content

The computer database DiaNIK was developed at Vernadsky Institute of Geochemistry and Analytical Chemistry and Institute of Experimental Mineralogy of Russian Academy of Sciences. DiaNIK is an interactive research information system of chemical thermodynamic data for minerals and mineral-forming substances. The structure of the thermodynamic database DiaNIK is based on the principles developed by CODATA, the International Group on Geothermodynamic Data, for working out thermodynamic information. The accepted structure allows use of the consistency procedure both for the individual substance or the individual chemical reaction (local consistency), and for chemical

systems containing a set of substances and reactions (global consistency). The core code of the DiaNIK system supports the work of separate blocks, which can provide different opportunities and alternatives for the user. At present successive local consistency procedures are used for treatment of thermodynamic data in the database.

A substantial portion of the thermodynamic values recommended by the DiaNIK experts, for the substances in the User Version 3.1, resulted from analysis of the literature data, using the original algorithms of the Expert Version 3.1.

All values accepted in the DiaNIK database are consistent with the CODATA key-values and IUPAC recommended values. Updating the database and improvements are performed annually.

The actinide database (expert version) consists of the following:

files of the primary experimental data on equilibrium constants of actinide hydrolysis, complex formation with inorganic anions CO_3^{2-}, SO_4^{2-}, PO_4^{3-}, and dissolution, total of 585 files (about 400 kB);

catalogue of the reactions studied experimentally in actinide aqueous systems (about 27 kB);

commentary files, substantiated the selection of the data, total of 46 files (about 100 kB);

program codes and files of extrapolation of the equilibrium constants to infinite dilution;

reference file;

selected data summarized in a catalogue of the reactions.

Our work on preparing the database is in now progress. It is planned in 1994 to include equilibrium constants for the dissolution and complex formation reactions in the following systems: actinides (U, Pu, Np etc.)–F^-–Cl^-–H_2O, actinides–CH_3COO^-–H_2O, and actinides–$C_2O_4^{2-}$–H_2O.

4. Discussion

In a number of cases the thermodynamic equilibrium constants have not been selected owing to the lack of experimental data or discrepancies between the data.

4.1. Probable sources of discrepancies

Probable sources of discrepancies between the experimental data, obtained by various researchers, should be taken into account during the data selection procedure.

The validity of experimental data (for instance the radionuclide compound solubility) is controlled by a series of factors. Among these the following should be considered primarily:

achievement of equilibrium in the studied system;

existence of ions in the system which are capable of complex formation with the cation of the solids (bottom phase);

existence of reducing or oxidizing species in the system (if containing solids with an element of variable valency);

method of separation of solid from the solution before analysis;

degree of dispersion of the solid;

influence of radioactivity (radiolysis, metamict phenomena, etc.).

Discrepancies between the experimental data obtained by various researchers may be determined by these factors. Other sources of discrepancies are the methods of extrapolation of experimental values of equilibrium constants to infinite dilution (Table 2) which are discussed above (Section 3.3).

Specific examples of the effect of some of these factors, which are the most significant for actinides, are considered elsewhere [9, 22, 23, 25, 45, 58].

Recent data obtained by Torrero et al. [59] most clearly demonstrate the influence of ionic medium on the solubility of crystalline UO_2: at pH < 4 the UO_2 solubility in chloride media (in 1 M NaCl and 5 M NaCl) is higher than that in perchlorate medium, and it does not depend on pH. This led the authors to suggest that U(IV)–OH–Cl complexes could be present in solutions. This suggestion seems realistic because our experimental studies of the UO_2(cr) solubility at 300–600 °C and $P = 1$ kbar [25] led us to the conclusion that in aqueous HCl media equilibrated with UO_2(cr), $U(OH)_3Cl$(ao) predominated:

$$UO_2(cr) + HCl(ao) + H_2O(l) = U(OH)_3Cl(ao)$$
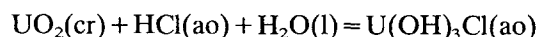
4.2. General remarks

The literature data analysis carried out while preparing our database permitted us to revise some of the recommendations of the IAEA volume [1]. Some of the selected values which differ from those of ref. 1 are summarized in Table 3. Based on the data analysis, the following can be noted.

(i) The uranium system has been studied experimentally more than those of plutonium and other actinides. The uranium systems have been studied experimentally by a number of authors and over a wide temperature range (283–873 K), whereas those of plutonium and other actinides have been studied mainly at 298 K.

(ii) In aqueous phase both uranium and other actinides have a tendency to hydrolysis and the formation of rather strong complexes with oxygen-containing ligands, found in natural waters. These include carbonate, sulfate, and phosphate.

TABLE 3. Selected values for actinide hydrolysis constants and stability constants of aqueous inorganic complexes at 298.15 K, 1 bar, and at infinite dilution

Reaction	lg K^0
Uranium	
$U^{4+} + H_2O(l) = UOH^{3+} + H^+$	-0.4 ± 0.2
$U^{4+} + 3H_2O(l) = U(OH)_3^+ + 3H^+$	NR
$U^{4+} + 4H_2O(l) = U(OH)_4^0 + 4H^+$	NR
$UO_2^{2+} + H_2O(l) = UO_2(OH)^+ + H^+$	-5.8 ± 0.1
$UO_2^{2+} + 3H_2O(l) = UO_2(OH)_3^- + 3H^+$	-19.7 ± 0.5
$3UO_2^{2+} + 5H_2O(l) = (UO_2)_3(OH)_5^+ + 5H^+$	-15.4 ± 0.1
$3UO_2^{2+} + 7H_2O(l) = (UO_2)_3(OH)_7^- + 7H^+$	-31.9 ± 0.8
$UO_2^{2+} + HPO_4^{2-} = UO_2HPO_4^0$	7.1 ± 0.2
$UO_2^{2+} + PO_4^{3-} = UO_2PO_4^-$	12.9 ± 0.3
Neptunium	
$NpO_2^+ + H_2O(l) = NpO_2OH^0 + H^+$	-9.0 ± 0.3
$NpO_2^+ + CO_3^{2-} = NpO_2CO_3^-$	4.7 ± 0.2
$NpO_2^+ + 2CO_3^{2-} = NpO_2(CO_3)_2^{3-}$	6.7 ± 0.4
Plutonium	
$Pu^{3+} + SO_4^{2-} = PuSO_4^+$	4.5 ± 0.5
$Pu^{3+} + 2SO_4^{2-} = Pu(SO_4)_2^-$	6.7 ± 0.6
$Pu^{4+} + HSO_4^- = PuSO_4^{2+} + H^+$	5.5 ± 0.5
$Pu^{4+} + 2HSO_4^- = Pu(SO_4)_2^0 + 2H^+$	7.7 ± 0.7
Americium	
$Am^{3+} + SO_4^{2-} = AmSO_4^+$	4.2 ± 0.4
$Am^{3+} + 2SO_4^{2-} = Am(SO_4)_2^-$	6.1 ± 0.5

NR not recommended.

(iii) Uranium is the most important "key" element for actinide thermochemistry, because many of the estimated values of standard entropies of actinide compounds are based on corresponding values for the uranium aqueous species. In turn, the thermodynamic values accepted for the aqueous uranyl ion are key values for uranium chemical thermodynamics. The Gibbs formation energies and entropies of all the uranium aqueous compounds and also of some of the uranium crystalline compounds are based on the values for aqueous UO_2^{2+}.

Recently O'Hare et al. [60] identified appreciable differences (of nearly an order of magnitude) in the values of the solubility product of $UO_2(OH)_2 \cdot H_2O$ (cr, schoepite). One value is calculated from thermochemical data and the other is obtained from the results of solubility measurements: lg $K_{so} = 4.77 \pm 0.23$ [60] and lg $K_{so} = 5.9 \pm 0.1$ [45].

Bruno and Sandino [45, 58] supported this conclusion with new experimental measurements of the solubility product of schoepite.

The cause of the divergence may be an error in the thermodynamic values of uranyl hydroxide $[UO_2(OH)_2(cr)]$ or in those of the uranyl ion. As has been shown by analysis of the experimental data from

thermochemistry and equilibrium measurements in the UO_3–H_2O system [61], the thermodynamic values of uranyl hydroxide, $UO_2(OH)_2 \cdot H_2O$, agree well with those for other solids in the system UO_3–H_2O.

Since the CODATA recommended value of formation enthalpy of the UO_2^{2+} ion is accepted, there is a possibility that the CODATA recommended standard entropy value of the uranyl ion has a systematic error. That assumption is confirmed by calculations of standard entropies of the uranyl ion using thermodynamic information for reactions in the systems UO_3–CO_2–H_2O and UO_3–SO_3–H_2O [61].

It should be emphasized particularly that if the recommended entropy and Gibbs free energy values for the UO_2^{2+} ion are really erroneous, then the values of thermodynamic properties of many U(IV, VI) aqueous compounds should be revised. Also, the thermodynamic values of many aqueous Pu(IV, VI) and other actinide compounds, which were estimated based on corresponding values for U(IV, VI), should be revised.

All results used for the calculation of the value $S^0_{298.15}UO_2^{2+}(ao)$ are summarized in Table 4.

All three new independent routes used for calculations of the standard entropy of the uranyl ion show the obvious systematic difference between CODATA [62] and NEA-TDB [9] recommendations, both of which are based on data for reaction (1), see Table 4.

The resulting discrepancies are very large. For the equilibrium constant of solubility of the uranyl-bearing compound at 298.15 K they correspond to an order of magnitude difference.

Various explanations of this phenomenon have been proposed by different investigators.

(1) "the disagreement may reflect, inter alia, the difficulty of achieving equilibrium between sparingly soluble compounds and the aqueous solution" [60].

(2) The difference between the solubility product obtained by calorimetric measurements and that obtained directly from solubility measurements "can be interpreted as a result of surface tension effects" [45].

(3) "The assumption, that the entropy of $UO_2(NO_3)_2 \cdot 6H_2O(cr)$ at 0.0 K is equal to zero, is

erroneous as it is known, the zero point (K) entropies of $Na_2CO_3 \cdot 10H_2O(cr)$ and $Na_2HPO_4 \cdot 12H_2O(cr)$ differ from zero" [61].

From our point of view, we lack evidence to explain clearly the discrepancies and to come to a final resolution of the problem.

As can be seen from Table 4 the value calculated for reaction (4) has a large uncertainty. This requires further investigation. The key measurements needed are low heat-capacity measurements for $UO_2SO_4(cr)$ and $UO_2SO_4 \cdot 2.5H_2O(cr)$ as well as measurements of the enthalpy of solution of these compounds in pure water and perchloric acid solutions.

Thus, analysis of the data has enabled us to determine areas where new experimental data are needed: the necessity of further and more careful studies of the solubility of actinide compounds ($ThO_2(cr)$, $UO_2(cr)$, $PuO_2(cr)$) over a wide temperature range and refinement of the values of standard entropy of UO_2^{2+} and U^{4+}, and Th^{4+} aqueous ions follows from the data analysis carried out within the framework of DiaNIK.

References

1 J. Fuger, I.L. Khodakovsky, E.I. Sergeyeva, V.A. Medvedev and J.D. Navratil, in V.A. Medvedev, M.H. Rand and E.F. Westrum, Jr., (eds.), The Chemical Thermodynamics of Actinide Elements and Compounds, Part 12, The Actinide Aqueous Inorganic Complexes, International Atomic Energy Agency, Vienna, 1992.

2 L.V. Gurvich, Proc. Int. Conf. Actinides-93, Santa Fe, NM, September 1993, 1993, Abs. of oral presentations, 41.

3 G.B. Naumov, B.N. Ryzhenko and I.L. Khodakovsky, in A.I. Tugarinov (ed.), Handbook of Thermodynamic Data, Atom-izdat, Moscow, 1971 (in Russian). Translated into English: G.B. Naumov, B.N. Ryzhenko, I.L. Khodakovsky, in G.J. Soleimani, I. Barnes and V. Speltz (eds.), Handbook of Thermodynamic Data, Rep. WRD-74-01, 1974 (US Geological Survey, Menlo Park, CA).

4 J. Fuger and F.R. Oetting, in V.A. Medvedev, M.H. Rand and E.F. Westrum, Jr., (eds.), The Chemical Thermodynamics of Actinide Elements and Compounds, Part 2, The Actinide Aqueous Ions, International Atomic Energy Agency, Vienna, 1976.

5 D.D. Wagman, W.H. Evans, V.B. Parker, R.H. Schumm and R.L. Nuttall, Selected values of chemical thermodynamic properties: compounds of uranium, protactinium, thorium, actinium, and the alkali metals, NBS Technical Note 270-8, May 1981, US Government printing office.

6 I.L. Khodakovsky, V.A. Medvedev, A.F. Vorob'ev, A.P. Zhi-dikova, O.A. Devina, I.A. Lebedev, S.Ya. Vasina, V.M. Ger-ovich and E.I. Sergeyeva, in V.P. Glushko (ed.), Thermal Constants of the Substances, Vols. VIII–X, AN SSSR, Viniti, Moscow, 1978–1982 (in Russian).

7 Y.K. Kharaka, W.D. Gunter, P.K. Aggarwal, E.H. Perkins and J.D. DeBraal, SOLMINEQ. 88: A Computer Program for Geochemical Modeling of Water–Rock Interactions, US Geological Survey (Report 89-616), Menlo Park, CA, 1988.

TABLE 4. Summary of the aqueous uranyl ion entropy evaluations

No.	Reaction	$S^0_{298.15}UO_2^{2+}(ao)$
1	$UO_2(NO_3)_2 \cdot 6H_2O(cr)$ $= UO_2^{2+} + 2NO_3^- + 6H_2O(l)$	-98.2 ± 3.0
2	$UO_2(OH)_2 \cdot H_2O(cr) + 2H^+$ $= UO_2^{2+} + 3H_2O(l)$	-77.3 ± 3.0
3	$UO_2CO_3(cr) = UO_2^{2+} + CO_3^{2-}$	-71 ± 10
4	$UO_2SO_4 \cdot 2.5H_2O(cr)$ $= UO_2^{2+} + SO_4^{2-} + 2.5H_2O(l)$	-77 ± 15

8 I. Puigdomenech and J. Bruno, *Plutonium solubility, SKB Tech. Rep. 91-04*, 1991 (Swedish Nuclear Fuel and Waste Management Co, Stockholm).

9 I. Grenthe, J. Fuger, R.J.M. Konings, R.J. Lemire, A.B. Muller, C. Nguyen-Trung and H. Wanner, in H. Wanner and J. Forest (eds.), *Chemical Thermodynamics of Uranium*, North-Holland, Amsterdam, 1992.

10 E.H.P. Cordfunke, R.J.M. Konings, P.E. Potter, G. Prins and M.H. Rand, in E.H.P. Cordfunke and R.J.M. Konings (eds.), *Thermochemical Data for Reactor Materials and Fission Products*, North-Holland, Amsterdam, 1990.

11 L.V. Gurvich, I.V. Veyts, V.A. Medvedev *et al.*, in V.P. Glushko (ed.), *Thermodynamic Properties of the Individual Substances*, Vol. 4 (second book), Nauka, Moscow, 1982.

12 R.J. Lemire and P.R. Tremain, *J. Chem. Eng. Data*, 25 (1980) 361.

13 R.J. Lemire and F. Garisto, *Atomic Energy of Canada Ltd.*, Whiteshell Nucl. Res. Estbl., Pinawa, Manitoba ROE 1LO, AECL-10009, 1989, p. 123.

14 A.D. Gel'man, A.I. Moskvin, L.M. Zaitsev and M.P. Mefod'eva, *Complex Compounds of the Transuranium Elements*, Izd. AN SSSR, Moscow, 1961 (in Russian).

15 A.P. Moskvin, *Coordination Chemistry of Actinides*, Atomizdat, Moscow, 1975 (in Russian).

16 P.N. Paley, *Zh. Analyt. Khim.*, 12 (1957) 647 (in Russian).

17 M.S. Milyukova, N.I. Gusev, I.G. Sentyurin and I.S. Sklyarenko, in P.N. Paley (ed.), *Analytical Chemistry and Plutonium*, Nauka, Moscow, 1965 (in Russian).

18 B.F. Myasoedov, L.I. Guseva, I.A. Lebedev, M.S. Milyukova and M.K. Chmutova, *Analytical Chemistry of the Transplutonium Elements*, Nauka, Moscow, 1972 (in Russian).

19 R.P. Rafal'sky, *Physico-Chemical Investigation of Conditions of the Uranium Ore Formation*, Gosatomizgat, Moscow, 1963 (in Russian).

20 G.B. Naumov and O.F. Mironova, *Geokhimiya, N3* (1960) 241 (in Russian).

21 G.B. Naumov and O.F. Mironova, in N.I. Khitarov (ed.), *Problems of Geochemistry*, Nauka, Moscow, 1965, p. 158 (in Russian).

22 A.A. Nikitin, E.I. Sergeyeva, I.L. Khodakovsky and G.B. Naumov, *Geokhimiya* (1972) 297. Translated into English, *Geochem. Int.*, 9 (1972) 301.

23 E.I. Sergeyeva, A.A. Nikitin, I.L. Khodakovsky and G.B. Naumov, *Geokhimiya* (1972) 1340. Translated into English, *Geochem. Int.*, 9 (1972) 900.

24 A.P. Zhidikova, G.M. Kolesov and I.L. Khodakovsky, *Geokhimiya* (1980) 821 (in Russian).

25 A.F. Red'kin, N.I. Savelyeva, E.I. Sergeyeva, B.I. Omelyanenko, I.P. Ivanov and I.L. Khodakovsky, *Sci. Geol. Bull. Strasbourg*, 42 (1989) 329.

26 O.A. Devina, M.E. Efimov, V.A. Medvedev and I.L. Khodakovsky, *Geokhimiya* (1982) 1454. Translated into English, *Geochem. Int.*, 19 (1982) 161.

27 O.A. Devina, M.E. Efimov, V.A. Medvedev and I.L. Khodakovsky, *Geokhimiya* (1983) 677. Translated into English, *Geochem. Int.*, 20 (1983) 10.

28 V.M. Gurevich, E.I. Sergeyeva, K.S. Gavrichev, V.E. Gorbunov and I.L. Khodakovsky, *Zh. Fiz. Khim.*, 61 (1987) 1643 (in Russian).

29 E.I. Sergeyeva, O.A. Devina, K.S. Gavrichev, V.E. Gorbunov, V.M. Gurevich, M.E. Efimov, V.A. Medvedev and I.L. Khodakovsky, in B.N. Laskorin and B.F. Myasoedov (eds.), *Chemistry of Uranium*, Nauka, Moscow, 1989, p. 36 (in Russian).

30 E.I. Sergeyeva, A.V. Zotov and I.L. Khodakovsky, *Proc. IUPAC Conf. Chem. Thermodynamics and 39 Calorimetry Conf., Hamilton, Canada, August 1984*, 1984, p. 203.

31 O.A. Devina, V.A. Dorofeeva, A.P. Zhidikova, G.B. Naumov, A.A. Nikitin, E.I. Sergeyeva and I.L. Khodakovsky, *Thermokhimiya*, Report, Vernadsky Institute, Moscow, 1976 (in Russian).

32 H. Nitsche and E.M. Standifer, *Radiochim. Acta*, 46 (1989) 185.

33 G. Scatchard, *Chem. Rev.*, 19 (1936) 309.

34 S. Ahrland, *Acta Chem. Scand.*, 5 (1951) 1151.

35 E.W. Davies and C.B. Monk, *Trans. Faraday Soc.*, 53 (1957) 442.

36 L. Bernarczyk and I. Fidelis, *J. Radioanal. Chem.*, 45 (1978) 325.

37 S.P. Awasthi and M. Sundaresan, *Indian J. Chem.*, 20A (1981) 378.

38 V.N. Krylov, E.V. Komarov and M.F. Puchlenkov, *Radiokhimiya*, 10 (1968) 708.

39 S.K. Patil and V.V. Ramakrishna, *J. Inorg. Nucl. Chem.*, 38 (1976) 1075.

40 K. Schlyter and K. Tekn, *Hogskol. Handl.*, 195 (1962) 21.

41 R.M. Rush and J.C. Johnson, *J. Phys. Chem.*, 67 (1963) 821.

42 L. Ciavatta, D. Ferri, M. Grimaldi, R. Palombari and F. Salvatore, *J. Inorg. Nucl. Chem.*, 41 (1979) 1175.

43 A. Vainiotalo and O. Makitie, *Finn. Chem. Lett.*, (1981) 102.

44 L. Maya, *Inorg. Chem.*, 21 (1982) 2895.

45 A. Sandino and J. Bruno, *Geochim. Cosmochim. Acta*, 56 (1992) 4135.

46 S. Ahrland, *Acta Chem. Scand.*, 3 (1949) 374.

47 H.S. Dunsmore, S. Hietanen and L.G. Sillen, *Acta Chem. Scand.*, 17 (1963) 2644.

48 S. Hietanen, B.R.L. Row and L.G. Sillen, *Acta Chem. Scand.*, 17 (1963) 2735.

49 R. Arnek and K. Schlyter, *Acta Chem. Scand.*, 22 (1968) 1331.

50 G. Ostacoli, E. Campi and M.C. Gennaro, *Gaz. Chim. Ital.*, 98 (1968) 301.

51 C. Tsymbal, *PhD dissertation*, Université de Grenoble, Grenoble, CEA-R-3479, 1969.

52 M. Maeda, T. Amaya, H. Ohtaki and H. Kakihana, *Bull. Chem. Soc. Jpn.*, 45 (1972) 2464.

53 L.H.J. Lajunen and S. Parhi, *Finn. Chem. Lett.*, (1979) 143.

54 L. Maya, *Inorg. Chem.*, 22 (1983) 2093.

55 G. Bidoglio, G. Tanet and A. Chatt, *Radiochim. Acta*, 38 (1985) 21.

56 Y. Inoye and O. Tochiyama, *Bull. Chem. Soc. Jpn.*, 58 (1985) 588.

57 C. Riglet, *Thèse de Doctorat*, Université Paris 6, March 17, 1989 (quoted in ref. 31).

58 A.A. Nikitin, E.I. Sergeeva, I.L. Khodakovsky and G.B. Naumov, *Geokhimiya* (1972) 297. Translated into English: *Geochem. Int.*, 9 (1972) 301.

59 E.I. Sergeeva, A.A. Nikitin, I.L. Khodakovsky and G.B. Naumov, *Geokhimiya* (1972) 1340. Translated into English: *Geochem. Int.*, 9 (1972) 900.

60 A.F. Red'kin, N.I. Savelyeva, E.I. Sergeyeva, B.I. Omelyanenko, I.P. Ivanov and I.L. Khodakovsky, *Sci. Geol. Bull. Strasbourg*, 42 (1989) 329.

61 P.A.G. O'Hare, B.M. Lewis and S.N. Nguyen, *J. Chem. Thermodyn.*, 20 (1988) 1287.

62 I.L. Khodakovsky, *Abstracts of the 12th IUPAC Conf. on Chemical Thermodynamics and of the 47th Annual Calorimetry Conf., Snowbird, UT, August 1992*, 1992, p. 157.

63 J.D. Cox, D.D. Wagman and V.A. Medvedev (eds.), *CODATA Key Values for Thermodynamics*, Hemisphere, 1989.