TDB-2

GUIDELINES FOR THE EXTRAPOLATION TO ZERO IONIC STRENGTH

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Version of 18 June 2013

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Contents

Guidelines for the Extrapolation to Zero Ionic Strength

1 Purpose of this Guideline

The objective of this guideline is to describe the scientific basis and illustrate the standard procedure in the NEA TDB Project for the extrapolation and correction of equilibrium data to the infinite dilution standard state. This procedure is known as the SIT approach (Specific Ion Interaction Theory) and is derived from the Brønsted-Guggenheim-Scatchard specific ion interaction method. This method has been chosen because of its robustness in analysing experimental data from diverse sources, its capacity to provide good estimates of activity coefficients, its simplicity of use and the possibility, by using charge/ion size correlations, to estimate unknown values for its parameters, the so-called ion interaction coefficients.

In addition, this guideline describes other methods of extrapolation to zero ionic strength commonly encountered in the literature and gives arguments to justify the method preferred in the NEA TDB Reviews.

Recommended values of the SIT parameters stemming from the literature and the previous TDB Reviews are also given in Tables.

Members of the NEA TDB teams performing the review are requested to adhere to the procedure specified in this Guideline, thus contributing to preserve the consistency of the NEA Thermochemical Database.

2 Background to the problem

The compilation of a database including aqueous species is invariably related to activity coefficient calculations, since it is generally impossible to study equilibria in standard state conditions (*i.e.*, at unit concentrations and zero interactions between dissolved species). In general, equilibrium constants are determined at a constant value of ionic strength, decided by the experimentalist and related to the complexity of the system to be studied. The equilibrium constants thus determined are conditional constants, *i.e.* valid only for the conditions in which they have been determined.

Complex formation, redox or solubility equilibrium studies are based on the determination of the *activity* of the ligand, the free metal ion or of the complexes formed in test solutions of known total concentrations, as well as *mass-balance* equations for these components. In order to use the former in combination with the latter, it is necessary to have information on the activity coefficients of reactants and products. In addition, one needs experimental information of one or more of the free concentrations of these species. As thermodynamic data are based on *activities* it is necessary to find methods that relate concentrations and activities – this is the key issue discussed in the present text. These methods include among others: ion selective electrodes, redox electrodes, measurements in two-phase systems and spectrophotometric techniques of various types.

The aim of the experimental studies is the simultaneous determination of the complexes formed (chemical model) and their stability constants. Calculation methods are based on the comparison of the experimental data with a pertinent chemical model, through graphical methods and/or computer programs. The *ionic medium method* is the most common method to relate concentrations and activities. According to this method, precise thermodynamic information for a given system can be obtained in the presence of an inert electrolyte (the *ionic medium*) of sufficiently high concentration (0.5 to 4 mol·L^{-1}, much higher than that of reactants and products in the reaction studied), in order to ensure that activity coefficients of the reacting species remain reasonably constant during the measurements. As shown in Section 2.1, it is practical to define a *conditional* standard state, where the activity coefficients of reactants and products are unity *in the selected ionic medium*. These data must then be recalculated to the common standard state in a pure water solvent.

The TDB reviewers cope with the issue of extrapolating data obtained in different ionic media to the standard state of zero interactions (infinite dilute aqueous solution) using methods briefly described in the following.

2.1   Ion interaction and ion association approaches

Thermodynamic data always refer to a selected standard state. The definition given by IUPAC [1982LAF] is adopted in the NEA TDB project as outlined in the TDB-5 guideline [2000WAN/OST2]. According to this definition, the standard state for a solute B in a water solution is a hypothetical solution, at the standard state pressure, in which $m_B = m^o = 1$ mol·kg^{-1}, and the activity coefficient γ_B is that at infinite dilution (unity). However, as stated in the preceding paragraphs, for

many reactions, measurements cannot be made accurately (or at all) in dilute solutions from which the necessary extrapolation to the standard state would be simple.

Mean activity coefficients for pure electrolytes can be determined experimentally, but this is not the case for metal-ligand systems where in general several complexes are present, the relative amounts of which vary depending on the total ligand and ionic medium concentrations. Currently, all practical methods for the estimation of activity coefficients in such systems are semi-empirical (that is to say, although they are plausible based on current electrolyte theories, their practical use involves parameters whose numerical value cannot be determined without recourse to experimental measurements).

Several methods have been developed to describe mean activity coefficients (and single-ion activity coefficients) both for single and mixed electrolyte systems and these will be discussed in the following section. However, the focus will be on systems where complex formation occurs, which have been studied experimentally using the ionic medium method. For a detailed discussion of these, see Chapter IX at the NEA TDB Project publication "Modelling in aquatic chemistry" [1997ALL/BAN]. Two of them are frequently encountered and each of them in various formulations[1]:

All thermodynamic discussions require a detailed specification of the system under scrutiny, such as temperature, pressure and chemical composition under *standard state conditions*. The latter is often different from the conditions used in experimental investigations and it is necessary to apply corrections of these data so that tabulated values refer to standard state conditions. The methods for doing so will be described in the following text, but before a general survey outlining the basic principles for such corrections is required. For pure substances the standard state is usually 25 °C and 0.1 MPa and, thus, corrections to standard state conditions are straightforward. This is not the case for reactions in solution because the interactions between the components and between these and the solvent are strongly dependent on their nature and concentrations, and they are particularly important in systems that contain charged species. The magnitude of the interactions decreases with decreasing concentration of the species in solution and it is therefore natural to select the infinite dilute solution as the standard state. That is, the standard state is the *hypothetical* condition where there are no

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[1] Other methods have been proposed in the literature, such as, for example, the ion-hydration method [1959ROB/STO].

interactions between the species in solution and between these and the solvent; the standard state for the solvent is accordingly *the pure solvent*. Deviations from standard state conditions are described with *activity factors*. Tabulated thermodynamic data refer to one mol of substance. In the following the focus will be on reactions in aqueous solution, such as complex formation, solubility and redox reactions.

Interactions between charged species are much larger than those between uncharged species and the activity coefficient correction for the latter is therefore both simpler and more accurate. The majority of the data in the NEA TDB refer to ionic species and their reactions. Here the ion–ion interactions are very strong and extremely dilute systems are necessary to minimize them; for electrolytes with charge ± 1, the interactions are small for concentration smaller than 10^{-3} M. Not surprisingly the magnitude of the ion–ion interactions increases with the charge of the interacting species and for ions with charges higher than ± 1, much lower concentrations are necessary to minimize their interactions; concentrations that are so low that it is difficult or impossible, to obtain accurate experimental information. Experimental studies of such systems have been carried out using the so-called *ionic-medium* method. In this method, the standard state for the solvent is defined as unity in an aqueous solution containing an electrolyte (usually a 1:1 strong electrolyte like $NaClO_4$, NaCl or $NaNO_3$ at a certain ionic strength, *I*), where the ionic strength is much larger than the concentration of reactants and products in the reactions studied. Because of the low concentration of the reactants/products, their mutual interactions are much smaller than their interactions with ions in the ionic medium and these interactions will be relatively constant for moderate variations of the concentrations of reactants and products in an experiment. An important effect of this is that the solutions can be described as "infinite" dilute if the reactants/products have concentrations that are less than a few percent of that of the ionic medium. Experimental solution chemical data obtained using the ionic-medium method therefore refers to standard state conditions, one for each ionic medium used, where the activity factors of reactants/products are defined as one and the activity of the ionic medium as unity; each of these standard states are different and also different from "pure water". This approximation is only valid if the concentration of the ionic medium is much larger than that of the reactants/products, a condition usually met in experimental studies of systems with strong complex formation, but *not* in systems where weak complexes are formed, because in these it is necessary to use high concentrations in order to identify the complexes formed and their equilibrium constants.

Many reactions in the NEA TDB reviews have been studied in different ionic media where the standard states differ, hence, it is necessary to provide a link between them in order to compare them on an equal footing. For this purpose, the NEA TDB has selected the "pure water/infinite dilution" standard state.

The nature of ion–ion, ion–dipole and dipole–dipole interactions are well-known and can therefore be described with scientifically sound microscopic models, as described in the following section. The models include parameters that describe these interactions, but these cannot be determined from first principles, and have to be determined by experiment. As thermodynamic data have been obtained under very many different experimental conditions it is essential to ensure that these parameters can be transferred from one condition to others.

2.1.1   The basic science behind the models for estimation of deviations from ideality in electrolyte solutions

The Debye-Hückel model

The models used to describe deviations from ideality and activity coefficients in electrolyte systems all have the simple Debye-Hückel model as starting point. The Debye-Hückel model/equation has a firm theoretical basis and does not contain any empirical parameters. It is based on three assumptions:

- All ions can be considered as point charges
- The only interactions between ions are electrostatic
- The effect of counterions, *j*, on a particular ion, *i*, of opposite charge can be described as due to a static ion-cloud.

These assumptions lead to the limiting Debye-Hückel equation where the single-ion activity coefficient for an ion, γ_i, with charge z_i is:

$$\log_{10} \gamma_i = A z_i^2 \sqrt{I_m} \tag{1}$$

where the quantity A has the same value for all ions and I_m refers to the ionic strength of the solution. Experimental data show deviations from this fundamental relationship outside the extreme dilution range, and also the activity factors are not the same for all ions at a given ionic strength. Different empirical methods have been used to extend the range of validity of the Debye-Hückel model, the first one by including an ion-size parameter, resulting in the following expression:

$$\log_{10} \gamma_i = \frac{A z_i^2 \sqrt{I_m}}{1 + B a_i \sqrt{I_m}} \tag{2}$$

The quantity B is given by theory and has the value of 0.3283 kg$^{1/2}$·mol$^{-1/2}$·Å^{-1}, however, a_i (ionic size) does not have a standard value, and also, no experimental or theoretical data are known. There is a qualitative theoretical basis for taking the finite size into account, but no quantitative method of doing this, thus, a_i has to be treated as an empirical parameter.

The Davies model

The Davies equation [1962DAV] has been used extensively to calculate activity coefficients of electrolytes at fairly low ionic strengths, in combination with an ion-association approach. At 25 °C and for an ion i of charge z_i, the activity coefficient is equal to:

$$\log_{10} \gamma_i = -Az_i^2 \left(\frac{\sqrt{I_m}}{1+\sqrt{I_m}} - 0.3I_m \right). \tag{3}$$

The equation is empirical, but is found to work fairly well up to ionic strengths of 0.1 mol·kg^{-1} for single electrolytes; it is, however, not able to take electrolyte-specific effects into account. To describe these, one is forced to introduce the concept of *ion pairing*, described by equilibrium constants between the single electrolyte anion and cation, *cf.* Section 3.1. The weakness of this method is that there is rarely independent information on ion-pair formation – in addition these complexes are so weak that it is necessary to make large changes in the ionic medium in order to identify them. For reasons discussed further down, the Davies equation should not be used in the NEA TDB reviews.

Ion association approaches

Ion association approaches consider ion-pair formation in order to account for differences in mean-activity coefficients between electrolytes at the same ionic strength and as a result the ion-pairs must also be taken into account in the calculation of a reduced (effective) ionic strength. They rely on the use of functions where the activity coefficients depend only on the ionic strength, *cf.* [1962DAV], [1962LIE/STO] and [1967HEL]. This approach has been used extensively in marine chemistry, *cf.* [1979JOH/PYT], [1979MIL], [1979PYT], and [1979WHI]. The activity or osmotic coefficients are interpreted using association constants and an expression for the dependence of activity coefficients of all species only on an effective ionic strength. The free ions (i) and ion pairs (j) are assumed to be in equilibrium and an effective ionic strength, I_e, instead of the stoichiometric I, is defined as:

$$I_e = 0.5 \; [\Sigma_i \, z_i^2 \, m_i(\text{free ions}) + \Sigma_j \, z_j^2 \, m_j(\text{ion pairs})].$$

To formulate an ion association model, in practice, it is necessary to specify:

- The solution components (including complexes and ion pairs, assumed to exist).

- Activity data for all model species as functions of effective ionic strength.

- Stability constants for ion pairs and other equilibria under infinite dilution conditions.

Therefore, the first choice that needed to be made for the NEA TDB Project was whether to adopt an *ion association* or an *ion interaction* approach. As stated in the preceding section, the problem most often encountered in the NEA TDB review work is the estimation of activity coefficients of metal and ligand ions and complexes in trace concentrations in the presence of a concentrated ionic media. For such cases, ion interaction approaches are more advantageous (see arguments presented by Harvie *et al.* [1984HAR/MOL]. For this reason, an *ion interaction* approach seems a more adequate and flexible choice compared to an *ion association* one. In particular, as the latter requires the introduction of a large number of ion pairs while fewer interaction coefficients are required in ion interaction approaches.

Specific ion-interaction methods

These methods take both long-range electrostatic and short-range specific ion-ion interactions into account and are based on the following assumptions:
- The interactions between ions A and B are specific for those particular ions and the same even in the presence of other ion species.
- The magnitude of the deviation from ideality depends on the concentration of the solutes (and the solvent).
- Deviations from ideality can be described with virial equations, where the first term is based on the Debye-Hückel theory.
- All methods for the estimation of deviations from ideality, such as activity coefficients, must approach the Debye-Hückel limit with increasing dilution.

In the first approximation of the virial expansion, only one interaction term is used to describe the non-electrostatic interactions between *two* species; the interaction parameters are considered to be independent of the ionic strength and

for a given pair of ions to be independent of the presence of other ions. This is the basis for the specific ion interaction theory developed by Brønsted, Guggenheim and Scatchard and described in Section 2.4. The specific ion interaction parameters are *empirical*, and have to be determined experimentally, either from activity coefficient data or from equilibrium constants determined in different ionic media and at different ionic strength; however, they do have a theoretical basis.

When experimental data are sufficiently accurate it may be possible to take into account the concentration dependence of the specific ion interaction coefficients and also the interactions between three, or more species. The Pitzer model, described in Section 3.2, takes these interactions into account. The parameters have to be determined experimentally and this is in general only possible from activity coefficient data in systems of strong electrolytes but *not* from equilibrium constants, *cf.* Chapter IX of [1997ALL/BAN]. It is important to note that interaction coefficients for complexes also in the Brønsted, Guggenheim and Scatchard approach must be determined from the ionic medium dependence of equilibrium constants.

2.2   Formulations of the ion interaction approach

The following formulations of the specific ion interaction approach have been described in the literature[2]:

1. The Brønsted-Guggenheim-Scatchard approach (abbreviated "B-G-S equation" in this document, and "SIT" derived there from), *cf.* this section.

2. The Pitzer and Brewer "B-method" (abbreviated "P-B" in this document) *cf.* Section 3.1.

3. The Pitzer virial coefficient method, *cf.* Section 3.2.

Formulations 1 and 2 are equivalent and differ only in the form of the denominator in the Debye-Hückel term. Formulation 3, involving quadratic terms in the virial expansion in molalities, requires more parameters for the description of the activity coefficients. While most of the required parameters for implementing calculations with the Pitzer virial expansion (Formulation 3) can be

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[2]   The approaches followed by Mesmer [1971MES], Bromley [1973BRO] and Vasiliev [1962VAS] are also formulations of this method, as are some others. All of them can be roughly described as giving the logarithm of activity coefficient as a sum of a calculated extended Debye-Hückel term plus a virial expansion in the molalities of ions with coefficients depending on the nature of the ions.

obtained by measuring excess properties of pure solutions, a problem arises in the case of equilibria involving formation of metal ion complexes, because the corresponding solutions of these complexes and a counter-ion can in general not be prepared in the laboratory. An extensive comparison of formulations 1 and 3 can be found in Chapter IX of [1997ALL/BAN].

The specific ion interaction formulations are reliable for the inter-comparison of experimental data from different experimental sources in a given concentration range. Moreover, calculations with all three formulations are easily applied: formulations 1 and 2 (the SIT and the P-B models) can be implemented by linear regression procedures; formulation 3 requires, in general, non-linear procedures. The robustness of the SIT model is the basis for its adoption for the NEA TDB Review work, where there is a frequent need to ascertain whether measurements of equilibrium constants by different authors in different ionic media are chemically consistent and can be jointly extrapolated to obtain values at zero ionic strength. In some cases, these extrapolations include data at rather low ionic strengths, $I = 0.03$ to 0.1 M, *cf.* Figure 1, while in other cases, notably for ions of high charge ($\geq + 4$ and $\leq - 4$), the lowest available ionic strength is 0.2 M or higher (see for example Figures V.12 and V.13 in [1992GRE/FUG]), resulting in a larger uncertainty in the extrapolation to zero ionic strength. The extrapolation uncertainty has two components: experimental and uncertainties in the extrapolation model. The latter seems to be rather small for many systems, less than 0.1 in $\log_{10} K^{\mathrm{o}}$. For reactions involving ions of high charge, which may be extensively hydrolysed, and where experiments at low ionic strengths cannot be performed, it is not possible to estimate the extrapolation uncertainty, a feature that is shared with all methods used to estimate activity corrections. Systematic model uncertainties of this type are not included in the uncertainties assigned to the selected data in the NEA TDB Reviews.

2.3   The SIT formulation in the TDB Project

The method used in the NEA Thermochemical Data Base Reviews is the specific ion interaction theory in the form of the Brønsted-Guggenheim-Scatchard approach ("specific ion interaction" or "SIT" method). Early in the development of the NEA TDB Project, two reasons led to the adoption of this method over the other formulations of the ion interaction approach: first, it can be formulated in linear terms offering a substantial degree of numerical uniqueness and robustness in the fitted coefficients; second, reasonably good estimates of ion interaction coefficients can be obtained from various correlation laws, which offers a

particular advantage not only for prediction but also for checking the reliability of experimentally determined values.

It should be emphasised that the "B-G-S equation" or "SIT" specific ion interaction approach is a model and, as such, an approximation. Extensions and modifications have been proposed. Modification, for example, by introducing the equations suggested by Ciavatta [1990CIA] (Eqs. (11) and (14), *cf.* Section 2.7), would result in slightly different values for the ion interaction coefficients. However, as these modifications have no theoretical basis, they should be avoided.

NEA TDB reviewers may sometimes have access to the parameters required for ionic strength corrections using other ion interaction formulations such as the Pitzer approach [1979PIT] for solubility product data or Baes and Mesmer [1976BAE/MES][3] for hydrolysis equilibria. In these cases, the reviewer should compare the results of the calculations using the B-G-S equation and the other ion interaction formulations, *cf.* Chapter IX of [1997ALL/BAN]. If the results of the extrapolated constants differ more than the experimental uncertainty, this should be brought to the attention of the NEA TDB Executive Group.

2.4   Fundamental assumptions

The Debye-Hückel term, which is the dominant term in the expression for the activity coefficients in dilute solution, accounts for long-range electrostatic interactions. At higher concentrations, short range, non-electrostatic interactions between ions have to be taken into account. This is usually done by adding ionic strength dependent terms to the Debye-Hückel expression (see below), as outlined by Brønsted ([1922BRO], [1922BRO2]) and elaborated by Scatchard [1936SCA] and Guggenheim [1966GUG]. The two basic assumptions in the specific ion interaction method are described below.

Assumption 1:   The activity coefficient γ_j of an ion j of charge z_j in a solution of ionic strength I_m may be described by Eq. (4)

$$\log_{10} \gamma_j = -z_j^2 D + \sum_k \varepsilon(j,k,I_m)m_k \tag{4}$$

where D is the Debye-Hückel term:

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[3]   The main difference between the formulation by Baes and Mesmer [1976BAE/MES] and the SIT is the numerical value of the constants in the denominator of the extended Debye-Hückel term.

$$D = \frac{A\sqrt{I_m}}{1+1.5\sqrt{I_m}}, \tag{5}$$

A is the Debye-Hückel constant, which is temperature dependent as listed in Table 2.

The value 1.5 in the Debye-Hückel term was proposed by Scatchard [1976SCA] and accepted by Biedermann [1975BIE] and Ciavatta [1980CIA] and has been used in the NEA TDB Reviews. The origin of this empirical choice is that it is found to minimize the ionic strength dependence of $\varepsilon(j,k,I_m)$ between I_m = 0.5 and 3.5 m. In the Pitzer model it is assumed that the first virial coefficient, B_{MX}^{γ}, is concentration dependent (see Eq. IX.13 in Chapter IX of [1997ALL/BAN]). It should be mentioned that some authors have proposed different values, ranging from 1.0 [1935GUG] to 1.6 [1962VAS]. However, the parameter is empirical and as such correlated to the value of $\varepsilon(j,k,I_m)$. Hence, the different values do not represent an uncertainty range, but rather indicate that several different sets of values in the denominator of the Debye-Hückel term and $\varepsilon(j,k,I_m)$ may describe the experimental mean activity coefficients of a given electrolyte equally well. The ion interaction coefficients listed in Table 4 through to Table 6 have thus to be used with the value 1.5 $kg^{1/2} \cdot mol^{-1/2}$.

The summation in Eq. (4) extends over all ions k present in the solution, with molalities denoted m_k. The concentrations of the ions of the ionic medium is in general a lot larger compared to those of the reacting species. Hence, the ionic medium ions will make the main contribution to the value of $\log_{10} \gamma_j$ for the reacting ions. This fact often makes it possible to simplify the summation $\sum_k \varepsilon(j,k,I_m)m_k$ so that only ion interaction coefficients between the reactants/products in the chemical reactions and the ionic medium ions are included, as shown in Eqs. (11) to (15), *cf* Section 2.7.

Assumption 2: According to the Brønsted principle of specific interactions [1922BRO], the ion interaction coefficients $\varepsilon(j,k,I_m)$ are expected to be small for ions of the same charge sign. Similarly they should be small for interactions between uncharged species (such as dipole – dipole interactions between neutral complexes or dissolved gases) and electro-neutral combinations of ions. However, when analysing data at very high concentrations or in systems where high experimental precision has been attained, it may be necessary to verify quantitatively the validity of this assumption.

The rationale behind this assumption for ions of the same charge sign is that the ε interaction parameters, which describe specific short-range interactions, must be small since ions of the same charge sign are usually far from one another due to electrostatic repulsion. The need to describe systems at high concentrations and recent progress in experimental techniques leading to high precision measurements, make it necessary to allow for the possibility of modifying Brønsted's original proposal and to estimate the deviations between experimental and the SIT data. However, the systematic addition of extra terms to describe these deviations is not foreseen in the NEA TDB Review work; reviewers should be prepared to encounter small but significant differences in $\Delta\varepsilon$ values determined in different ionic media, that may be used to obtain interaction coefficients in each ionic medium and to estimate the uncertainty in the thermodynamic quantities at zero ionic strength. These interaction coefficients should be reported with a note in the tables compiled by the NEA TDB specifying the medium in which the corresponding value is obtained.

2.5   Activity coefficients for uncharged species

For uncharged solutes in the ionic medium, the SIT Eq.(4) is reduced to only one term, which is equivalent to the Setschenow equation [1952LON/MCD]. In this case a linear dependence of $\log_{10}\gamma_N$ on the electrolyte concentration is observed. If γ_N is the activity coefficient of the uncharged molecule in an aqueous electrolyte solution MX of molality m_{MX}, then:

$$\log_{10}\gamma_N = \varepsilon\left(N,\ M^+ +\ X^-\right)m_{MX} = \varepsilon\left(N,\ MX\right)I_m$$

In practice, for NEA TDB review work, it should be noted that for a large majority of systems encountered in the literature, the Brønsted principle of specific interactions (leading to the basic Assumption 2) is expected to hold. Reviewers should therefore not use interaction coefficients between ions of the same charge type, or for neutral molecules unless the experimental accuracy justifies this. In these cases, reviewers should explicitly mention in their reports the corresponding assumptions and supporting calculations.

In general, Eq. (4) should allow fairly accurate estimates of the activity coefficients in mixtures of electrolytes if the ion interaction coefficients are known. Ion interaction coefficients for simple ions can be obtained from tabulated data of mean activity coefficients of strong electrolytes or from the corresponding osmotic coefficients. Ion interaction coefficients for complexes can either be estimated from the charge and size of the ion or determined experimentally from

the variation of the equilibrium constant with the ionic strength.

2.6 Ionic strength dependence of ion interaction coefficients

Ion interaction coefficients are not strictly constant but may vary slightly with the ionic strength. The extent of this variation depends on the charge type and is small for 1:1, 1:2 and 2:1 electrolytes for molalities less than 3.5 mol·kg^{-1} and can, thus, often be neglected. This point was emphasized by Guggenheim [1966GUG], who presented a considerable amount of experimental material in support of it. The concentration dependence is larger for electrolytes of higher charge. In order to accurately reproduce their activity coefficient data, concentration-dependent ion interaction coefficients have to be used, *cf.* Pitzer and Brewer [1961LEW/RAN], Baes and Mesmer [1976BAE/MES], or Ciavatta [1980CIA]. The latter author has proposed, for cases where the uncertainties in the ion interaction coefficients exceed ± 0.03 kg·mol^{-1}, that these coefficients are taken as functions of the ionic strength according to the expression:

$$\varepsilon = \varepsilon_1 + \varepsilon_2 \cdot \log_{10} I_m. \tag{6}$$

According to this equation $\varepsilon \to -\infty$ when $I_m \to 0$, which is not acceptable. The NEA TDB does not recommend the use of this equation, even if it has been used in some cases in previous evaluations. If the experimental data justify ionic strength-dependent interaction parameters, the NEA TDB suggests the use of a virial expansion as outlined in [1997ALL/BAN]. For a binary electrolyte (*i,j*) this results in the following expression for the mean-activity coefficient $\gamma_\pm$:

$$\log_{10} \gamma_\pm = -\frac{A|z_+ z_-|\sqrt{I_m}}{1+1.5\sqrt{I_m}} + \varepsilon_{1,i,j} I_m + \varepsilon_{2,i,j} I_m^{3/2} \tag{7}$$

where the second and third terms can be written as:

$$\varepsilon I_m = \left(\varepsilon_{1,i,j} + \varepsilon_{2,i,j}\sqrt{I_m}\right) I_m. \tag{8}$$

This expression has the required property that $\varepsilon \to \varepsilon_{1,i,j}$ when $I_m \to 0$.

In cases where the extrapolation of experimental equilibrium constants at different ionic strength does not follow the "standard" SIT model one should use a function where $\Delta\varepsilon$ is replaced by $\Delta\varepsilon = \Delta\varepsilon_1 + \Delta\varepsilon_2\sqrt{I_m}$, rather than the Ciavatta equation.

2.7   Ionic strength corrections with SIT: complex formation equilibria

The way in which the activity coefficient corrections are performed in the NEA TDB reviews, according to the specific ion interaction method, is illustrated below for the general case of a complex formation reaction (charges are omitted for brevity):

$$m\text{M} + q\text{L} + n\text{H}_2\text{O} \rightleftharpoons \text{M}_m\text{L}_q(\text{OH})_n + n\text{H}^+. \tag{9}$$
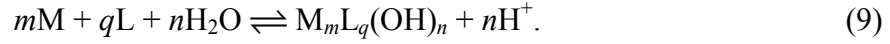
The formation constant of $\text{M}_m\text{L}_q(\text{OH})_n$, $^*\beta_{q,n,m}$, determined in an ionic medium (1:1 salt NX) of ionic strength I_m, is related to the corresponding value at zero ionic strength, $^*\beta^o_{q,n,m}$, by Eq. (10):

$$\begin{aligned}
\log_{10} {}^*\beta_{q,n,m} &= \log_{10} {}^*\beta^o_{q,n,m} + m\log_{10}\gamma_\text{M} + q\log_{10}\gamma_\text{L} \\
&\quad + n\log_{10}a_{\text{H}_2\text{O}} - \log_{10}\gamma_{q,n,m} - n\log_{10}\gamma_\text{H}
\end{aligned} \tag{10}$$

The subscript (q,n,m) denotes the stoichiometry of the complex ion $\text{M}_m\text{L}_q(\text{OH})_n$. If the concentrations of N and X are much greater than the concentrations of M, L, $\text{M}_m\text{L}_q(\text{OH})_n$ and H, only the molalities m_N and m_X have to be taken into account for the calculation of the term $\sum \varepsilon(j,k,I)m_k$ in Eq. (4). For example, for the activity coefficient of metal cation M, γ_M, Eq. (11) is obtained.

$$\log_{10}\gamma_\text{M} = \frac{-z_\text{M}^2 A\sqrt{I_m}}{1+1.5\sqrt{I_m}} + \varepsilon(\text{M},\text{X},I_m)m_\text{X} \tag{11}$$

Under these conditions, $I_m \approx m_\text{X} = m_\text{N}$. Substituting the $\log_{10}\gamma_j$ values in Eq. (10) with the corresponding forms of Eq. (11) and rearranging leads to:

$$\log_{10} {}^*\beta_{q,n,m} - \Delta z^2 D - p\log_{10}a_{\text{H}_2\text{O}} = \log_{10} {}^*\beta^o_{q,n,m} - \Delta\varepsilon I_m \tag{12}$$

where at 25 °C:

$$D = \frac{0.509\sqrt{I_m}}{1+1.5\sqrt{I_m}} \tag{13}$$

$$\Delta z^2 = (mz_\text{M} - qz_\text{L} - n)^2 + n - mz_\text{M}^2 - qz_\text{L}^2 \tag{14}$$

$$\Delta\varepsilon = \varepsilon(q,n,m,\text{N or X}) + n\varepsilon(\text{H},\text{X}) - q\varepsilon(\text{N},\text{L}) - m\varepsilon(\text{M},\text{X}) \tag{15}$$

Here $(mz_\text{M} - qz_\text{L} - n)$, z_M and z_L are the charges of complex $\text{M}_m\text{L}_q(\text{OH})_n$, the metal ion M and the ligand L, respectively.

2.8   Taking into account the activity of water

Equilibria involving H_2O (l) as a reactant or product require a correction for the activity of water, a_{H_2O}. The activity of water in an electrolyte mixture can be calculated as

$$\log_{10} a_{H_2O} = -\phi_m M_{H_2O} \sum_k m_k / \ln(10) \tag{16}$$

where ϕ is the osmotic coefficient of the mixture and the summation extends over all ions k with molality m_k present in the solution. In the presence of an ionic medium NX in dominant concentration, Eq. (13) can be simplified by neglecting the contributions of all minor species, *i.e.*, the reacting ions. Hence, for a 1:1 electrolyte of ionic strength $I_m \approx m_{NX}$, Eq. (16) becomes

$$\log_{10} a_{H_2O} = -2m_{NX} \phi_m M_{H_2O} / \ln(10) \tag{17}$$

Values of osmotic coefficients for single electrolytes have been compiled by various authors, *e.g.*, Robinson and Stokes [1959ROB/STO]. The activity of water is obtained by inserting Eq. (16) into Eq. (17). It should be mentioned that in mixed electrolytes with several components at high concentrations, it may be necessary to use Pitzer's equation to calculate the activity of water from the known activity coefficients of the dissolved species. For convenience, water activities have been listed in Table 1 for some common ionic media. These have been calculated applying Pitzer's ion interaction model and the interaction parameters given in [1991PIT]. On the other hand, a_{H_2O} is nearly constant (and close to 1) in most experimental equilibrium studies in dilute aqueous solutions, where an ionic medium is used in large excess with respect to the reactants. The medium electrolyte concentration thus determines the osmotic coefficient of the solvent.

In natural waters the situation is similar, but the ionic strength of most surface waters is so low that the activity of H_2O (l) can be set equal to unity. A correction may be necessary in the case of seawater, where a sufficiently good approximation for the osmotic coefficient may be obtained by considering NaCl as the dominant electrolyte.

In more complex solutions of high ionic strengths with more than one electrolyte at significant concentrations, *e.g.*, $(Na^+, Mg^{2+}, Ca^{2+})(Cl^-, SO_4^{2-})$, Pitzer's equations may be used to estimate the osmotic coefficient; the necessary interaction coefficients are known for most systems of geochemical interest.

Table 1: Water activities a_{H_2O} at 298.15 K for the most common ionic media at various concentrations calculated using Pitzer's ion interaction approach and the interaction parameters given in [1991PIT]. Data in italics have been calculated for concentrations beyond the validity of the parameter set applied. These data are therefore extrapolations and should be used with care.

Water activities a_{H_2O} at 298.15 K							
c (M)	$HClO_4$	$NaClO_4$	$LiClO_4$	NH_4ClO_4	$Ba(ClO_4)_2$	HCl	$NaCl$	$LiCl$
0.10	0.9966	0.9966	0.9966	0.9967	0.9953	0.9966	0.9966	0.9966
0.25	0.9914	0.9917	0.9912	0.9920	0.9879	0.9914	0.9917	0.9915
0.50	0.9821	0.9833	0.9817	0.9844	0.9740	0.9823	0.9833	0.9826
0.75	0.9720	0.9747	0.9713	0.9769	0.9576	0.9726	0.9748	0.9731
1.00	0.9609	0.9660	0.9602	0.9694	0.9387	0.9620	0.9661	0.9631
1.50	0.9357	0.9476	0.9341	0.9542	0.8929	0.9386	0.9479	0.9412
2.00	0.9056	0.9279	0.9037		*0.8383*	0.9115	0.9284	0.9167
3.00	0.8285	0.8840	0.8280		*0.7226*	0.8459	0.8850	0.8589
4.00	0.7260	0.8331	*0.7309*			0.7643	0.8352	0.7991
5.00	*0.5982*	*0.7744*				0.6677	0.7782	0.7079
6.00	*0.4513*	*0.7075*				*0.5592*		*0.6169*

c (M)	KCl	NH_4Cl	$MgCl_2$	$CaCl_2$	$NaBr$	HNO_3	$NaNO_3$	$LiNO_3$
0.10	0.9966	0.9966	0.9953	0.9954	0.9966	0.9966	0.9967	0.9966
0.25	0.9918	0.9918	0.9880	0.9882	0.9916	0.9915	0.9919	0.9915
0.50	0.9836	0.9836	0.9744	0.9753	0.9830	0.9827	0.9841	0.9827
0.75	0.9754	0.9753	0.9585	0.9605	0.9742	0.9736	0.9764	0.9733
1.00	0.9671	0.9669	0.9399	0.9436	0.9650	0.9641	0.9688	0.9635
1.50	0.9500	0.9494	0.8939	0.9024	0.9455	0.9439	0.9536	0.9422
2.00	0.9320	0.9311	0.8358	0.8507	0.9241	0.9221	0.9385	0.9188
3.00	0.8933	0.8918	0.6866	0.7168	0.8753	0.8737	0.9079	0.8657
4.00	0.8503	0.8491	0.5083	0.5511	*0.8174*	0.8196	0.8766	0.8052
5.00		*0.8037*		0.3738	*0.7499*	0.7612	0.8446	0.7390
6.00					*0.6728*	*0.7006*	*0.8120*	*0.6696*

c (M)	NH_4NO_3	Na_2SO_4	$(NH_4)_2SO_4$	Na_2CO_3	K_2CO_3	$NaSCN$
0.10	0.9967	0.9957	0.9958	0.9956	0.9955	0.9966
0.25	0.9920	0.9900	0.9902	0.9896	0.9892	0.9915
0.50	0.9843	0.9813	0.9814	0.9805	0.9789	0.9828
0.75	0.9768	0.9732	0.9728	0.9720	0.9683	0.9736
1.00	0.9694	0.9653	0.9640	0.9637	0.9570	0.9641
1.50	0.9548	0.9491	0.9455	0.9467	0.9316	0.9438
2.00	0.9403		0.9247	0.9283	0.9014	0.9215
3.00	0.9115		0.8735		0.8235	0.8708
4.00	0.8829		0.8050		0.7195	*0.8115*
5.00	*0.8545*				*0.5887*	*0.7436*
6.00	*0.8266*					*0.6685*

2.9 Ionic strength corrections with SIT: analysing osmotic coefficient data

In the presence of an ionic medium $N_{\nu_+}X_{\nu_-}$ of a concentration much larger than that of the reacting ions, the osmotic coefficient can be calculated according to Eqs. (23-39), (23-40) and (A4-2), in [1961LEW/RAN]). That is:

$$1-\phi_m = \frac{A\ln(10)|z_+z_-|}{I_m(1.5)^3}\left[1+1.5\sqrt{I_m} - 2\ln(1+1.5\sqrt{I_m})-\frac{1}{1+1.5\sqrt{I_m}}\right]$$
$$-\ln(10)\varepsilon(N,X)m_{NX}\left(\frac{\nu_+\nu_-}{\nu_+ + \nu_-}\right) \tag{18}$$

where ν_+ and ν_- are the number of cations and anions in the salt formula $(\nu_+ z_+ = \nu_-|z_-|)$, and in this case

$$I_m = \frac{1}{2}|z_+z_-|m_{NX}(\nu_+ + \nu_-) \tag{19}$$

2.10 Electroneutrality needs to be respected

Note that in all ion interaction approaches, the equation for mean activity coefficients can be split up to give equations for conventional single ion activity coefficients in mixtures, *e.g.*, Eq. (4). The latter are strictly valid only when used in combinations which yield electroneutrality. Thus, while estimating medium effects on standard potentials, a combination of redox equilibria with $H^+ + e^- \rightleftharpoons$ ½H$_2$(g) is necessary (*cf.* Section 2.14).

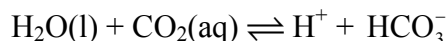## 2.11 Complex formation equilibria involving uncharged species

For a complex formation reaction in a NX medium salt with an uncharged species **Un**:

$$qL^{l-} + rH_2O(l) + sUn \rightleftharpoons L_qUn_s(OH)_r^{lq-r} + rH^+$$

$$\log_{10}\beta_{p,q,r} - \Delta z_i^2 D(I) - r\log_{10}a_{H_2O} = \log_{10}\beta_{p,q,r}^o + \Delta\varepsilon I \tag{20}$$
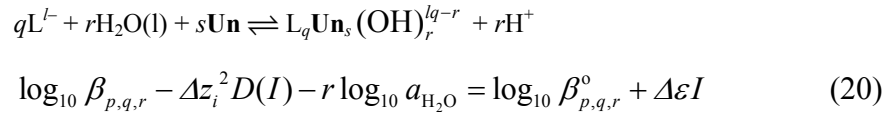
where: $\Delta z_i^2 = (lq-r)^2 + r^2 - ql^2$, and

$$\Delta\varepsilon = \varepsilon\left[L_qUn_s(OH)_r^{-(lq+r)}, Na^+\right] + r\varepsilon(H^+, X^-) - q\varepsilon(N^+, L^-) - s\varepsilon(U, NX).$$

This would apply to the analysis of equilibria such as:

$$H_2O(l) + CO_2(aq) \rightleftharpoons H^+ + HCO_3^-$$

where the equilibrium constant includes a neutral molecule, $CO_2(aq)$, and its interaction with the ionic medium NaCl should be included in the calculations. Experimental data on the solubility of $CO_2(g)$ in NaCl solutions were used to obtain the value $\varepsilon(CO_2(aq), Na^+ + Cl^-) = 0.083$ kg·mol^{-1} (see Chapter IX of [1997ALL/BAN]).

2.12　Ionic strength corrections at temperatures other than 298.15 K

Values of the Debye-Hückel parameters A in Eqs. (4) and (5) for different temperatures are listed in Table 2, at a pressure of 1 bar for temperatures below 100 °C and at the steam saturated pressure for $t \geq 100$ °C. The values in Table 2 may be calculated from the static dielectric constant and the density of water as a function of temperature and pressure, and are also found for example in Refs. [1974HEL/KIR2], [1979BRA/PIT], [1981HEL/KIR], [1984ANA/ATK], and [1990ARC/WAN].

The variation of $\varepsilon(j,k,I_m)$ with temperature is discussed by Lewis and Randall [1961LEW/RAN], Millero [1979MIL], Helgeson *et al.* [1981HEL/KIR], [1990OEL/HEL], Giffaut *et al.* [1993GIF/VIT2] and Grenthe and Plyasunov [1997GRE/PLY]. The absolute values for the reported ion interaction parameters differ in these studies due to the fact that the Debye-Hückel term used by these authors is not exactly the same. Nevertheless, common to all these studies is the fact that values of $(\partial \varepsilon / \partial T)_p$ are usually ≤ 0.005 kg·mol^{-1}·K^{-1} for temperatures below 200 °C. In order to reduce the uncertainties on solubility calculations at $t = 25$ °C, studies on the variation of $\varepsilon(j,k,I_m)$-values with temperature should be undertaken. As the values of $\varepsilon(j,k,I_m)$ and the value 1.5 in the denominator of the Debye-Hückel term are strongly correlated, there is no basis in selecting a value different from 1.5 at different temperatures, so any temperature variation is, included in the ε-term. This review recommends the use of the value 1.5 kg$^{1/2}$·mol$^{-1/2}$ for the temperature interval 0-200 °C.

Table 2: The Debye-Hückel constant, *A*, as a function of temperature at a pressure of 1 bar below 100 °C or steam saturated pressure for $t \geq 100$ °C. The uncertainty in the parameter is estimated by this review to be ± 0.001 at 25 °C, and ± 0.006 at 300 °C.

$t/°C$	p/bar	$A/\mathrm{kg}^{1/2}\cdot\mathrm{mol}^{-1/2}$
0	1.00	0.491
5	1.00	0.494
10	1.00	0.498
15	1.00	0.501
20	1.00	0.505
25	1.00	0.509
30	1.00	0.513
35	1.00	0.518
40	1.00	0.525
50	1.00	0.534
75	1.00	0.564
100	1.013	0.600
125	2.32	0.642
150	4.76	0.690
175	8.92	0.746
200	15.5	0.810
250	29.7	0.980
300	85.8	1.252

2.13 Estimation methods for ion interaction coefficients

For an extensive discussion on various correlations between interaction coefficients in various ionic media, scaling laws with ion potential and correlations between coefficients for successive complexes with the same ligand, see Section IX.5 in [1997GRE/PLY]. This reference also contains the indication that $\Delta\varepsilon$ values for chemical reactions between ions of same charge type are similar in value within an uncertainty between ± 0.05 and ± 0.1 kg·mol^{-1}. All these correlations may be used by Reviewers to estimate unknown values of ion

interaction coefficients and their combinations whose consistency with experimental data should be verified and reported explicitly.

2.13.1   Estimation from mean activity coefficient data

The ion interaction coefficient $\varepsilon(H^+, Cl^-)$ can be obtained from published values of $\gamma_{\pm,HCl}$ *vs.* m_{HCl}.

$$2\log_{10}\gamma_{\pm,HCl} = \log_{10}\gamma_{H^+} + \log_{10}\gamma_{Cl^-}$$
$$= -D + \varepsilon(H^+, Cl^-)m_{Cl^-} - D + \varepsilon(Cl^-, H^+)m_{H^+} \tag{21}$$

$$\log_{10}\gamma_{\pm,HCl} = -D + \varepsilon(H^+, Cl^-)m_{HCl} \tag{22}$$

By plotting $(\log_{10}\gamma_{\pm,HCl} + D)$ *vs.* m_{HCl} a straight line with the slope $\varepsilon(H^+, Cl^-)$ is obtained. The degree of linearity should in itself indicate the range of validity of the specific ion interaction approach. Osmotic coefficient data can be treated in an analogous way.

2.13.2   Estimations based on experimental values of equilibrium constants at different ionic strengths

Equilibrium constants for the reaction below are given in Table 3.

$$UO_2^{2+} + 2CO_3^{2-} \rightleftharpoons UO_2(CO_3)_2^{2-}. \tag{23}$$
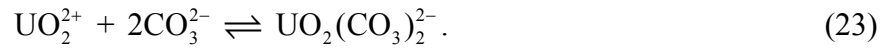
Then, the following formula is derived from Eq. (12) for the extrapolation to $I = 0$:

$$\log_{10}\beta_2 + 8D = \log_{10}\beta_2^{o} - \Delta\varepsilon I_m. \tag{24}$$

A linear regression gives

$$\log_{10}\beta_2^{o} = (16.94 \pm 0.12)$$

$$\Delta\varepsilon(23) = -(0.32 \pm 0.06) \text{ kg·mol}^{-1}$$

where the uncertainties are calculated as described in the NEA Guidelines for the Assignment of Uncertainties [1999NEA].

The experimental data are depicted in Figure 1.

Table 3: The preparation of the experimental equilibrium constants for the extrapolation to $I = 0$ with the specific ion interaction method at 25 °C and 1 bar according to Reaction (23). The linear regression of this set of data is shown in Figure 1.

Method	Ionic medium	$\log_{10} \beta_2$ [a]	$\log_{10} \beta_2^\circ$ [a]	Reference
sol	0		14.6	[1956MCC/BUL]
sol	0.2 M NH_4NO_3	15.6		[1960BAB/KOD]
emf, gl	0.1 M $NaClO_4$	16.2 ± 0.3 [b,d]		[1969TSY]
sol	0.03 M	16.7 ± 0.3 [d]		[1972SER/NIK]
sol	var.	4.0		[1973ALM/GAR]
dis	0.1 M $NaNO_3$	16.22 ± 0.30 [d]		[1977SCA]
emf, gl	0.1 M $NaClO_4$	16.15 ± 0.30 [d]		[1982MAY]
sol	0.5 M $NaClO_4$	15.56 ± 0.15 [b,c]		[1984GRE/FER]
	3.0 M $NaClO_4$	16.20 ± 0.15 [b,c]		
emf, gl	0.5 M $NaClO_4$	14.93 ± 0.30		[1991GRE/LAG]
rev	0		17.0	[1978LAN]
rev	0		17.1 ± 0.4	[1980LEM/TRE]

(a) Refers to the reaction indicated, $\log_{10} K$ in the ionic medium given and $\log_{10} K^\circ$ (molal units) at $I = 0$ and 25 °C.

(b) Re-evaluated in [1992GRE/FUG].

(c) The reported constant is corrected for the different protonation constants of carbonate used in [1992GRE/FUG].
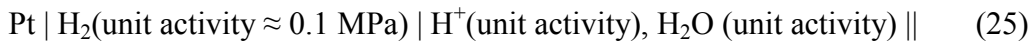
(d) Uncertainties estimated in [1992GRE/FUG].

Figure 1: Extrapolation to $I = 0$ of experimental data for the formation of $UO_2(CO_3)_2^{2-}$ using the specific ion interaction theory. The shaded area represent the uncertainty range obtained by propagating the resulting uncertainties from $I = 0$ back to $I = 4$ m.
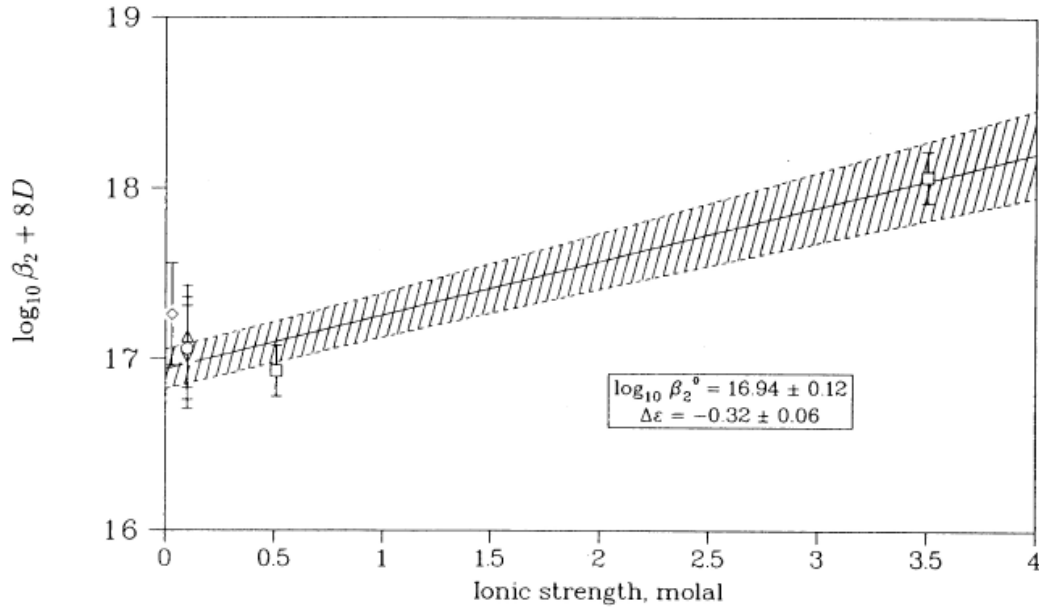
2.14 Redox equilibria

Electrochemical data for redox couples are reported as *reduction potentials*, relative to the hypothetical *standard hydrogen electrode*. This is a half-cell:

$$Pt \mid H_2(\text{unit activity} \approx 0.1 \text{ MPa}) \mid H^+(\text{unit activity}), H_2O \text{ (unit activity)} \parallel \qquad (25)$$

This half-cell is difficult to prepare and is actually replaced by other half-cells, *e.g.*, Ag $\mid$ AgCl $\mid$ Ag$^+$ $\parallel$, and the calomel electrode. The potentials of these half-cells can be related to the normal hydrogen electrode, but are more practical to work with. In practice one can use the hydrogen electrode by using solutions at different *concentrations* of hydrogen ions and calculate the activity.

As an example, the relationship between the redox potential of the couple UO_2^{2+}/U^{4+} in a medium of ionic strength I_m and the corresponding quantity at $I_m = 0$ should be calculated in the following way. The reaction in the galvanic cell

$$Pt,H_2 \,|\, H^+ :: UO_2^{2+}, U^{4+} \,|\, Pt \tag{26}$$

is

$$UO_2^{2+} + H_2(g) + 2H^+ \rightleftharpoons U^{4+} + 2H_2O(l) \tag{27}$$
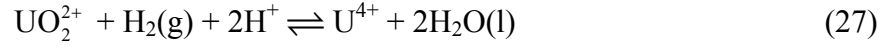
For this reaction:

$$\log_{10} K^\circ = \log_{10}\left(\frac{a_{U^{4+}} \times a_{H_2O}^2}{a_{UO_2^{2+}} \times a_{H^+}^2 \times f_{H_2}} \right), \tag{28}$$

$$\log_{10} K^\circ = \log_{10} K + \log_{10} \gamma_{U^{4+}} - \log_{10} \gamma_{UO_2^{2+}} - 2\log_{10} \gamma_{H^+} \\ - \log_{10} f_{H_2} + 2\log_{10} a_{H_2O} \tag{29}$$

$f_{H_2} \approx p_{H_2}$ at reasonably low partial pressure of $H_2(g)$, $a_{H_2O} \approx 1$, and

$$\log_{10} \gamma_{U^{4+}} = -16D + \varepsilon(U^{4+}, ClO_4^-)\, m_{ClO_4^-}$$

$$\log_{10} \gamma_{UO_2^{2+}} = -4D + \varepsilon(UO_2^{2+}, ClO_4^-)\, m_{ClO_4^-}$$

$$\log_{10} \gamma_{H^+} = -D + \varepsilon(H^+, ClO_4^-)\, m_{ClO_4^-}.$$

Hence,

$$\log_{10} K^\circ = \log_{10} K - 10D \\ + [\varepsilon(U^{4+}, ClO_4^-) - \varepsilon(UO_2^{2+}, ClO_4^-) - 2\varepsilon(H^+, ClO_4^-)] m_{ClO_4^-} \tag{30}$$

The relationship between the equilibrium constant and the standard potential is

$$\ln K = \frac{nF}{RT} E \tag{31}$$

$$\ln K^\circ = \frac{nF}{RT} E^\circ \tag{32}$$

E is the standard potential in a medium of ionic strength I_m, E° is the corresponding quantity at $I_m = 0$, and n is the number of transferred electrons in the reaction considered. Combining Eqs. (30) and (32) and rearranging them leads to Eq. (33).

$$E - 10D\left(\frac{RT\ln(10)}{nF} \right) = E^\circ - \Delta\varepsilon m_{ClO_4^-}\left(\frac{RT\ln(10)}{nF} \right) \tag{33}$$

For $n = 2$ in the present example and $T = 298.15$ K, Eq. (33) becomes

$$E/mV - 295.8\,D = E^\circ/mV - 29.58\Delta\varepsilon m_{ClO_4^-} \tag{34}$$

where:

$$\Delta\varepsilon = \left(\varepsilon(U^{4+}, ClO_4^-) - \varepsilon(UO_2^{2+}, ClO_4^-) - 2\varepsilon(H^+, ClO_4^-) \right).$$

3   Other methods for ionic strength corrections

As discussed, the method used in the NEA Thermochemical DataBase Reviews is the specific ion interaction method in the form of the Brønsted-Guggenheim-Scatchard formulation (SIT). A number of other formulations for ionic strength corrections have been developed in the literature and may be encountered by NEA TDB reviewers in the course of their work. Some of the most common ones are briefly discussed in the following sections as an *aide memoire* to the reviewers. See also the discussion under Section IX.4 of [1997GRE/PLY].

For certain systems, NEA TDB reviewers may find that, in addition to the analysis using SIT, additional ones are also possible with several other ion interaction formulations. A comparison of the results of such analyses is encouraged, and in case of significant differences between the parameters obtained from the various formulations, should be followed by a discussion with the NEA TDB Project Executive Group.

3.1   The Pitzer and Brewer equation

The P-B equation is very similar to the SIT equation. The expression for the activity coefficient of an ion i of charge z_i takes the form:

$$\log_{10} \gamma_i = \frac{-z_i^2 0.5107\sqrt{I_m}}{1+\sqrt{I_m}} + \sum_j B(i,j)m_j \tag{35}$$

where the summation over j covers all anions for the case that i is a cation and vice versa. Tables of $B(i,j)$ are given by Pitzer and Brewer [1961LEW/RAN] and by Baes and Mesmer [1976BAE/MES]. The Debye-Hückel term, *cf.* Eq. (4), is different from that in the SIT equation. Apart from a slightly different value for A, the factor in the denominator of the Debye-Hückel term has been chosen equal to 1.0 in the Pitzer-Brewer equation compared to 1.5 in the SIT equation. The SIT equation is preferred to the Pitzer-Brewer equation in the critical evaluations of the NEA-TDB Project for the reasons given in Section 2.

3.2   The Pitzer equations

By using a more elaborate virial expansion, Pitzer and co-workers ([1973PIT], [1973PIT/MAY], [1974PIT/KIM], [1974PIT/MAY], [1975PIT], [1976PIT/SIL], [1978PIT/PET], [1979PIT]) have described the measured activity coefficients of a large number of electrolytes with high precision over a large concentration range. An extensive comparison of the SIT and Pitzer formulations of the ion interaction approach can be found in Sections IX.6 to IX.9 of [1997GRE/PLY]. The key problem when using the Pitzer model to describe activity factors for complexes is to determine the concentration dependence of the second virial coefficient B_{MX}^{γ} for complexes, as seen from Eq. IX.13 in Chapter IX of [1997ALL/BAN]. This requires experimental data at low ionic strength in order to have a reliable value of $\beta_{MX}^{(1)}$ and this is often difficult or impossible, for instance for high charged ions in salt-brine systems.

3.3   The equations used by Baes and Mesmer

Baes and Mesmer [1976BAE/MES] used the function $F(I_m)$ proposed by Pitzer to express the ionic strength dependence of the ion interaction coefficient B_{MX} in Guggenheim's equations. For a single electrolyte:

$$\log_{10} \gamma_{\pm MX}^{o} = -\left|z_M z_X\right| \frac{0.511\sqrt{I_m}}{1+\sqrt{I_m}} + \frac{2\nu_M \nu_X}{\nu} B_{MX} m_{MX} \tag{36}$$

where

$$B_{MX} = B_{MX}^{\infty} + (B_{MX}^{o} - B_{MX}^{\infty})F(I_m) \tag{37}$$

$$F(I_m) = \frac{1-(1+2\sqrt{I_m}-2I_m)e^{(-2\sqrt{I_m})}}{4I_m}, F(0)=1, F(\infty)=0. \tag{38}$$

The Pitzer function linearises the dependence of the ion interaction coefficient on the ionic strength quite well, even in the cases of 4:1 and 5:1 electrolytes, where constant $\varepsilon(M,X)$ values, *cf.* Eq. (4), are not obtained at high ionic strengths. The parameters B_{MX}^{o} and B_{MX}^{∞} can be determined from a single electrolyte activity coefficient by calculating first B_{MX}. (Note that $B_{MX} \neq \varepsilon(M,X)$, since the Debye-Hückel term in Eq. (36) does not have the factor of 1.5 in the denominator). By plotting $B_{MX}(I_m)$ values against $F(I_m)$, B_{MX}^{∞} is obtained as the intercept while B_{MX}^{o} is obtained from the slope of the straight line, *cf.* Eq. (37). The equation for a mixture is similar to Eq. (38) and $B_{MX} = 0$ if M and X are of the

same charge sign. In the case of equilibrium constant measurements, ΔB values are expressed by equations similar to Eq. (12).

The corresponding ΔB^{o} and ΔB^{∞} can be obtained together with the β^{o} values from the system of equations:

$$\log_{10} \beta(I_m) - \Delta z_i^2 \frac{0.511\sqrt{I_{m,n}}}{1+\sqrt{I_{m,n}}} - r \log_{10}(a_{\mathrm{H_2O}})_n =$$

$$\log_{10} \beta^{\mathrm{o}} + \Delta B^{\infty}[1 - F(I_{m,n})]I_{m,n} + \Delta B^{\mathrm{o}} F(I_{m,n})I_{m,n} \tag{39}$$

where $\beta(I_m)$ and $(a_{\mathrm{H_2O}})_n$ refer to the values of β and $a_{\mathrm{H_2O}}$ at ionic strength $I_{m,n}$. From the values obtained for ΔB^{o} and ΔB^{∞} and equations similar to Eq.(15), one may estimate the unknown $B^{\mathrm{o}}_{\mathrm{MX}}$ and B^{∞}_{MX} values.

4   Weak complexes within an ion-interaction approach: ion interaction coefficients *versus* equilibrium constants for ion pairs

A problem often encountered in practice is that of adequately modelling systems where weak complexes are formed. In these cases the distinction between complex formation and activity coefficient variations is unclear or even arbitrary. As long as the fraction associated is rather small, the mathematical effect of an ion association is the same as that of a negative contribution to a virial coefficient [1981PIT]. This means that chloride salts have lower interaction coefficients than perchlorates for the same cation, since they are partially associated.

Usually, large changes of the ionic medium are necessary to study weak complex formation by substituting in most cases completely the medium anion by the ligand. This causes changes of the activity coefficients of the species involved, even though the stoichiometric ionic strength is usually maintained constant. In this case, it is recommended to use the general formulation of the SIT equation, Eq.(4), and not the simplified form, Eq. (11). Then, the reviewer has to decide what terms, *e.g.* ε (j,k) $[k]$, can be neglected among all the SIT terms. If only L^- has a non-negligible concentration compared with that of ClO_4^-, then the procedure of extrapolation should be as follows.

The reviewer is advised to estimate first the changes of activity coefficients during the experimental determination of the constants at each ionic strength. For practical reasons [1985SPA], it is advantageous to carry out this part

of the calculation in molar scale. The problem involves estimation of the activity coefficient changes for the equilibrium:

$$M^{m+} + nL^- \rightleftharpoons ML_n^{(m-n)} , \tag{40}$$
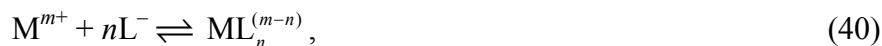
$$\beta_n^{\mathrm{o}} = \frac{[ML_n^{(m-n)}]}{[M^{m+}] \cdot [L^-]^n} \cdot \frac{\gamma_{cML_n^{(m-n)}}}{\gamma_{cM^{m+}} \cdot \gamma_{cL}^n} \tag{41}$$

in mixtures with a common cation N and of total ionic strength I M during the substitution of perchlorate by the anion L of the weak complex. The reference state is I M NaClO$_4$, *i.e.* activity coefficients tend to unity when [L] goes to zero, and the composition of the medium becomes that of the reference state. For both the SIT and Pitzer approaches, at the concentrations relevant for most studies of weak complexes, the ion interaction part is dominated by linear terms in $[ClO_4^-]$ or $[L^-]$ (ε in SIT and $\beta^{(0)} + \theta_{i,j}$ in the Pitzer approach) as all the other species are at trace concentrations. Since $[ClO_4^-] = I - [L^-]$ and because I and also $D_{\mathrm{H}}(I)$ are constant, the value of $\log_{10}\beta_n$ at constant ionic strength must vary linearly with $[L^-]$. In some cases, as in spectrophotometric studies, this change in $\log_{10}\beta_n$ during the titration was interpreted as an experimental error, since the spectra did not show evidence of new complexes. In many cases, however, the variation of activity coefficients at constant ionic strength has been misinterpreted as the formation of one or several (up to three) complexes.

By using as a reference state the pure background electrolyte (*e.g.*, NaClO$_4$) at ionic strength I, it is possible to obtain an expression for the activity coefficient of species i in (NaClO$_4$ − NaL) mixtures at the same ionic strength:

$$
\begin{aligned}
\log_{10} \gamma_{i,\mathrm{mix}} - \log_{10} \gamma_{i,\mathrm{perchl}} \;&= -z_i^2 \{D_{\mathrm{H}}(I) - D_{\mathrm{H}}(I)\} + \varepsilon(i, L^-) [L^-] \\
&\quad + \varepsilon(i, ClO_4^-) (I - [L^-]) - \varepsilon(i, ClO_4^-) I \\
&= -\{\varepsilon(i, ClO_4^-) - \varepsilon(i, L^-)\} [L^-].
\end{aligned} \tag{42}
$$

Substitution of these expressions for all species participating in the complex formation equilibrium (40) gives relatively simple linear expressions relating $\log_{10}\beta_n$ to $\log_{10}\beta_n^{\mathrm{o}}$ from which a value of the constant β_n^{o} at the given ionic medium level and trace concentrations of the ligand is obtained.

The values of the constants thus obtained may then be converted to molal scale and used in the standard SIT extrapolation at zero ionic strength. An example (for the formation of NpNO$_3^{3+}$) is shown in Figure 2, which contains reported and corrected formation constants for Np^{4+} + NO$_3^-$ $\rightleftharpoons$ NpNO$_3^{3+}$. It can be seen that such corrections are not very large (compare filled and empty symbols at each ionic strength level) and no real loss of accuracy in the value of

the constant at zero ionic strength, which is finally selected in the review, is expected to originate from not carrying out this kind of corrections.

However, what the reviewer gains is: firstly, a more consistent set of data; secondly, in the process, several very weak higher-order complexes, which have no independent chemical validation, are excluded and thirdly, the values of $\Delta\varepsilon$ obtained do not result in the inconsistencies commented in Chapter V of the Organics review [2005HUM/AND].

Figure 2: Extrapolation to infinite dilution using the SIT (empty squares) and data recalculated in [2001LEM/FUG] at trace nitrate concentrations (filled circles).
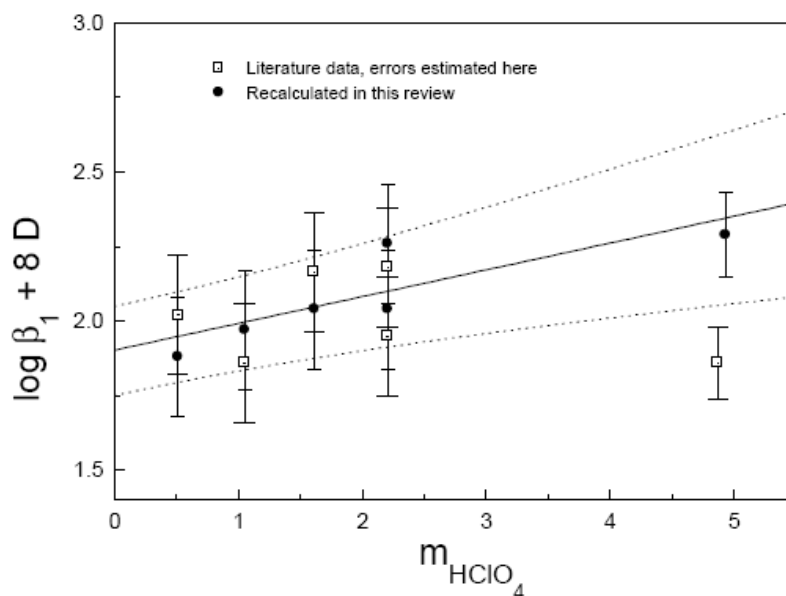
In conclusion, for the analysis of systems where weak complexes are suspected, the following procedure should be followed:

- The review of the original work should preferably include an estimation of the activity coefficient changes occurring during the addition of the weak ligand at each constant ionic strength. If, during the course of an experiment, more than 10% of the background electrolyte is replaced by the ligand, calculation of an independent association constant value cannot usually be justified.

- A standard SIT treatment on a molar scale at each ionic strength level should allow the value of the equilibrium constant at trace ligand concentration to be estimated. If this calculation shows that the system can be described equally well without recourse to complexation, this should be stated in the Review. Otherwise, the data thus obtained for each ionic strength should be used to obtain by extrapolation the value at zero ionic strength with the usual procedure (and statistical tests).

5   Tables of ion interaction coefficients

Tables 4, 5 and 7 contain the selected specific ion interaction coefficients used in the TDB reviews, according to the specific ion interaction theory described. Table 4 contains cation interaction coefficients with Cl^-, ClO_4^-, and NO_3^-, Table 5 anion interaction coefficients with Li^+, Na^+ (or NH_4^+) and K^+, and Table 7 neutral species—electroneutral combination of ions. The coefficients have the units of $kg \cdot mol^{-1}$ and are valid at 298.15 K and 1 bar. The species are ordered by charge and appear, within each charge class, in the standard order of arrangement, *cf.* Section I.1.10 of [2000WAN/OST2].

In some cases, the ionic interaction can be better described by assuming ion interaction coefficients as functions of the ionic strength rather than as constants. Ciavatta [1980CIA] proposed the use of Eq. (43) for cases where the uncertainties in Table 4 and Table 5 are ± 0.03 $kg \cdot mol^{-1}$ or greater.

$$\varepsilon = \varepsilon_1 + \varepsilon_2 \log_{10} I_m \qquad\qquad (43)$$

As stated in the previous sections, this procedure is doubtful as it introduces a second fitting parameter resulting in apparent better agreement between experimental data and extrapolation model. This is not really an improvement in the accuracy, but, nevertheless, the procedure has been used in the NEA TDB as shown in Table 6.

Table 4: Ion interaction coefficients $\varepsilon(j,k)\,(\text{kg·mol}^{-1})$ for cations j with $k = \text{Cl}^-$, ClO_4^- and NO_3^-. The uncertainties represent 95% confidence level. The ion interaction coefficients marked with † can be described more accurately with an ionic strength dependent function, listed in Table 6. The coefficients $\varepsilon(\text{M}^{n+},\ \text{Cl}^-)$ and $\varepsilon(\text{M}^{n+},\ \text{NO}_3^-)$ reported by Ciavatta [1980CIA] were evaluated without taking chloride and nitrate complexation into account, as discussed in Section 4.

j	k	$\varepsilon(j,k)$	Comments
H^+	Cl^-	0.12 ± 0.01	
	ClO_4^-	0.14 ± 0.02	Reported by Ciavatta [1980CIA].
	NO_3^-	0.07 ± 0.01	
NH_4^+	Cl^-	-0.01 ± 0.01	Reported by Ciavatta [1980CIA].
	ClO_4^-	$-0.08 \pm 0.04^\dagger$	
	NO_3^-	$-0.06 \pm 0.03^\dagger$	
H_2gly^+	Cl^-	-0.06 ± 0.02	Reported by Ciavatta [1988CIA].
	ClO_4^-	—	
	NO_3^-	—	
H_5edta^+	Cl^-	-0.23 ± 0.15	
	ClO_4^-	-0.23 ± 0.15	See Section VIII.3.7 of [2005HUM/AND].
	NO_3^-	-0.23 ± 0.15	
SnOH^+	Cl^-	—	
	ClO_4^-	-0.07 ± 0.13	See Section VII.1.1 of [2012GAM/GAJ].
	NO_3^-	—	
SnF^+	Cl^-	—	
	ClO_4^-	0.14 ± 0.10	See Section VIII.3.1.1 of [2012GAM/GAJ].
	NO_3^-	—	
SnCl^+	Cl^-	—	
	ClO_4^-	0.08 ± 0.07	See Section VIII.3.2.1 of [2012GAM/GAJ].
	NO_3^-	—	
SnBr^+	Cl^-	—	
	ClO_4^-	0.15 ± 0.07	See Section VIII.3.3.1 of [2012GAM/GAJ].
	NO_3^-	—	
SnNO_3^+	Cl^-	—	
	ClO_4^-	0.17 ± 0.09	See Section X.1.1 of [2012GAM/GAJ].
	NO_3^-	—	
SnSCN^+	Cl^-	—	
	ClO_4^-	0.17 ± 0.29	See Section XI.1.1 of [2012GAM/GAJ].
	NO_3^-	—	

(Continued on next page)

Table 4 (continued)

j	k	$\varepsilon(j,k)$	Comments
Tl^+	Cl^-	—	
	ClO_4^-	$-0.21 \pm 0.06^\dagger$	
	NO_3^-	—	
$ZnHCO_3^+$	Cl^-	0.2	Taken from Ferri *et al.* [1985FER/GRE].
	ClO_4^-	—	
	NO_3^-	—	
$CdCl^+$	Cl^-	—	
	ClO_4^-	0.25 ± 0.02	Reported by Ciavatta [1980CIA].
	NO_3^-	—	
CdI^+	Cl^-	—	
	ClO_4^-	0.27 ± 0.02	Reported by Ciavatta [1980CIA].
	NO_3^-	—	
$CdSCN^+$	Cl^-	—	
	ClO_4^-	0.31 ± 0.02	Reported by Ciavatta [1980CIA].
	NO_3^-	—	
$HgCl^+$	Cl^-	—	
	ClO_4^-	0.19 ± 0.02	Reported by Ciavatta [1988CIA].
	NO_3^-	—	
Cu^+	Cl^-	—	
	ClO_4^-	0.11 ± 0.01	Reported by Ciavatta [1980CIA].
	NO_3^-	—	
Ag^+	Cl^-	—	
	ClO_4^-	0.00 ± 0.01	Reported by Ciavatta [1980CIA].
	NO_3^-	$-0.12 \pm 0.05^\dagger$	
$NiOH^+$	Cl^-	-0.01 ± 0.07	Evaluated in [2005GAM/BUG] (Section V.3.1.1) for the reaction Ni^{2+} +
	ClO_4^-	0.14 ± 0.07	$H_2O \rightleftharpoons NiOH^+ + H^+$ from $\Delta\varepsilon$ in chloride media/perchlorate media.
	NO_3^-	—	
NiF^+	Cl^-	—	
	ClO_4^-	0.34 ± 0.08	Derived from $\Delta\varepsilon = \varepsilon(NiF^+, ClO_4^-) - \varepsilon(Ni^{2+}, ClO_4^-) - \varepsilon(Na^+, F^-) =$
			$-(0.049 \pm 0.060)$ kg·mol^{-1} (see Section V.4.2.3 of [2005GAM/BUG]).
	NO_3^-	—	
$NiCl^+$	Cl^-	—	
	ClO_4^-	0.47 ± 0.06	See details in Section V.4.2.4 of [2005GAM/BUG].
	NO_3^-	—	

(Continued on next page)

Table 4 (continued)

j	k	$\varepsilon(j,k)$	Comments
$NiNO_3^+$	Cl^-	—	
	ClO_4^-	0.44 ± 0.14	See details in Section V.6.1.2 of [2005GAM/BUG], specially sub-section V.6.1.2.1 for an alternative treatment of this system.
	NO_3^-	—	
$Ni(H_2cit)^+$	Cl^-	—	
	ClO_4^-	0.12 ± 0.50	See Section VII.7 in [2005HUM/AND].
	NO_3^-	—	
$NiBr^+$	Cl^-	—	
	ClO_4^-	0.59 ± 0.10	See details in [2005GAM/BUG], *cf.* Section V.4.2.5, specially sub-section V.4.2.5.1 for an alternative treatment of this system.
	NO_3^-	—	
$NiHS^+$	Cl^-	—	
	ClO_4^-	-0.85 ± 0.39	See details in [2005GAM/BUG], Section V.5.1.1.2.
	NO_3^-	—	
$NiSCN^+$	Cl^-	—	
	ClO_4^-	0.31 ± 0.04	Derived from $\Delta\varepsilon = \varepsilon(NiSCN^+,ClO_4^-) - \varepsilon(Na^+,SCN^-) - \varepsilon(Ni^{2+},ClO_4^-) = -(0.109\pm0.025)\,kg\cdot mol^{-1}$ (see [2005GAM/BUG], Section V.7.1.3.1).
	NO_3^-	—	
$Fe(OH)_2^+$	Cl^-	—	
	ClO_4^-	0.37 ± 0.18	Determined in Section VII.1.3.1 of [2013LEM/BER]..
	NO_3^-	—	
FeF^+	Cl^-	—	
	ClO_4^-	0.34 ± 0.07	Determined in Section VIII.2.1.3 of [2013LEM/BER].
	NO_3^-	—	
$FeCl_2^+$	Cl^-	—	
	ClO_4^-	0.52 ± 0.05	Determined in Section VIII.2.3.2.2.1 of [2013LEM/BER]..
	NO_3^-	—	
$FeSO_4^+$	Cl^-	—	
	ClO_4^-	0.4 ± 0.1	Determined in Section IX.1.2.1.4.1 of [2013LEM/BER]..
	NO_3^-	—	
YCO_3^+	Cl^-	—	
	ClO_4^-	0.17 ± 0.04	Taken from Spahiu [1983SPA].
	NO_3^-	—	

Table 4 (continued)

j	k	$\varepsilon(j,k)$	Comments
$Am(OH)_2^+$	Cl^-	-0.27 ± 0.20	Evaluated in [2003GUI/FAN] (*cf.* Section 12.3.1.1) from $\Delta\varepsilon$ (in NaCl solution) for the reactions $An^{3+} + nH_2O(l) \rightleftharpoons An(OH)_n^{(3-n)} + nH^+$ (An = Am, Cm).
	ClO_4^-	0.17 ± 0.04	Estimated in [1995SIL/BID].
	NO_3^-	—	
AmF_2^+	Cl^-	—	
	ClO_4^-	0.17 ± 0.04	Estimated in [1995SIL/BID].
	NO_3^-	—	
$AmSO_4^+$	Cl^-	—	
	ClO_4^-	0.22 ± 0.08	Evaluated in [1995SIL/BID].
	NO_3^-	—	
$AmCO_3^+$	Cl^-	0.01 ± 0.05	Evaluated in [2003GUI/FAN] (Section 12.6.1.1.1) from $\Delta\varepsilon$ (in NaCl solution) for the reactions $An^{3+} + nCO_3^{2-} \rightleftharpoons An(CO_3)_n^{(3-2n)}$ (based on $\varepsilon(Am^{3+}, Cl^-) = (0.23 \pm 0.02)$ kg·mol^{-1} and $\varepsilon(Na^+, CO_3^{2-}) = -(0.08 \pm 0.03)$ kg·mol^{-1}.
	ClO_4^-	0.17 ± 0.04	Estimated in [1995SIL/BID].
	NO_3^-	—	
$Am(ox)^+$	Cl^-	—	
	ClO_4^-	0.08 ± 0.10	See Section VI.13 of [2005HUM/AND].
	NO_3^-	—	
PuO_2^+	Cl^-	—	
	ClO_4^-	0.24 ± 0.05	Derived from $\Delta\varepsilon = \varepsilon(PuO_2^{2+}, ClO_4^-) - \varepsilon(PuO_2^+, ClO_4^-) = (0.22 \pm 0.03)$ kg·mol^{-1} [1995CAP/VIT]. In [1992GRE/FUG], $\varepsilon(PuO_2^+, ClO_4^-) = (0.17 \pm 0.05)$ kg·mol^{-1} was tabulated based on [1989ROB], [1989RIG/ROB] and [1990RIG]. Capdevila and Vitorge's data [1992CAP], [1994CAP/VIT] and [1995CAP/VIT] were unavailable at that time.
	NO_3^-	—	
PuO_2F^+	Cl^-	—	
	ClO_4^-	0.29 ± 0.11	Estimated in [2001LEM/FUG] by analogy with $\Delta\varepsilon$ of the corresponding Np(IV) reaction.
	NO_3^-	—	
PuO_2Cl^+	Cl^-	—	
	ClO_4^-	0.50 ± 0.09	From $\Delta\varepsilon$ evaluated by Giffaut [1994GIF].
	NO_3^-	—	

Table 4 (continued)

j	k	$\varepsilon(j,k)$	Comments
NpO_2^+	Cl^-	0.09 ± 0.05	See Section 12.1 of [2001LEM/FUG].
	ClO_4^-	0.25 ± 0.05	Derived from $\Delta\varepsilon = \varepsilon(NpO_2^{2+}, ClO_4^-) - \varepsilon(NpO_2^+, ClO_4^-) = (0.21 \pm 0.03)$ $kg \cdot mol^{-1}$ [1987RIG/VIT], [1989RIG/ROB] and [1990RIG].
	NO_3^-	—	
NpO_2OH^+	Cl^-	—	
	ClO_4^-	-0.06 ± 0.40	Estimated in [2001LEM/FUG].
	NO_3^-	—	
$(NpO_2)_3(OH)_5^+$	Cl^-	—	
	ClO_4^-	0.45 ± 0.20	See Section 8.1.2 of [2001LEM/FUG].
	NO_3^-	—	
NpO_2F^+	Cl^-	—	
	ClO_4^-	0.29 ± 0.12	Estimated in [2001LEM/FUG] by analogy with $\Delta\varepsilon$ of the corresponding U(IV) reaction.
	NO_3^-	—	
NpO_2Cl^+	Cl^-	—	
	ClO_4^-	0.50 ± 0.14	Estimated in [2001LEM/FUG] by analogy with $\Delta\varepsilon$ of the corresponding Pu(VI) reaction.
	NO_3^-	—	
$NpO_2IO_3^+$	Cl^-	—	
	ClO_4^-	0.33 ± 0.04	Estimated in [2001LEM/FUG] by assuming $\varepsilon(NpO_2IO_3^+, ClO_4^-) \approx \varepsilon(UO_2IO_3^+, ClO_4^-)$.
	NO_3^-	—	
$Np(SCN)_3^+$	Cl^-	—	
	ClO_4^-	0.17 ± 0.04	Estimated in [2001LEM/FUG] by assuming $\varepsilon(Np(SCN)_3^+, ClO_4^-) \approx \varepsilon(AmF_2^+, ClO_4^-)$.
	NO_3^-	—	
UO_2^+	Cl^-	—	
	ClO_4^-	0.26 ± 0.03	Evaluated in [1992GRE/FUG], using $\varepsilon(UO_2^{2+}, ClO_4^-) = (0.46 \pm 0.03)$ $kg \cdot mol^{-1}$.
	NO_3^-	—	
UO_2OH^+	Cl^-	—	
	ClO_4^-	-0.06 ± 0.40	Evaluated in [1992GRE/FUG], using $\varepsilon(UO_2^{2+}, X) = (0.46 \pm 0.03)$ $kg \cdot mol^{-1}$, where $X = Cl^-, ClO_4^-$ and NO_3^-.
	NO_3^-	0.51 ± 1.4	
$(UO_2)_3(OH)_5^+$	Cl^-	0.81 ± 0.17	
	ClO_4^-	0.45 ± 0.15	Evaluated in [1992GRE/FUG], using $\varepsilon(UO_2^{2+}, X) = (0.46 \pm 0.03)$ $kg \cdot mol^{-1}$, where $X = Cl^-, ClO_4^-$ and NO_3^-.
	NO_3^-	0.41 ± 0.22	

Table 4 (continued)

j	k	$\varepsilon(j,k)$	Comments
UF_3^+	Cl^-	0.1 ± 0.1	Estimated in [1992GRE/FUG].
	ClO_4^-	0.1 ± 0.1	
	NO_3^-	—	
UO_2F^+	Cl^-	0.04 ± 0.07	Taken from Riglet *et al.* [1989RIG/ROB], where the following assumptions were made: $\varepsilon(Np^{3+}, ClO_4^-) \approx \varepsilon(Pu^{3+}, ClO_4^-) = 0.49$ kg·mol^{-1} as for other (M^{3+}, ClO_4^-) interactions, and $\varepsilon(NpO_2^{2+}, ClO_4^-) \approx \varepsilon(PuO_2^{2+}, ClO_4^-) \approx \varepsilon(UO_2^{2+}, ClO_4^-) = 0.46$ kg·mol^{-1}.
	ClO_4^-	0.28 ± 0.04	See Section 9.4.2.2.1 of [2003GUI/FAN].
	NO_3^-	—	
UO_2Cl^+	Cl^-	—	
	ClO_4^-	0.33 ± 0.04	Evaluated in [1992GRE/FUG], using $\varepsilon(UO_2^{2+}, X) = (0.46 \pm 0.03)$ kg·mol^{-1}, where X = Cl^-, ClO_4^- and NO_3^-.
	NO_3^-	—	
$UO_2ClO_3^+$	Cl^-	—	
	ClO_4^-	0.33 ± 0.04	Estimated in [1992GRE/FUG].
	NO_3^-	—	
UO_2Br^+	Cl^-	—	
	ClO_4^-	0.24 ± 0.04	Estimated in [1992GRE/FUG].
	NO_3^-	—	
$UO_2BrO_3^+$	Cl^-	—	
	ClO_4^-	0.33 ± 0.04	Estimated in [1992GRE/FUG].
	NO_3^-	—	
$UO_2IO_3^+$	Cl^-	—	
	ClO_4^-	0.33 ± 0.04	Estimated in [1992GRE/FUG].
	NO_3^-	—	
$UO_2N_3^+$	Cl^-	—	
	ClO_4^-	0.3 ± 0.1	Estimated in [1992GRE/FUG].
	NO_3^-	—	
$UO_2NO_3^+$	Cl^-	—	
	ClO_4^-	0.33 ± 0.04	Estimated in [1992GRE/FUG].
	NO_3^-	—	
UO_2SCN^+	Cl^-	—	
	ClO_4^-	0.22 ± 0.04	Estimated in [1992GRE/FUG].
	NO_3^-	—	

Table 4 (continued)

j	k	$\varepsilon(j,k)$	Comments
$Th(OH)_3^+$	Cl^-	0.06 ± 0.05	
	ClO_4^-	0.15 ± 0.10	See Table VII-16 in Section VII.3.6.1 of [2008RAN/FUG].
	NO_3^-	0.05 ± 0.15	
ThF_3^+	Cl^-	—	
	ClO_4^-	0.1 ± 0.1	See Table VIII-8 in Section VIII.1.2.1 of [2008RAN/FUG].
	NO_3^-	0.0 ± 0.2	
$Th(NO_3)_3^+$	Cl^-	—	
	ClO_4^-	0.25 ± 0.15	Evaluated in Section X.1.3.3 of [2008RAN/FUG], using $\varepsilon(Th^{4+},X) =$
	NO_3^-	0.25 ± 0.15	(0.70 ± 0.10) kg·mol^{-1} where X = ClO_4^- and NO_3^-.
H_6edta^{2+}	Cl^-	-0.20 ± 0.16	
	ClO_4^-	-0.20 ± 0.16	Evaluated in [2005HUM/AND] (Section VIII.3.7).
	NO_3^-	-0.20 ± 0.16	
Sn^{2+}	Cl^-	0.19 ± 0.04	See Section VI.2.1 of [2013LEM/BER].
	ClO_4^-	0.19 ± 0.04	See Section VI.2.1 of [2013LEM/BER].
	NO_3^-	—	
$Sn_3(OH)_4^{2+}$	Cl^-	—	
	ClO_4^-	-0.02 ± 0.16	See Section VII.1.1 of [2013LEM/BER].
	NO_3^-	—	
Pb^{2+}	Cl^-	—	
	ClO_4^-	0.15 ± 0.02	Reported by Ciavatta [1980CIA].
	NO_3^-	$-0.20 \pm 0.12^\dagger$	
$AlOH^{2+}$	Cl^-	0.09	Taken from Hedlund [1988HED].
	ClO_4^-	0.31	
	NO_3^-	—	
$Al_2CO_3(OH)_2^{2+}$	Cl^-	0.26	Taken from Hedlund [1988HED].
	ClO_4^-	—	
	NO_3^-	—	
Zn^{2+}	Cl^-	—	
	ClO_4^-	0.33 ± 0.03	Reported by Ciavatta [1980CIA].
	NO_3^-	0.16 ± 0.02	
$ZnCO_3^{2+}$	Cl^-	0.35 ± 0.05	Taken from Ferri *et al.* [1985FER/GRE].
	ClO_4^-	—	
	NO_3^-	—	
Cd^{2+}	Cl^-	—	
	ClO_4^-	—	
	NO_3^-	0.09 ± 0.02	Reported by Ciavatta [1980CIA].

Table 4 (continued)

j	*k*	$\varepsilon(j,k)$	Comments
Hg^{2+}	Cl^-	—	
	ClO_4^-	0.34 ± 0.03	Reported by Ciavatta [1980CIA].
	NO_3^-	$-0.1 \pm 0.1^\dagger$	
Hg_2^{2+}	Cl^-	—	
	ClO_4^-	0.09 ± 0.02	Reported by Ciavatta [1980CIA].
	NO_3^-	$-0.2 \pm 0.1^\dagger$	
Cu^{2+}	Cl^-	0.08 ± 0.01	
	ClO_4^-	0.32 ± 0.02	Reported by Ciavatta [1980CIA].
	NO_3^-	0.11 ± 0.01	
Ni^{2+}	Cl^-	0.17 ± 0.02	Reported by Ciavatta [1980CIA].
	ClO_4^-	0.370 ± 0.032	Derived from the ionic strength dependence of the osmotic and mean activity coefficient of $Ni(ClO_4)_2$ solution ([2005GAM/BUG], Section V.4.3).
	NO_3^-	0.182 ± 0.010	Derived from the ionic strength dependence of the osmotic and mean activity coefficient of $Ni(NO_3)_2$ solution ([2005GAM/BUG], Section V.6.1.2.1).
Co^{2+}	Cl^-	0.16 ± 0.02	
	ClO_4^-	0.34 ± 0.03	Reported by Ciavatta [1980CIA].
	NO_3^-	0.14 ± 0.01	
Fe^{2+}	Cl^-	0.17 ± 0.01	Determined in Section VI.4.3 of [2013LEM/BER].
	ClO_4^-	0.37 ± 0.04	Determined in Section VI.4.4 of [2013LEM/BER].
	NO_3^-	—	
$FeOH^{2+}$	Cl^-	—	
	ClO_4^-	0.46 ± 0.09	Section VII.1.3.1 of [2013LEM/BER]
	NO_3^-	—	
$FeCl^{2+}$	Cl^-	0.64 ± 0.06	Determined in Section VIII.2.3.1.3 of [2013LEM/BER].
	ClO_4^-	0.63 ± 0.05	Determined in Section VIII.2.3.2.2.1 of [2013LEM/BER].
	NO_3^-	—	
$FeSCN^{2+}$	Cl^-	—	
	ClO_4^-	0.45	Taken from Spahiu [1983SPA].
	NO_3^-	—	
Mn^{2+}	Cl^-	0.13 ± 0.01	Reported by Ciavatta [1980CIA].
	ClO_4^-	—	
	NO_3^-	—	
$YHCO_3^{2+}$	Cl^-	—	
	ClO_4^-	0.39 ± 0.04	Taken from Spahiu [1983SPA].
	NO_3^-	—	

(Continued on next page)

Table 4 (continued)

j	k	$\varepsilon(j,k)$	Comments
$AmOH^{2+}$	Cl^-	-0.04 ± 0.07	Evaluated in [2003GUI/FAN] (*cf.* Section 12.3.1.1) from $\Delta\varepsilon$ (in NaCl solution) for the reactions $An^{3+} + n\,H_2O(l) \rightleftharpoons An(OH)_n^{(3-n)} + n\,H^+$.
	ClO_4^-	0.39 ± 0.04	Estimated in [1995SIL/BID].
	NO_3^-	—	
AmF^{2+}	Cl^-	—	
	ClO_4^-	0.39 ± 0.04	Estimated in [1995SIL/BID].
	NO_3^-	—	
$AmCl^{2+}$	Cl^-	—	
	ClO_4^-	0.39 ± 0.04	Estimated in [1995SIL/BID].
	NO_3^-	—	
AmN_3^{2+}	Cl^-	—	
	ClO_4^-	0.39 ± 0.04	Estimated in [1995SIL/BID].
	NO_3^-	—	
$AmNO_2^{2+}$	Cl^-	—	
	ClO_4^-	0.39 ± 0.04	Estimated in [1995SIL/BID].
	NO_3^-	—	
$AmNO_3^{2+}$	Cl^-	—	
	ClO_4^-	0.39 ± 0.04	Estimated in [1995SIL/BID].
	NO_3^-	—	
$AmH_2PO_4^{2+}$	Cl^-	—	
	ClO_4^-	0.39 ± 0.04	Estimated in [1995SIL/BID].
	NO_3^-	—	
$AmSCN^{2+}$	Cl^-	—	
	ClO_4^-	0.39 ± 0.04	Estimated in [1995SIL/BID].
	NO_3^-	—	
PuO_2^{2+}	Cl^-	—	
	ClO_4^-	0.46 ± 0.05	By analogy with $\varepsilon(UO_2^{2+}, ClO_4^-)$ as derived from isopiestic measurements in [1992GRE/FUG]. The uncertainty is increased because the value is estimated by analogy.
	NO_3^-	—	
PuF_2^{2+}	Cl^-	—	
	ClO_4^-	0.36 ± 0.17	Estimated in [2001LEM/FUG] by analogy with $\Delta\varepsilon$ of the corresponding U(IV) reaction.
	NO_3^-	—	

Table 4 (continued)

j	k	$\varepsilon(j,k)$	Comments
$PuCl^{2+}$	Cl^-	—	
	ClO_4^-	0.39 ± 0.16	Estimated in [2001LEM/FUG] by analogy with $\Delta\varepsilon$ of the corresponding Am(III) reaction.
	NO_3^-	—	
PuI^{2+}	Cl^-	—	
	ClO_4^-	0.39 ± 0.04	Estimated in [2001LEM/FUG] by assuming $\varepsilon(PuI^{2+}, ClO_4^-) \approx \varepsilon(AmSCN^{2+}, ClO_4^-)$ and $\varepsilon(NH_4^+, I^-) \approx \varepsilon(Na^+, SCN^-)$.
	NO_3^-	—	
$PuSCN^{2+}$	Cl^-	—	
	ClO_4^-	0.39 ± 0.04	Estimated in [2001LEM/FUG] by assuming $\varepsilon(PuSCN^{2+}, ClO_4^-) \approx \varepsilon(AmSCN^{2+}, ClO_4^-)$.
	NO_3^-	—	
NpO_2^{2+}	Cl^-	—	
	ClO_4^-	0.46 ± 0.05	By analogy with $\varepsilon(UO_2^{2+}, ClO_4^-)$ as derived from isopiestic measurements noted in [1992GRE/FUG]. The uncertainty is increased because the value is estimated by analogy.
	NO_3^-	—	
$(NpO_2)_2(OH)_2^{2+}$	Cl^-	—	
	ClO_4^-	0.57 ± 0.10	See Section 8.1.2 in [2001LEM/FUG].
	NO_3^-	—	
NpF_2^{2+}	Cl^-	—	
	ClO_4^-	0.38 ± 0.17	Estimated in [2001LEM/FUG] by analogy with $\Delta\varepsilon$ of the corresponding U(IV) reaction.
	NO_3^-	—	
$NpSO_4^{2+}$	Cl^-	—	
	ClO_4^-	0.48 ± 0.11	Estimated on Section 10.1.2.1 of [2001LEM/FUG].
	NO_3^-	—	
$Np(SCN)_2^{2+}$	Cl^-	—	
	ClO_4^-	0.38 ± 0.20	Estimated in [2001LEM/FUG] by analogy with $\Delta\varepsilon$ of the corresponding U(IV) reaction.
	NO_3^-	—	
UO_2^{2+}	Cl^-	0.21 ± 0.02	Reported by Ciavatta [1980CIA].
	ClO_4^-	0.46 ± 0.03	Reported by Ciavatta [1980CIA].
	NO_3^-	0.24 ± 0.03	Reported by Ciavatta [1980CIA].
			These coefficients were not used in [1992GRE/FUG] because they were evaluated by Ciavatta [1980CIA] without taking chloride and nitrate complexation into account. Instead, Grenthe *et al.* used $\varepsilon(UO_2^{2+}, X) = (0.46 \pm 0.03)$ kg·mol^{-1}, for X = Cl^-, ClO_4^- and NO_3^-.

Table 4 (continued)

j	k	$\varepsilon(j,k)$	Comments
$(UO_2)_2(OH)_2^{2+}$	Cl^-	0.69 ± 0.07	Evaluated in [1992GRE/FUG], using $\varepsilon(UO_2^{2+}, X) = (0.46 \pm 0.03)$ $kg \cdot mol^{-1}$, where $X = Cl^-$, ClO_4^- and NO_3^-.
	ClO_4^-	0.57 ± 0.07	
	NO_3^-	0.49 ± 0.09	
$(UO_2)_3(OH)_4^{2+}$	Cl^-	0.50 ± 0.18	Evaluated in [1992GRE/FUG], using $\varepsilon(UO_2^{2+}, X) = (0.46 \pm 0.03)$ $kg \cdot mol^{-1}$, where $X = Cl^-$, ClO_4^- and NO_3^-.
	ClO_4^-	0.89 ± 0.23	
	NO_3^-	0.72 ± 1.0	
UF_2^{2+}	Cl^-	—	
	ClO_4^-	0.3 ± 0.1	Estimated in [1992GRE/FUG].
	NO_3^-	—	
USO_4^{2+}	Cl^-	—	
	ClO_4^-	0.3 ± 0.1	Estimated in [1992GRE/FUG].
	NO_3^-	—	
$U(NO_3)_2^{2+}$	Cl^-	—	
	ClO_4^-	0.49 ± 0.14	Evaluated in [1992GRE/FUG] using $\varepsilon(U^{4+}, ClO_4^-) = (0.76 \pm 0.06)$ $kg \cdot mol^{-1}$.
	NO_3^-	—	
$Th(OH)_2^{2+}$	Cl^-	0.13 ± 0.05	Calculated in Section VII.3.6.1 of [2008RAN/FUG].
	ClO_4^-	0.33 ± 0.10	
	NO_3^-	0.10 ± 0.15	
ThF_2^{2+}	Cl^-	—	See Table VIII-8 in Section VIII.1.2.1 of [2008RAN/FUG].
	ClO_4^-	0.3 ± 0.1	
	NO_3^-	0.15 ± 0.20	
$ThSO_4^{2+}$	Cl^-	0.14 ± 0.15	See Section IX.1.3.2 of [2008RAN/FUG].
	ClO_4^-	0.3 ± 0.1	
	NO_3^-	—	
$Th(N_3)_2^{2+}$	Cl^-	—	
	ClO_4^-	0.40 ± 0.15	Estimated in Section X.1.2 of [2008RAN/FUG].
	NO_3^-	—	
$Th(NO_3)_2^{2+}$	Cl^-	—	Estimated in Section X.1.3.3 of [2008RAN/FUG], using $\varepsilon(Th^{4+}, X) =$ (0.70 ± 0.10) $kg \cdot mol^{-1}$ for $X = ClO_4^-$ and NO_3^-.
	ClO_4^-	0.43 ± 0.18	
	NO_3^-	0.43 ± 0.18	
$Th(H_2PO_4)_2^{2+}$	Cl^-	—	
	ClO_4^-	0.4 ± 0.1	Estimated in Section X.2.3.2 of [2008RAN/FUG].
	NO_3^-	—	

Table 4 (continued)

j	k	$\varepsilon(j,k)$	Comments
$Th(SCN)_2^{2+}$	Cl^-	—	
	ClO_4^-	0.38 ± 0.20	See Section XI.1.3.6.1 of [2008RAN/FUG].
	NO_3^-	—	
Be^{2+}	Cl^-	—	
	ClO_4^-	0.30 ± 0.04	Taken from [1986BRU], where it appears to have been based on the average of the values for $\varepsilon(Mg^{2+}, ClO_4^-)$ and $\varepsilon(Ca^{2+}, ClO_4^-)$ [1980CIA].
	NO_3^-	—	
Mg^{2+}	Cl^-	0.19 ± 0.02	
	ClO_4^-	0.33 ± 0.03	Reported by Ciavatta [1980CIA].
	NO_3^-	0.17 ± 0.01	
Ca^{2+}	Cl^-	0.14 ± 0.01	
	ClO_4^-	0.27 ± 0.03	Reported by Ciavatta [1980CIA].
	NO_3^-	0.02 ± 0.01	
Ba^{2+}	Cl^-	0.07 ± 0.01	
	ClO_4^-	0.15 ± 0.02	Reported by Ciavatta [1980CIA].
	NO_3^-	-0.28 ± 0.03	
Al^{3+}	Cl^-	0.33 ± 0.02	Reported by Ciavatta [1980CIA].
	ClO_4^-	—	
	NO_3^-	—	
Ni_2OH^{3+}	Cl^-	—	
	ClO_4^-	0.59 ± 0.15	By assuming $\varepsilon(Ni_2OH^{3+},ClO_4^-) \approx \varepsilon(Be_2OH^{3+},ClO_4^-)$, see Section V.3.1.1 in [2005GAM/BUG].
	NO_3^-	—	
Fe^{3+}	Cl^-	0.76 ± 0.03	Determined in Section VI.4.2.2 of [2013LEM/BER].
	ClO_4^-	0.73 ± 0.04	Determined in Sections VI.1.2.1.1.1 and VI.4.1 of [2013LEM/BER].
	NO_3^-	—	
Cr^{3+}	Cl^-	0.30 ± 0.03	Reported by Ciavatta [1980CIA].
	ClO_4^-	—	
	NO_3^-	0.27 ± 0.02	Reported by Ciavatta [1980CIA].
La^{3+}	Cl^-	0.22 ± 0.02	
	ClO_4^-	0.47 ± 0.03	Reported by Ciavatta [1980CIA].
	NO_3^-	—	
$La^{3+} \rightarrow Lu^{3+}$	Cl^-	—	
	ClO_4^-	$0.47 \rightarrow 0.52$	Taken from Spahiu [1983SPA].
	NO_3^-	—	

Table 4 (continued)

j	*k*	$\varepsilon(j,k)$	Comments
Am^{3+}	Cl^-	0.23 ± 0.02	The $\varepsilon(An^{3+}, Cl^-)$ for An = Am and Cm is assumed to be equal to $\varepsilon(Nd^{3+}, Cl^-)$ which is calculated from trace activity coefficients of Nd^{3+} ion in 0 −4 m NaCl. These trace activity coefficients are based on the Pitzer ion interaction parameters evaluated in [1997KON/FAN] from osmotic coefficients in aqueous $NdCl_3 - NaCl$ and $NdCl_3 - CaCl_2$.
	ClO_4^-	0.49 ± 0.03	Estimated in [1995SIL/BID].
	NO_3^-	—	
Pu^{3+}	Cl^-	—	
	ClO_4^-	0.49 ± 0.05	Estimated by analogy with $\varepsilon(Ho^{3+}, ClO_4^-)$ [1983SPA] as in [1992GRE/FUG], [1995SIL/BID]. The uncertainty is increased because the value is estimated by analogy.
	NO_3^-	—	
$PuOH^{3+}$	Cl^-	—	
	ClO_4^-	0.50 ± 0.05	Estimated in [2001LEM/FUG].
	NO_3^-	—	
PuF^{3+}	Cl^-	—	
	ClO_4^-	0.56 ± 0.11	Estimated in [2001LEM/FUG].
	NO_3^-	—	
$PuCl^{3+}$	Cl^-	—	
	ClO_4^-	0.85 ± 0.09	Derived from the $\Delta\varepsilon$ evaluated in [2001LEM/FUG].
	NO_3^-	—	
$PuBr^{3+}$	Cl^-	—	
	ClO_4^-	0.58 ± 0.16	Estimated in [2001LEM/FUG] by analogy with $\Delta\varepsilon$ of the corresponding U(IV) reaction, and by assuming $\varepsilon(H^+, Br^-) \approx \varepsilon(Na^+, Br^-)$.
	NO_3^-	—	
Np^{3+}	Cl^-	—	
	ClO_4^-	0.49 ± 0.05	Estimated by analogy with $\varepsilon(Ho^{3+}, ClO_4^-)$ [1983SPA] as in previous books in this series [1992GRE/FUG], [1995SIL/BID]. The uncertainty is increased because the value is estimated by analogy.
	NO_3^-	—	
$NpOH^{3+}$	Cl^-	—	
	ClO_4^-	0.50 ± 0.05	Estimated in [2001LEM/FUG].
	NO_3^-	—	
NpF^{3+}	Cl^-	—	
	ClO_4^-	0.58 ± 0.07	Evaluated in [2001LEM/FUG].
	NO_3^-	—	

(Continued on next page)

Table 4 (continued)

j	k	$\varepsilon(j,k)$	Comments
$NpCl^{3+}$	Cl^-	—	
	ClO_4^-	0.81 ± 0.09	Derived from the $\Delta\varepsilon$ selected in [2001LEM/FUG].
	NO_3^-	—	
NpI^{3+}	Cl^-	—	
	ClO_4^-	0.77 ± 0.26	Estimated in [2001LEM/FUG] by analogy with $\Delta\varepsilon$ of the corresponding Np(IV) chloride reaction, and by assuming $\varepsilon(H^+,I^-) \approx \varepsilon(Na^+,I^-)$.
	NO_3^-	—	
$NpSCN^{3+}$	Cl^-	0.76 ± 0.12	Estimated in [2001LEM/FUG] by analogy with $\Delta\varepsilon$ of the corresponding U(IV) reaction.
	ClO_4^-	—	
	NO_3^-	—	
U^{3+}	Cl^-	—	
	ClO_4^-	0.49 ± 0.05	Evaluated in [2001LEM/FUG] by analogy with $\varepsilon(Am^{3+}, ClO_4^-)$.
	NO_3^-	—	
UOH^{3+}	Cl^-	—	
	ClO_4^-	0.48 ± 0.08	Evaluated in [1992GRE/FUG].
	NO_3^-	—	
UF^{3+}	Cl^-	—	
	ClO_4^-	0.48 ± 0.08	Estimated in [1992GRE/FUG].
	NO_3^-	—	
UCl^{3+}	Cl^-	—	
	ClO_4^-	0.50 ± 0.10	Estimated in [2003GUI/FAN].
	NO_3^-	—	
UBr^{3+}	Cl^-	—	
	ClO_4^-	0.52 ± 0.10	Estimated in [1992GRE/FUG] using $\varepsilon(U^{4+},X) = (0.76 \pm 0.06)$ kg·mol^{-1}, for $X = Br^-$ and ClO_4^-.
	NO_3^-	—	
UI^{3+}	Cl^-	—	
	ClO_4^-	0.55 ± 0.10	Estimated in [1992GRE/FUG] using $\varepsilon(U^{4+},X) = (0.76 \pm 0.06)$ kg·mol^{-1}, for $X = I^-$ and ClO_4^-.
	NO_3^-	—	
UNO_3^{3+}	Cl^-	—	
	ClO_4^-	0.62 ± 0.08	Evaluated in [1992GRE/FUG] using $\varepsilon(U^{4+},X) = (0.76 \pm 0.06)$ kg·mol^{-1} for $X = NO_3^-$ and ClO_4^-.
	NO_3^-	—	

Table 4 (continued)

j	k	$\varepsilon(j,k)$	Comments
$ThOH^{3+}$	Cl^-	0.19 ± 0.05	
	ClO_4^-	0.48 ± 0.08	See Table VII-18 in Section VII.3.6.1 of [2008RAN/FUG].
	NO_3^-	0.20 ± 0.15	
ThF^{3+}	Cl^-	—	
	ClO_4^-	0.48 ± 0.08	Estimated in Section VIII.1.2.1 of [2008RAN/FUG]
	NO_3^-	0.25 ± 0.20	(Table VIII-8).
$ThCl^{3+}$	Cl^-	0.62 ± 0.11	Calculated in Section VIII.2.2.1.2 of [2008RAN/FUG] using
	ClO_4^-	0.62 ± 0.11	$\varepsilon(Th^{4+}, X) = (0.70 \pm 0.10)$ kg·mol^{-1}, for X = Cl$^-$ and ClO$_4^-$
	NO_3^-	—	
$ThClO_3^{3+}$	Cl^-	—	
	ClO_4^-	0.62 ± 0.11	Calculated in Section VIII.2.2.2 of [2008RAN/FUG] using
			$\varepsilon(Th^{4+}, X) = (0.70 \pm 0.10)$ kg·mol^{-1}, for X = ClO$_3^-$ and ClO$_4^-$
	NO_3^-	—	
$ThBr^{3+}$	Cl^-	—	
	ClO_4^-	0.62 ± 0.11	Calculated in Section VIII.3.2.1 of [2008RAN/FUG] using
			$\varepsilon(Th^{4+}, X) = (0.70 \pm 0.10)$ kg·mol^{-1}, for X = Br$^-$ and ClO$_4^-$
	NO_3^-	—	
$ThBrO_3^{3+}$	Cl^-	—	
	ClO_4^-	0.62 ± 0.08	Calculated in Section VIII.3.2.2 of [2008RAN/FUG] using
			$\varepsilon(Th^{4+}, X) = (0.70 \pm 0.10)$ kg·mol^{-1}, for X = BrO$_3^-$ and ClO$_4^-$
	NO_3^-	—	
ThN_3^{3+}	Cl^-	—	
	ClO_4^-	0.55 ± 0.15	See Section X.1.2 of [2008RAN/FUG].
	NO_3^-	—	
$Th(NO_3)^{3+}$	Cl^-	—	
	ClO_4^-	0.56 ± 0.14	Calculated in Section X.1.3.3 of [2008RAN/FUG] using
	NO_3^-	0.56 ± 0.14	$\varepsilon(Th^{4+}, X) = (0.70 \pm 0.10)$ kg·mol^{-1}, for X = ClO$_4^-$ and NO$_3^-$.
$Th(H_2PO_4)^{3+}$	Cl^-	—	
	ClO_4^-	0.5 ± 0.1	Estimated in Section X.2.3.2 of [2008RAN/FUG].
	NO_3^-	—	
$Th(H_2PO_4)(H_3PO_4)^{3+}$	Cl^-	—	
	ClO_4^-	0.5 ± 0.1	Estimated in Section X.2.3.2 of [2008RAN/FUG].
	NO_3^-	—	
$Th(SCN)^{3+}$	Cl^-	—	
	ClO_4^-	0.50 ± 0.10	See Section XI.1.3.6.1 of [2008RAN/FUG].
	NO_3^-	—	

Table 4 (continued)

j	*k*	$\varepsilon(j,k)$	Comments
Be_2OH^{3+}	Cl^-	—	
	ClO_4^-	0.50 ± 0.05	Taken from [1986BRU], where the assumption was made that $\varepsilon(Be^{2+}, ClO_4^-) = 0.30$ kg·mol^{-1}, apparently based on the average of the values for $\varepsilon(Mg^{2+}, ClO_4^-)$ and $\varepsilon(Ca^{2+}, ClO_4^-)$ [1980CIA].
	NO_3^-	—	
$Be_3(OH)_3^{3+}$	Cl^-	—	
	ClO_4^-	0.51 ± 0.05	Taken from [1986BRU], where the assumption was made that $\varepsilon(Be^{2+}, ClO_4^-) = 0.30$ kg·mol^{-1}, apparently based on the average of the values for $\varepsilon(Mg^{2+}, ClO_4^-)$ and $\varepsilon(Ca^{2+}, ClO_4^-)$ [1980CIA].
	NO_3^-	—	
Sn^{4+}	Cl^-	—	
	ClO_4^-	0.7 ± 0.2	See Section VI.3.1 of [2013LEM/BER].
	NO_3^-	—	
$Al_3HCO_3(OH)_4^{4+}$	Cl^-	0.41	Taken from Hedlund [1988HED].
	ClO_4^-	—	
	NO_3^-	—	
$Ni_4(OH)_4^{4+}$	Cl^-	—	
	ClO_4^-	1.08 ± 0.08	Derived from $\Delta\varepsilon = 4\varepsilon(H^+, ClO_4^-) - \varepsilon(Ni_4OH_4^{4+}, ClO_4^-) - 4\varepsilon(Ni^{2+}, ClO_4^-) = (0.16 \pm 0.05)$ kg·mol^{-1} (see [2005GAM/BUG], Section V.3.1.1.1).
	NO_3^-	—	
$Fe_2(OH)_2^{4+}$	Cl^-	—	
	ClO_4^-	1.04 ± 0.09	Determined in Section VII.1.3.3 of [2013LEM/BER].
	NO_3^-	—	
$Y_2CO_3^{4+}$	Cl^-	—	
	ClO_4^-	0.80 ± 0.04	Taken from Spahiu [1983SPA].
	NO_3^-	—	
Pu^{4+}	Cl^-	0.37 ± 0.05	Calculated in Section VI.3.1 of [2008RAN/FUG].
	ClO_4^-	0.82 ± 0.07	Derived from $\Delta\varepsilon = \varepsilon(Pu^{4+}, ClO_4^-) - \varepsilon(Pu^{3+}, ClO_4^-) = (0.33 \pm 0.035)$ kg·mol^{-1} [1995CAP/VIT]. Uncertainty estimated in [2001LEM/FUG]. In the [1992GRE/FUG], $\varepsilon(Pu^{3+}, ClO_4^-) = (1.03 \pm 0.05)$ kg·mol^{-1} was tabulated based on references [1989ROB], [1989RIG/ROB], [1990RIG]. Capdevila and Vitorge's data [1992CAP], [1994CAP/VIT] and [1995CAP/VIT] were unavailable at that time.
	NO_3^-	—	

Table 4 (continued)

j	k	$\varepsilon(j,k)$	Comments
Np^{4+}	Cl^-	—	
	ClO_4^-	0.84 ± 0.06	Derived from $\Delta\varepsilon = \varepsilon(Np^{4+},ClO_4^-) - \varepsilon(Np^{3+},ClO_4^-) = (0.35 \pm 0.03)$ kg·mol^{-1} [1989ROB], [1989RIG/ROB], [1990RIG].
	NO_3^-	—	
U^{4+}	Cl^-	—	
	ClO_4^-	0.76 ± 0.06	Estimated in [1992GRE/FUG]. Using the measured value of $\Delta\varepsilon = \varepsilon(U^{4+},ClO_4^-) - \varepsilon(U^{3+},ClO_4^-) = (0.35 \pm 0.06)$ kg·mol^{-1} p.89 [1990RIG], where the uncertainty is recalculated in [2001LEM/FUG] from the data given in this thesis, and $\varepsilon(U^{3+},ClO_4^-) = (0.49 \pm 0.05)$ kg·mol^{-1}, a value for $\varepsilon(U^{4+},ClO_4^-)$ can be calculated in the same way as is done for $\varepsilon(Np^{4+},ClO_4^-)$ and $\varepsilon(Pu^{4+},ClO_4^-)$. This value, $\varepsilon(U^{4+},ClO_4^-) = (0.84 \pm 0.06)$ kg·mol^{-1} is consistent with that tabulated $\varepsilon(U^{4+},ClO_4^-) = (0.76 \pm 0.06)$ kg·mol^{-1}, since the uncertainties overlap. The authors of [2001LEM/FUG] do not believe that a change in the previously selected value for $\varepsilon(U^{4+},ClO_4^-)$ is justified at present.
	NO_3^-	—	
Th^{4+}	Cl^-	0.25 ± 0.03	Reported by Ciavatta [1980CIA].
	ClO_4^-	0.70 ± 0.10	Evaluated in Section VI.3.1 of [2008RAN/FUG].
	NO_3^-	0.31 ± 0.12	Evaluated in Section VI.3.1 of [2008RAN/FUG].
$Th_4(OH)_{12}^{4+}$	Cl^-	0.25 ± 0.20	
	ClO_4^-	0.56 ± 0.42	See Section VII.3.4.1.3 of [2008RAN/FUG].
	NO_3^-	0.42 ± 0.50	
$Th(H_3PO_4)^{4+}$	Cl^-	—	
	ClO_4^-	0.7 ± 0.1	Estimated in Section X.2.3.2 of [2008RAN/FUG].
	NO_3^-	—	
$Al_3(OH)_4^{5+}$	Cl^-	0.66	Taken from Hedlund [1988HED]
	ClO_4^-	1.30	Taken from Hedlund [1988HED]
	NO_3^-	—	
$Th_2(OH)_3^{5+}$	Cl^-	0.29 ± 0.09	
	ClO_4^-	0.91 ± 0.21	Calculated in Section VII.3.4.1.1 of [2008RAN/FUG].
	NO_3^-	0.69 ± 0.25	
$Th_2(OH)_2^{6+}$	Cl^-	0.40 ± 0.16	
	ClO_4^-	1.22 ± 0.24	Evaluated in Section VII.3.4.1.1 of [2008RAN/FUG].
	NO_3^-	0.69 ± 0.26	
$Th_4(OH)_8^{8+}$	Cl^-	0.70 ± 0.20	
	ClO_4^-	1.69 ± 0.42	Evaluated in Section VII.3.4.1.3 of [2008RAN/FUG].
	NO_3^-	1.59 ± 0.51	

Table 4 (continued)

j	k	$\varepsilon(j,k)$	Comments
$Th_6(OH)_{15}^{9+}$	Cl^-	0.72 ± 0.30	
	ClO_4^-	1.85 ± 0.74	See details in Section VII.3.4.1.4 of [2008RAN/FUG].
	NO_3^-	2.20 ± 0.77	
$Th_6(OH)_{14}^{10+}$	Cl^-	0.83 ± 0.30	
	ClO_4^-	2.2 ± 0.3	Estimated in Section VII.3.4.1.4 of [2008RAN/FUG].
	NO_3^-	2.9 ± 0.5	

Table 5: Ion interaction coefficients, $\varepsilon(j,k)$ (kg·mol^{-1}), for anions j with $k = $ Li$^+$, Na$^+$ and K$^+$. The uncertainties represent 95% confidence level. The ion interaction coefficients marked with † can be described more accurately with an ionic strength dependent function, listed in Table 6.

j	k	$\varepsilon(j,k)$	Comments
OH$^-$	Li$^+$	-0.02 ± 0.03†	
	Na$^+$	0.04 ± 0.01	Reported by Ciavatta [1980CIA].
	K$^+$	0.09 ± 0.01	
F$^-$	Li$^+$	—	
	Na$^+$	0.02 ± 0.02	Evaluated in [1992GRE/FUG].
	K$^+$	0.03 ± 0.02	[1988CIA]
HF$_2^-$	Li$^+$	—	
	Na$^+$	-0.11 ± 0.06	Evaluated in [1992GRE/FUG].
	K$^+$	—	
Cl$^-$	Li$^+$	0.10 ± 0.01	
	Na$^+$	0.03 ± 0.01	Reported by Ciavatta [1980CIA].
	K$^+$	0.00 ± 0.01	
ClO$_3^-$	Li$^+$	—	
	Na$^+$	-0.01 ± 0.02	Reported by Ciavatta [1980CIA].
	K$^+$	—	
ClO$_4^-$	Li$^+$	0.15 ± 0.01	
	Na$^+$	0.01 ± 0.01	Reported by Ciavatta [1980CIA].
	K$^+$	—	
Br$^-$	Li$^+$	0.13 ± 0.02	
	Na$^+$	0.05 ± 0.01	Reported by Ciavatta [1980CIA].
	K$^+$	0.01 ± 0.02	
BrO$_3^-$	Li$^+$	—	
	Na$^+$	-0.06 ± 0.02	Reported by Ciavatta [1980CIA].
	K$^+$	—	
I$^-$	Li$^+$	0.16 ± 0.01	
	Na$^+$	0.08 ± 0.02	Reported by Ciavatta [1980CIA].
	K$^+$	0.02 ± 0.01	
IO$_3^-$	Li$^+$	—	
	Na$^+$	-0.06 ± 0.02	Estimated in [1992GRE/FUG].
	K$^+$	—	

Table 5 (continued)

j	k	$\varepsilon(j,k)$	Comments
HSO_4^-	Li^+	— [4]	
	Na^+	-0.01 ± 0.02 [1]	Reported by Ciavatta [1980CIA].
	K^+	— [1]	
N_3^-	Li^+	—	
	Na^+	0.015 ± 0.020	See Section X.1.2 of [2008RAN/FUG].
	K^+	—	
NO_2^-	Li^+	0.06 ± 0.04†	
	Na^+	0.00 ± 0.02	Reported by Ciavatta [1980CIA].
	K^+	-0.04 ± 0.02	Reported by Ciavatta [1988CIA].
NO_3^-	Li^+	0.08 ± 0.01	Reported by Ciavatta [1980CIA].
	Na^+	-0.04 ± 0.03†	
	K^+	-0.11 ± 0.04†	
$H_2PO_4^-$	Li^+	—	
	Na^+	-0.08 ± 0.04†	
	K^+	-0.14 ± 0.04†	
HCO_3^-	Li^+	—	
	Na^+	0.00 ± 0.02	These values differ from those reported in [1992GRE/FUG]. See the discussion in [1995GRE/PUI]. Values for CO_3^{2-} and HCO_3^- are based on [1980CIA].
	K^+	-0.06 ± 0.05	Calculated in [2001LEM/FUG] from Pitzer coefficients [1998RAI/FEL].
Hox^-	Li^+	-0.28 ± 0.09	
	Na^+	-0.07 ± 0.01	Evaluated in Section VI.3.5 of [2005HUM/AND].
	K^+	-0.01 ± 0.08	
H_2cit^-	Li^+	-0.11 ± 0.03	
	Na^+	-0.05 ± 0.01	Evaluated in Section VII.3.6 of [2005HUM/AND].
	K^+	-0.04 ± 0.01	
CN^-	Li^+	—	
	Na^+	0.07 ± 0.03	As reported in [1992BAN/BLI].
	K^+	—	
SCN^-	Li^+	—	
	Na^+	0.05 ± 0.01	Reported by Ciavatta [1980CIA].
	K^+	-0.01 ± 0.01	

(Continued on next page)

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[4] No value is tabulated here for $\varepsilon(H^+, HSO_4^-)$; possible values are discussed in the footnote to the Appendix A entry for [1955LIS/RIV2].

Table 5 (continued)

j	k	$\varepsilon(j,k)$	Comments
HCOO$^-$	Li$^+$	—	
	Na$^+$	0.03 ± 0.01	Reported by Ciavatta [1980CIA].
	K$^+$	—	
CH$_3$COO$^-$	Li$^+$	0.05 ± 0.01	
	Na$^+$	0.08 ± 0.01	Reported by Ciavatta [1980CIA].
	K$^+$	0.09 ± 0.01	
H$_3$edta$^-$	Li$^+$	—	
	Na$^+$	-0.33 ± 0.14	Evaluated in Section VIII.3.7 of [2005HUM/AND].
	K$^+$	-0.14 ± 0.17	
SiO(OH)$_3^-$	Li$^+$	—	
	Na$^+$	-0.08 ± 0.03	Evaluated in [1992GRE/FUG].
	K$^+$	—	
Si$_2$O$_2$(OH)$_5^-$	Li$^+$	—	
	Na$^+$	-0.08 ± 0.04	Estimated in [1992GRE/FUG].
	K$^+$	—	
Sn(OH)$_3^-$	Li$^+$	—	
	Na$^+$	0.22 ± 0.03	See Section VII.1.1 of [2012GAM/GAJ].
	K$^+$	—	
SnCl$_3^-$	Li$^+$	—	
	Na$^+$	0.04 ± 0.07	See Section VIII.3.2.1 of [2012GAM/GAJ].
	K$^+$	—	
SnBr$_3^-$	Li$^+$	—	
	Na$^+$	0.16 ± 0.08	See Section VIII.3.3.1 of [2012GAM/GAJ].
	K$^+$	—	
B(OH)$_4^-$	Li$^+$	—	
	Na$^+$	-0.07 ± 0.05†	
	K$^+$	—	
Ni(SCN)$_3^-$	Li$^+$	—	
	Na$^+$	0.66 ± 0.13	Evaluated in [2005GAM/BUG] (see Section V.7.1.3.1).
	K$^+$	—	
Ni(cit)$^-$	Li$^+$	—	
	Na$^+$	0.22 ± 0.50	Evaluated in Section VII.7 of [2005HUM/AND].
	K$^+$	—	
Fe(SO$_4$)$_2^-$	Li$^+$	—	
	Na$^+$	0.24 ± 0.14	Estimated in Section IX.1.2.1.4.3 of [2013LEM/BER].
	K$^+$	—	

Table 5 (continued)

j	k	$\varepsilon(j,k)$	Comments
$Am(SO_4)_2^-$	Li^+	—	
	Na^+	-0.05 ± 0.05	Estimated in [1995SIL/BID].
	K^+	—	
$Am(CO_3)_2^-$	Li^+	—	
	Na^+	-0.14 ± 0.06	Evaluated inSection 12.6.1.1.1 [2003GUI/FAN], from $\Delta\varepsilon_n$ in NaCl solution for the reactions $An^{3+} + n\,CO_3^{2-} \rightleftharpoons An(CO_3)_n^{(3-2n)}$ (An = Am, Cm) based on $\varepsilon(Am^{3+}, Cl^-) = (0.23 \pm 0.02)$ kg·mol^{-1} and $\varepsilon(Na^+, CO_3^{2-}) = -(0.08 \pm 0.03)$ kg·mol^{-1}.
	K^+	—	
$Am(ox)_2^-$	Li^+	—	
	Na^+	-0.21 ± 0.08	Evaluated in Section VI.13 of [2005HUM/AND].
	K^+	—	
$Am(edta)^-$	Li^+	—	
	Na^+	0.01 ± 0.16	Evaluated in Section VIII.13.2.1 of [2005HUM/AND].
	K^+	0.01 ± 0.16	Estimated in [2005HUM/AND] Section VIII.13.2.1 by assuming $\varepsilon(K^+, Am(edta)^-) \approx \varepsilon(Na^+, Am(edta)^-)$.
$PuO_2CO_3^-$	Li^+	—	
	Na^+	-0.18 ± 0.18	Estimated in [2001LEM/FUG] by analogy with $\varepsilon(Na^+, NpO_2CO_3^-)$.
	K^+	—	
$Pu(edta)^-$	Li^+	—	
	Na^+	—	
	K^+	0.01 ± 0.16	Estimated in [2005HUM/AND], Section VIII.12.2.1 by assuming $\varepsilon(K^+, Pu(edta)^-) \approx \varepsilon(Na^+, Am(edta)^-)$.
$NpO_2(OH)_2^-$	Li^+	—	
	Na^+	-0.01 ± 0.07	Estimated in [2001LEM/FUG] (Section 8.1.3).
	K^+	—	
$NpO_2CO_3^-$	Li^+	—	
	Na^+	-0.18 ± 0.15	Calculated in [2001LEM/FUG] (Section 12.1.2.1.3).
	K^+	—	
$NpO_2(ox)^-$	Li^+	—	
	Na^+	-0.4 ± 0.1	Evaluated in Section VI.11.2.3 of [2005HUM/AND].
	K^+	—	
$NpO_2(H_2edta)^-$	Li^+	—	
	Na^+	-0.18 ± 0.16	Evaluated in Section VIII.11.2.3 of [2005HUM/AND].
	K^+	—	

Table 5 (continued)

j	k	$\varepsilon(j,k)$	Comments
$(NpO_2)_2CO_3(OH)_3^-$	Li^+	—	
	Na^+	0.00 ± 0.05	Estimated by analogy in [2001LEM/FUG] (Section 12.1.2.1.2).
	K^+	—	
$UO_2(OH)_3^-$	Li^+	—	
	Na^+	-0.09 ± 0.05	Estimated in [1992GRE/FUG].
	K^+	—	
$UO_2F_3^-$	Li^+	—	
	Na^+	-0.14 ± 0.05	Evaluated in [2003GUI/FAN], Section 9.4.2.2.1.1.
	K^+	—	
$UO_2(N_3)_3^-$	Li^+	—	
	Na^+	0.0 ± 0.1	Estimated in [1992GRE/FUG].
	K^+	—	
$(UO_2)_2CO_3(OH)_3^-$	Li^+	—	
	Na^+	0.00 ± 0.05	Estimated in [1992GRE/FUG].
	K^+	—	
UO_2cit^-	Li^+	—	
	Na^+	-0.11 ± 0.09	Evaluated in [2005HUM/AND].
	K^+	—	
$Th(OH)_3(CO_3)^-$	Li^+	—	
	Na^+	-0.05 ± 0.20	See Section XI.1.3.2 of [2008RAN/FUG].
	K^+	—	
$Mg(cit)^-$	Li^+	—	
	Na^+	0.03 ± 0.03	Evaluated in [2005HUM/AND].
	K^+	—	
$UO_2(Hedta)^-$	Li^+	—	
	Na^+	-0.18 ± 0.16	Evaluated in Section VIII.10.2.4 of [2005HUM/AND].
	K^+	—	
$Mg(Hedta)^-$	Li^+	—	
	Na^+	0.11 ± 0.20	Estimated in Section VIII.5.1 of [2005HUM/AND]
	K^+	—	
SO_3^{2-}	Li^+	—	
	Na^+	-0.08 ± 0.05†	
	K^+	—	
SO_4^{2-}	Li^+	-0.03 ± 0.04†	
	Na^+	-0.12 ± 0.06†	
	K^+	-0.06 ± 0.02	Reported by Ciavatta [1988CIA].

Table 5 (continued)

j	k	$\varepsilon(j,k)$	Comments
$S_2O_3^{2-}$	Li^+	—	
	Na^+	-0.08 ± 0.05†	
	K^+	—	
HPO_4^{2-}	Li^+	—	
	Na^+	-0.15 ± 0.06†	
	K^+	-0.10 ± 0.06†	
CO_3^{2-}	Li^+	—	
	Na^+	-0.08 ± 0.03	These values differ from those reported in [1992GRE/FUG]. See the discussion in [1995GRE/PUI]. Values for CO_3^{2-} and HCO_3^- are based on [1980CIA].
	K^+	0.02 ± 0.01	Reported by Ciavatta [1980CIA].
ox^{2-}	Li^+	-0.51 ± 0.09	
	Na^+	-0.08 ± 0.01	Evaluated in Section VI.3.5 of [2005HUM/AND].
	K^+	0.07 ± 0.08	
$Hcit^{2-}$	Li^+	-0.17 ± 0.04	
	Na^+	-0.04 ± 0.02	Evaluated in Section VII.3.6 of [2005HUM/AND].
	K^+	-0.01 ± 0.02	
H_2edta^{2-}	Li^+	—	
	Na^+	-0.37 ± 0.14	Evaluated in Section VII.3.7 of [2005HUM/AND].
	K^+	-0.17 ± 0.18	
$SiO_2(OH)_2^{2-}$	Li^+	—	
	Na^+	-0.10 ± 0.07	Evaluated in [1992GRE/FUG].
	K^+	—	
$Si_2O_3(OH)_4^{2-}$	Li^+	—	
	Na^+	-0.15 ± 0.06	Estimated in [1992GRE/FUG].
	K^+	—	
$Ni(ox)_2^{2-}$	Li^+	—	
	Na^+	-0.26 ± 0.03	Evaluated in Section VI.7.2 of [2005HUM/AND].
	K^+	—	
$Ni(CN)_4^{2-}$	Li^+	—	
	Na^+	0.185 ± 0.081	Evaluated in [2005GAM/BUG] (see Section V.7.1.2.1.1).
	K^+	—	
$Fe(CO_3)_2^{2-}$	Li^+	—	
	Na^+	-0.05 ± 0.05	By analogy. See Appendix A entry for [1992BRU/WER].
	K^+	—	

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Table 5 (continued)

j	k	$\varepsilon(j,k)$	Comments
CrO_4^{2-}	Li^+	—	
	Na^+	-0.06 ± 0.04†	
	K^+	-0.08 ± 0.04†	
$NpO_2(HPO_4)_2^{2-}$	Li^+	—	
	Na^+	-0.1 ± 0.1	Estimated in [2001LEM/FUG].
	K^+	—	
$NpO_2(CO_3)_2^{2-}$	Li^+	—	
	Na^+	-0.02 ± 0.14	Estimated by analogy in [2001LEM/FUG] (Section 12.1.2.1.2).
	K^+	—	
$NpO_2\,cit^{2-}$	Li^+	—	
	Na^+	-0.06 ± 0.03	Evaluated in Section VII.11 of [2005HUM/AND].
	K^+	—	
$NpO_2(Hedta)^{2-}$	Li^+	—	
	Na^+	0.07 ± 0.16	Estimated in Section VIII.11.2.3 of [2005HUM/AND].
	K^+	—	
$UO_2F_4^{2-}$	Li^+	—	
	Na^+	-0.30 ± 0.06	Evaluated in [2003GUI/FAN], Section 9.4.2.2.1.1.
	K^+	—	
$UO_2(SO_4)_2^{2-}$	Li^+	—	
	Na^+	-0.12 ± 0.06	Estimated in [1992GRE/FUG].
	K^+	—	
$UO_2(N_3)_4^{2-}$	Li^+	—	
	Na^+	-0.1 ± 0.1	Estimated in [1992GRE/FUG].
	K^+	—	
$UO_2(ox)_2^{2-}$	Li^+	—	
	Na^+	-0.18 ± 0.07	Estimated in Section VI.1.2.4.1 of [2005HUM/AND].
	K^+	—	
$UO_2\,edta^{2-}$	Li^+	—	
	Na^+	-0.22 ± 0.18	Estimated in Section VIII.10.2.4 of [2005HUM/AND].
	K^+	—	
$UO_2(CO_3)_2^{2-}$	Li^+	—	
	Na^+	-0.02 ± 0.09	These values differ from those reported in [1992GRE/FUG]. See the discussion in [1995GRE/PUI]. Values for CO_3^{2-} and HCO_3^- are based on [1980CIA].
	K^+	—	

Table 5 (continued)

j	k	$\varepsilon(j,k)$	Comments
$(UO_2)_2(OH)_2(SO_4)_2^{2-}$	Li^+	—	
	Na^+	-0.14 ± 0.22	Evaluated in Section 9.5.1.1.2 of [2003GUI/FAN].
	K^+	—	
ThF_6^{2-}	Li^+	—	
	Na^+	-0.30 ± 0.06	See Table VIII-8 in Section VIII.1.2.1 of [2008RAN/FUG].
	K^+	—	
$Th(SO_4)_3^{2-}$	Li^+	-0.068 ± 0.003	In combination with $\varepsilon_2 = (0.093 \pm 0.007)$.
	Na^+	-0.091 ± 0.038	See Section IX.1.3.2 of [2008RAN/FUG].
	K^+	-0.091 ± 0.038	
$Th(OH)_2(CO_3)_2^{2-}$	Li^+	—	
	Na^+	-0.1 ± 0.2	See Section XI.1.3.2 of [2008RAN/FUG].
	K^+	—	
$Th(OH)_4(CO_3)^{2-}$	Li^+	—	
	Na^+	-0.1 ± 0.2	See Section XI.1.3.2 of [2008RAN/FUG].
	K^+	—	
$Mg(ox)_2^{2-}$	Li^+	—	
	Na^+	-0.15 ± 0.03	Estimated in Section VI.5.1 of [2005HUM/AND].
	K^+	-0.15 ± 0.10	Estimated in [2005HUM/AND], Section VI.5.1 by assuming $\varepsilon(K^+, Mg(ox)_2^{2-}) \approx \varepsilon(Na^+, Mg(ox)_2^{2-})$.
$Mg(edta)^{2-}$	Li^+	—	
	Na^+	-0.01 ± 0.15	Evaluated in Section VIII.5.2 of [2005HUM/AND].
	K^+	—	
$Ca(ox)_2^{2-}$	Li^+	—	
	Na^+	-0.15 ± 0.10	Estimated in [2005HUM/AND], Section VI.5.2 by assuming $\varepsilon(Na^+, Ca(ox)_2^{2-}) \approx \varepsilon(Na^+, Mg(ox)_2^{2-})$.
	K^+	-0.15 ± 0.10	Estimated in [2005HUM/AND], Section VI.5.2 by assuming $\varepsilon(K^+, Ca(ox)_2^{2-}) \approx \varepsilon(Na^+, Mg(ox)_2^{2-})$.
cit^{3-}	Li^+	-0.44 ± 0.15†	
	Na^+	-0.076 ± 0.030†	
	K^+	0.02 ± 0.02	Evaluated in Section VI.3.6 of [2005HUM/AND].
$Hedta^{3-}$	Li^+	—	
	Na^+	-0.10 ± 0.14	Evaluated in Section VIII.3.7 of [2005HUM/AND].
	K^+	0.31 ± 0.18	
PO_4^{3-}	Li^+	—	
	Na^+	-0.25 ± 0.03†	
	K^+	-0.09 ± 0.02	Reported by Ciavatta [1980CIA].

Table 5 (continued)

j	k	$\varepsilon(j,k)$	Comments
$Si_3O_6(OH)_3^{3-}$	Li^+	—	
	Na^+	-0.25 ± 0.03	Estimated in [1992GRE/FUG].
	K^+	—	
$Si_3O_5(OH)_5^{3-}$	Li^+	—	
	Na^+	-0.25 ± 0.03	Estimated in [1992GRE/FUG].
	K^+	—	
$Si_4O_7(OH)_5^{3-}$	Li^+	—	
	Na^+	-0.25 ± 0.03	Estimated in [1992GRE/FUG].
	K^+	—	
$Ni(CN)_5^{3-}$	Li^+	—	
	Na^+	0.25 ± 0.14	Evaluated in [2005GAM/BUG] (see Section V.7.1.2.1.1).
	K^+	—	
$Fe(CO_3)_3^{3-}$	Li^+	—	
	Na^+	-0.23 ± 0.07	By analogy. See Appendix A entry for [2005GRI].
	K^+	—	
$Am(CO_3)_3^{3-}$	Li^+	—	
	Na^+	-0.23 ± 0.07	Evaluated Section 12.6.1.1.1 [2003GUI/FAN], from $\Delta\varepsilon_n$ in NaCl solution for the reactions $An^{3+} + n\,CO_3^{2-} \rightleftharpoons An(CO_3)_n^{(3-2n)}$ (An = Am, Cm) based on $\varepsilon(Am^{3+},Cl^-) = (0.23 \pm 0.02)$ kg·mol^{-1} and $\varepsilon(Na^+,CO_3^{2-}) = -(0.08 \pm 0.03)$ kg·mol^{-1}.
	K^+	—	
$Am(ox)_3^{3-}$	Li^+	—	
	Na^+	-0.23 ± 0.10	Estimated in [2005HUM/AND], Section VI.13.2.1 by assuming $\varepsilon(Na^+, Am(ox)_3^{3-}) \approx \varepsilon(Na^+, Am(CO_3)_3^{3-})$.
	K^+	—	
$Np(CO_3)_3^{3-}$	Li^+	—	
	Na^+	—	
	K^+	-0.15 ± 0.07	Estimated by analogy in [2001LEM/FUG] (Section 12.1.2.1.5).
$NpO_2(CO_3)_2^{3-}$	Li^+	—	
	Na^+	-0.33 ± 0.17	Calculated in [2001LEM/FUG] (Section 12.1.2.1.3).
	K^+	—	
$NpO_2(CO_3)_2OH^{3-}$	Li^+	—	
	Na^+	-0.40 ± 0.19	Estimated in [2001LEM/FUG] by analogy with $NpO_2(CO_3)_3^{4-}$.
	K^+	—	
$NpO_2(ox)_2^{3-}$	Li^+	—	
	Na^+	-0.3 ± 0.2	Evaluated in Section VI.11.2.3 of [2005HUM/AND].
	K^+	—	

Table 5 (continued)

j	k	$\varepsilon(j,k)$	Comments
$NpO_2 edta^{3-}$	Li^+	—	
	Na^+	0.20 ± 0.16	Estimated in Section VIII.11.2.3 of [2005HUM/AND].
	K^+	—	
$edta^{4-}$	Li^+	—	
	Na^+	0.32 ± 0.14	Evaluated in Section VIII.3.7 of [2005HUM/AND].
	K^+	1.07 ± 0.19	
$P_2O_7^{4-}$	Li^+	—	
	Na^+	-0.26 ± 0.05	Reported by Ciavatta [1988CIA].
	K^+	-0.15 ± 0.05	Reported by Ciavatta [1988CIA].
$Fe(CN)_6^{4-}$	Li^+	—	
	Na^+	—	
	K^+	-0.17 ± 0.03	
$NpO_2(CO_3)_3^{4-}$	Li^+	—	
	Na^+	-0.40 ± 0.19	Calculated in [2001LEM/FUG] (Section 12.1.2.1.2).
	K^+	-0.62 ± 0.42	$\varepsilon(NH_4^+, NpO_2(CO_3)_3^{4-}) = -(0.78 \pm 0.25)$ kg·mol^{-1} is calculated in [2001LEM/FUG] (Section 12.1.2.2.1).
$U(CO_3)_4^{4-}$	Li^+	—	
	Na^+	-0.09 ± 0.10	These values differ from those estimated in [1992GRE/FUG]. See the discussion in [1995GRE/PUI]. Values for CO_3^{2-} and HCO_3^- are based on [1980CIA].
	K^+	—	
$UO_2(CO_3)_3^{4-}$	Li^+	—	
	Na^+	-0.01 ± 0.11	These values differ from those reported in [1992GRE/FUG]. See the discussion in [1995GRE/PUI]. Values for CO_3^{2-} and HCO_3^- are based on [1980CIA].
	K^+	—	
$UO_2(ox)_3^{4-}$	Li^+	—	
	Na^+	-0.01 ± 0.11	Estimated in [2005HUM/AND], Section VI.10.2.4.1 by assuming $\varepsilon(Na^+, UO_2(ox)_3^{4-}) \approx \varepsilon(Na^+, UO_2(CO_3)_3^{4-})$.
	K^+	—	
$(UO_2)_3(OH)_4(SO_4)_3^{4-}$	Li^+	—	
	Na^+	0.6 ± 0.6	Estimated in Section 9.5.1.1.2 of [2003GUI/FAN].
	K^+	—	

Table 5 (continued)

j	k	$\varepsilon(j,k)$	Comments
$NpO_2(CO_3)_3^{5-}$	Li^+	—	
	Na^+	-0.53 ± 0.19	Calculated in [2001LEM/FUG] (Section 12.1.2.1.3).
	K^+	-0.22 ± 0.03	Evaluated in [2003GUI/FAN] (discussion of [1998ALM/NOV] in Appendix A) from $\Delta\varepsilon$ for the reactions $KNpO_2CO_3(s) + 2CO_3^{2-} \rightleftharpoons NpO_2(CO_3)_3^{5-} + K^+$ (in K₂CO₃–KCl solution) and $K_3NpO_2(CO_3)_2(s) + CO_3^{2-} \rightleftharpoons NpO_2(CO_3)_3^{5-} + 3K^+$ (in K₂CO₃ solution) (based on $\varepsilon(K^+, CO_3^{2-}) = (0.02 \pm 0.01)$ kg·mol⁻¹).
$UO_2(CO_3)_3^{5-}$	Li^+	—	
	Na^+	-0.62 ± 0.15	These values differ from those reported in [1992GRE/FUG]. See the discussion in [1995GRE/PUI]. Values for CO_3^{2-} and HCO_3^- are based on [1980CIA].
	K^+	—	
$Th(OH)(CO_3)_4^{5-}$	Li^+	—	
	Na^+	-0.22 ± 0.13	Evaluated in Section XI.1.3.2.1 of [2008RAN/FUG].
	K^+	—	
$Np(CO_3)_5^{6-}$	Li^+	—	
	Na^+	—	
	K^+	-0.73 ± 0.68	Calculated in [2001LEM/FUG] (Section 12.1.2.1.4).
$(NpO_2)_3(CO_3)_6^{6-}$	Li^+	—	
	Na^+	-0.46 ± 0.73	Calculated in [2001LEM/FUG] (Section 12.1.2.1.2).
	K^+	—	
$U(CO_3)_5^{6-}$	Li^+	—	
	Na^+	-0.30 ± 0.15	These values differ from those reported in [1992GRE/FUG]. See the discussion in [1995GRE/PUI]. Values for CO_3^{2-} and HCO_3^- are based on [1980CIA].
	K^+	-0.70 ± 0.31	Calculated in [2001LEM/FUG] from Pitzer coefficients [1998RAI/FEL].
$(UO_2)_3(CO_3)_6^{6-}$	Li^+	—	
	Na^+	0.37 ± 0.11	These values differ from those reported in [1992GRE/FUG]. See the discussion in [1995GRE/PUI]. Values for CO_3^{2-} and HCO_3^- are based on [1980CIA].
	K^+	—	
$(UO_2)_2NpO_2(CO_3)_6^{6-}$	Li^+	—	
	Na^+	0.09 ± 0.71	Estimated by analogy in [2001LEM/FUG] (Section 12.1.2.2.1).
	K^+	—	
$(UO_2)_5(OH)_8(SO_4)_4^{6-}$	Li^+	—	
	Na^+	1.10 ± 0.5	Estimated in Section 9.5.1.1.2 of [2003GUI/FAN].
	K^+	—	

Table 5 (continued)

j	k	$\varepsilon(j,k)$	Comments
$Th(CO_3)_5^{6-}$	Li^+	—	
	Na^+	-0.30 ± 0.15	Estimated in Section XI.1.3.2.1 of [2008RAN/FUG].
	K^+	—	
$(UO_2)_4(OH)_7(SO_4)_4^{7-}$	Li^+	—	
	Na^+	2.80 ± 0.7	Estimated in Section 9.5.1.1.2 of [2003GUI/FAN].
	K^+	—	

Table 6: Ion interaction coefficients, $\varepsilon_1(j,k)$ and $\varepsilon_2(j,k)$, both in (kg·mol^{-1}), for cations j with $k = Cl^-$, ClO_4^- and NO_3^- (first part), and for anions j with $k = Li^+$, Na^+ and K^+ (second part), according to the relationship $\varepsilon = \varepsilon_1 + \varepsilon_2 \log_{10} I_m$. The data are taken from Ciavatta [1980CIA], [1988CIA] unless indicated otherwise. The uncertainties represent the 95% confidence level.

$j\ k \rightarrow$ $\downarrow$	Cl^-		ClO_4^-		NO_3^-	
	ε_1	ε_2	ε_1	ε_2	ε_1	ε_2
NH_4^+			-0.088 ± 0.002	0.095 ± 0.012	-0.075 ± 0.001	0.057 ± 0.004
Tl^+			-0.18 ± 0.02	0.09 ± 0.02		
$FeCl_2^+$			0.57 ± 0.05 [b]	-0.41 ± 0.05 [b]		
Ag^+					-0.1432 ± 0.0002	0.0971 ± 0.0009
Pb^{2+}					-0.329 ± 0.007	0.288 ± 0.018
Hg^{2+}					-0.145 ± 0.001	0.194 ± 0.002
Hg_2^{2+}					-0.2300 ± 0.0004	0.194 ± 0.002
$FeOH^{2+}$	0.42 ± 0.06 [c]	-0.20 ± 0.07 [c]				
$FeCl^{2+}$	0.72 ± 0.06 [d]	-0.55 ± 0.05 [d]	0.68 ± 0.05 [b]	-0.41 ± 0.05 [b]		
Fe^{3+}	0.84 ± 0.04 [e]	-0.59 ± 0.06 [e]	0.78 ± 0.05 [f]	-0.41 ± 0.05 [f]		
$j\ k \rightarrow$ $\downarrow$	Li^+		Na^+		K^+	
	ε_1	ε_2	ε_1	ε_2	ε_1	ε_2
OH^-	-0.039 ± 0.002	0.072 ± 0.006				
NO_2^-	0.02 ± 0.01	0.11 ± 0.01				
NO_3^-			-0.049 ± 0.001	0.044 ± 0.002	-0.131 ± 0.002	0.082 ± 0.006
$H_2PO_4^-$			-0.109 ± 0.001	0.095 ± 0.003	-0.1473 ± 0.0008	0.121 ± 0.004
$B(OH)_4^-$			-0.092 ± 0.002	0.103 ± 0.005		
SO_3^{2-}			-0.125 ± 0.008	0.106 ± 0.009		
SO_4^{2-}	-0.068 ± 0.003	0.093 ± 0.007	-0.184 ± 0.002	0.139 ± 0.006		
$S_2O_3^{2-}$			-0.125 ± 0.008	0.106 ± 0.009		
HPO_4^{2-}			-0.19 ± 0.01	0.11 ± 0.03	-0.152 ± 0.007	0.123 ± 0.016
CrO_4^{2-}			-0.090 ± 0.005	0.07 ± 0.01	-0.123 ± 0.003	0.106 ± 0.007
cit^{3-}	-0.55 ± 0.11 [a]	0.3 ± 0.2 [a]	-0.15 ± 0.03 [a]	0.13 ± 0.03 [a]		
PO_4^{3-}			-0.29 ± 0.02	0.10 ± 0.01		

(a)　See Section VII.3.6 of [2005HUM/AND].

(b)　See Section VIII.2.3.2.2.1 of [2013LEM/BER].

(c)　See Section VII.1.3 of [2013LEM/BER].

(d)　See Section VIII.2.3.1.3 of [2013LEM/BER].

(e)　See Section VI.4.2.2 of [2013LEM/BER].

(f)　See Section VI.1.2.1.1.1 of [2013LEM/BER].

Table 7: SIT interaction coefficients $\varepsilon(j,k)$ (kg·mol^{-1}) for neutral species, j, with k, electroneutral combination of ions.

$j \quad k \rightarrow$ ↓	Na$^+$ + ClO$_4^-$	Na$^+$ + Cl$^-$	K$^+$ + NO$_3^-$
H$_2$ox(aq)	0.00 ± 0.01 [b]	0.00 ± 0.01 [b]	0.00 ± 0.01 [b]
H$_3$cit(aq)	0.00 ± 0.01 [b]	0.00 ± 0.01 [b]	0.00 ± 0.01 [b]
H$_4$edta(aq)	-0.29 ± 0.14	-0.29 ± 0.14	-0.29 ± 0.14
SnBr$_2$(aq)	0.14 ± 0.07		
SnSO$_4$(aq)	0.19 ± 0.35		
Sn(NO$_3$)$_2$(aq)	0.130 ± 0.111		
Ni(ox)(aq)	-0.07 ± 0.03	-0.07 ± 0.03	
Ni(Hcit)(aq)	-0.07 ± 0.5		
Ni(SCN)$_2$(aq)	0.38 ± 0.06 [a]		
Am(cit)(aq)		0.00 ± 0.05	
Np(edta)(aq)	-0.19 ± 0.19 [g]		
UO$_2$ox(aq)	-0.05 ± 0.06	-0.05 ± 0.06	
Uedta(aq)	-0.19 ± 0.19		
Mg(ox)(aq)		0.00 ± 0.03	0.0 ± 0.1 [c]
Mg(Hcit)(aq)	0.02 ± 0.05	0.02 ± 0.05	
Ca(ox)(aq)	0.0 ± 0.1 [d]	0.0 ± 0.1 [e]	0.0 ± 0.1 [f]

(a) See Section V.7.1.3.1 in [2005GAM/BUG].

(b) Basic assumption made in [2005HUM/AND]. See Sections VI.3.5 and VII.3.6 of that review for discussions.

(c) Estimated in Section VI.5.2 of [2005HUM/AND] by assuming ε(Mg(ox)(aq), KNO$_3$) ≈ ε(Mg(ox)(aq), NaCl).

(d) Estimated in Section VI.5.2 of [2005HUM/AND] by assuming ε(Ca(ox)(aq), NaClO$_4$) ≈ ε(Mg(ox)(aq), NaCl).

(e): Estimated in Section VI.5.1 of [2005HUM/AND] by assuming ε(Ca(ox)(aq), NaCl) ≈ ε(Mg(ox)(aq), NaCl).

(f) Estimated in Section VI.5.2 of [2005HUM/AND] by assuming ε(Ca(ox)(aq), KNO$_3$) ≈ ε(Mg(ox)(aq), NaCl).

(g) Estimated in Section VIII.11.2.2 of [2005HUM/AND] by assuming ε(Np(edta)(aq), NaClO$_4$) ≈ ε(Uedta(aq), NaClO$_4$).

6 Conclusions

The specific ion interaction formulation is simple to use and gives a fairly good estimate of activity coefficients. By using size/charge correlations, it seems possible to estimate unknown ion interaction coefficients. The specific ion interaction theory has therefore been adopted as a standard procedure in the NEA

Thermochemical DataBase review for the extrapolation and correction of equilibrium data to the infinite dilution standard state.

Bibliography

[1922BRO]   Brønsted, J. N., Studies of solubility: IV. The principle of specific interaction of ions, *J. Am. Chem. Soc.*, **44**, (1922), 877-898. Cited on pages: 14, 15.

[1922BRO2]   Brønsted, J. N., Calculation of the osmotic and activity functions in solutions of uni-univalent salts, *J. Am. Chem. Soc.*, **44**, (1922), 938-948. Cited on page: 14.

[1935GUG]   Guggenheim, E. A., The specific thermodynamic properties of aqueous solutions of strong electrolytes, *Philos. Mag.*, **19**, (1935), 588-643. Cited on page: 15.

[1936SCA]   Scatchard, G., Concentrated solutions of strong electrolytes, *Chem. Rev.*, **19**, (1936), 309-327. Cited on page: 14.

[1952LON/MCD]   Long, F. A., McDevit, W. F., Activity coefficients of nonelectrolyte solutes in aqueous salt solutions, *Chem. Rev.*, **51**, (1952), 119-169. Cited on page: 16.

[1956MCC/BUL]   McClaine, L. A., Bullwinkel, E. P., Huggins, J. C., The carbonate chemistry of uranium: Theory and applications, Proc. International Conf. on the Peaceful Uses of Atomic Energy, held 8-20 August, in Geneva Switzerland, VIII, pp.26-37, United Nations, New York, (1956). Cited on page: 25.

[1959ROB/STO]   Robinson, R. A., Stokes, R. H., *Electrolyte solutions*, 2nd. Edition, Butterworths, London, (1959, revised 1970), 571 pp. Cited on page: 19.

[1960BAB/KOD]   Babko, A. K., Kodenskaya, V. S., Equilibria in solutions of uranyl carbonate complexes, *Russ. J. Inorg. Chem.*, **5**, (1960), 1241-1244. Cited on page: 25.

[1961LEW/RAN]   Lewis, G. N., Randall, M., *Thermodynamics, as revised by Pitzer, K. S. and Brewer, L.*, 2nd. Edition, McGraw-Hill, New York, (1961), 723 pp. Cited on pages: 17, 21, 22, 28.

[1962DAV]   Davies, C. W., *Ion association*, Butterworths, London, (1962), 190 pp. Cited on page: 10.

[1962LIE/STO]   Lietzke, M.H., Stoughton, R. W., The calculation of activity coefficients from osmotic coefficient data, *J. Phys. Chem.*, **66**, 3, (1962), 508-509. Cited on page: 10.

[1962VAS]   Vasil'ev, V. P., Influence of ionic strength on the instability constants of complexes, *Russ. J. Inorg. Chem.*, **7**, (1962), 924-927. Cited on page: 15.

[1966GUG]   Guggenheim, E. A., *Applications of Statistical Mechanics*, Clarendon Press, Oxford, (1966). Cited on pages: 14, 17.

[1967HEL]   Helgeson, H. C., Thermodynamics of complex dissociation in aqueous solution at elevated temperatures, *J. Phys. Chem.*, **71**, (1967), 3121-3136. Cited on page: 10.

[1969TSY]   Tsymbal, C., Contribution à la chimie de l'uranium(VI) en solution, Université de Grenoble, Report CEA-R-3479, (1969), 97 pp. Cited on page: 25.

[1972SER/NIK]   Sergeyeva, E. I., Nikitin, A. A., Khodakovskiy, I. L., Naumov, G. B., Experimental investigation of equilibria in 19the system UO_3-CO_2-H_2O in 1925-200°C temperature interval, *Geochem. Int.*, **4**, (1972), 900-910. Cited on page: 25.

[1973ALM/GAR]   Almagro, V., Garcia, F. S., Sancho, J., Estudio polarografico del ion UO_2^{2+} en medio carbonato sodico, *An. Quím.*, **69**, (1973), 709-716, in Spanish. Cited on page: 25.

[1973PIT/MAY]   Pitzer, K. S., Mayorga, G., Thermodynamics of electrolytes. II. Activity and osmotic coefficients for strong electrolytes with one or both ions univalent, *J. Phys. Chem.*, **77**, (1973), 2300-2308. Cited on page: 28.

[1973PIT]   Pitzer, K. S., Thermodynamics of electrolytes: I. Theoretical basis and general equations, *J. Phys. Chem.*, **77**, (1973), 268-277. Cited on page: 28.

[1974HEL/KIR2]   Helgeson, H. C., Kirkham, D. H., Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressures and temperatures: II. Debye-Hückel parameters for activity coefficients and relative partial molal properties, *Am. J. Sci.*, **274**, (1974), 1199-1261. Cited on page: 22.

[1974PIT/KIM]   Pitzer, K. S., Kim, J. J., Thermodynamics of electrolytes. IV. Activity and osmotic coefficients for mixed electrolytes, *J. Am. Chem. Soc.*, **96**, (1974), 5701-5707. Cited on page: 28.

[1974PIT/MAY]   Pitzer, K. S., Mayorga, G., Thermodynamics of electrolytes. III. Activity and osmotic coefficients for 2-2 electrolytes, *J. Solution Chem.*, **3**, (1974), 539-546. Cited on page: 28.

[1975BIE]   Biedermann, G., Ionic media, Dahlem workshop on the nature of seawater, pp.339-359, Dahlem Konferenzen, Berlin, (1975). Cited on page: 15.

[1975PIT]   Pitzer, K. S., Thermodynamics of electrolytes. V. Effects of higher-order electrostatic terms, *J. Solution Chem.*, **4**, (1975), 249-265. Cited on page: 28.

[1976BAE/MES]   Baes, C. F., Jr., Mesmer, R. E., *The hydrolysis of cations*, Wiley & Sons, New York, (1976), 489 pp. Cited on pages: 14, 17, 28, 29.

[1976PIT/SIL]   Pitzer, K. S., Silvester, L. F., Thermodynamics of electrolytes. VI. Weak electrolytes including H_3PO_4, *J. Solution Chem.*, **5**, (1976), 269-278. Cited on page: 28.

[1976SCA]   Scatchard, G., *Equilibrium in solutions: Surface and colloid chemistry*, Harvard University Press, Cambridge, Massachusetts, (1976), 306 pp. Cited on page: 15.

[1977SCA]   Scanlan, J. P., Equilibria in uranyl carbonate systems: II. The overall stability constant of $UO_2(CO_3)_2^{2+}$ and the third formation constant of $UO_2(CO_3)_3^{4+}$, *J. Inorg. Nucl. Chem.*, **39**, (1977), 635-639. Cited on page: 25.

[1978LAN]   Langmuir, D., Uranium solution - mineral equilibria at low temperatures with applications to sedimentary ore deposits, *Geochim. Cosmochim. Acta*, **42**, (1978), 547-569. Cited on page: 25.

[1978PIT/PET]   Pitzer, K. S., Peterson, J. R., Silvester, L. F., Thermodynamics of electrolytes: IX. Rare earth chlorides, nitrates, and perchlorates, *J. Solution Chem.*, **7**, (1978), 45-56. Cited on page: 28.

[1979BRA/PIT]   Bradley, D. J., Pitzer, K. S., Thermodynamics of electrolytes. 12. Dielectric properties of water and Debye-Hückel parameters to 350 °C and 1 kbar, *J. Phys. Chem.*, **83**, (1979), 1599-1603. Cited on page: 22.

[1979JOH/PYT]   Johnson, K. S., Pytkowicz, R. M., Ion association and activity coefficients in multicomponent solutions, *Activity coefficients in electrolyte solutions*, Pytkowicz, R. M., Ed., II, pp.1-62, CRC Press, Boca Raton, Florida, (1979). Cited on page: 10.

[1979MIL]   Millero, F. J., Effects of pressure and temperature on activity coefficients, *Activity coefficients in electrolyte solutions*, Pytkowicz, R. M., Ed., II, pp.63-151, CRC Press, Boca Raton, Florida, (1979). Cited on pages: 10, 22.

[1979PIT]   Pitzer, K. S., Theory: Ion Interaction Approach, *Activity coefficients in electrolyte solutions*, Pytkowicz, R. M., Ed., vol. 1, pp.157-208, CRC Press, Boca Raton, Florida, (1979). Cited on pages: 14, 28.

[1979PYT]   Pytkowicz, R. M., Activity coefficients, ionic media, and equilibria in solutions, *Activity coefficients in electrolyte solutions*, Pytkowicz, R. M., Ed., II, pp.301-305, CRC Press, Boca Raton, Florida, (1979). Cited on page: 10.

[1979WHI]   Whitfield, M., Activity coefficients in natural waters, *Activity coefficients in electrolyte solutions*, Pytkowicz, R. M., Ed., II, pp.153-299, CRC Press, Boca Raton, Florida, (1979). Cited on page: 10.

[1980CIA]   Ciavatta, L., The specific interaction theory in evaluating ionic equilibria, *Ann. Chim. (Rome)*, **70**, (1980), 551-567. Cited on pages: 15, 17, 33, 34, 35, 40, 41, 43, 45, 49, 50, 52, 53, 54, 57, 58, 59, 61, 62, 64.

[1980LEM/TRE]   Lemire, R. J., Tremaine, P. R., Uranium and plutonium equilibria in aqueous solutions to 200°C, *J. Chem. Eng. Data*, **25**, (1980), 361-370. Cited on page: 25.

[1981HEL/KIR]   Helgeson, H. C., Kirkham, D. H., Flowers, G. C., Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressures and temperatures: IV. Calculation of activity coefficients, osmotic coefficients, and apparent molal and standard and relative partial molal properties to 600°C and 5 kb, *Am. J. Sci.*, **281**, (1981), 1249-1516. Cited on page: 22.

[1981PIT]   Pitzer, K. S., Characteristics of very concentrated solutions, , (1981), 249-272. Cited on page: 30.

[1982LAF]   Laffitte, M., A report of IUPAC commission I.2 on thermodynamics: Notation for states and processes, significance of the word "standard" in chemical thermodynamics, and remarks on commonly tabulated forms of thermodynamic functions, *J. Chem. Thermodyn.*, **14**, (1982), 805-815. Cited on page: 6.

[1982MAY]   Maya, L., Hydrolysis and carbonate complexation of dioxouranium(VI) in the neutral-pH range at 25°C, *Inorg. Chem.*, **21**, (1982), 2895-2898. Cited on page: 25.

[1983SPA]   Spahiu, K., Carbonate complex formation in lanthanoid and actinoid systems, Ph. D. Thesis, The Royal Institute of Technology, (1983), Stockholm, Sweden. Cited on pages: 36, 41, 45, 46, 49.

[1984ANA/ATK]   Ananthaswamy, J., Atkinson, G., Thermodynamics of concentrated electrolyte mixtures. 4. Pitzer-Debye-Hückel limiting slopes for water from 0 to 100°C and from 1 atm to 1 kbar, *J. Chem. Eng. Data*, **29**, (1984), 81-87. Cited on page: 22.

[1984GRE/FER]   Grenthe, I., Ferri, D., Salvatore, F., Riccio, G., Studies on metal carbonate equilibria. Part 10. A solubility study of the complex formation in the uranium(VI) water-carbonate dioxide system at 25°C, *J. Chem. Soc., Dalton Trans.*, (1984), 2439-2443. Cited on page: 25.

[1984HAR/MOL]   Harvie, C. E., Møller, N., Weare, J. H., The prediction of mineral solubilities in natural waters: The Na-K-Mg-Ca-H-Cl-SO_4-OH- HCO_3-CO_3-CO_2-H_2O system to high ionic strengths at 25°C, *Geochim. Cosmochim. Acta*, **48**, (1984), 723-751. Cited on page: 11.

[1985FER/GRE]   Ferri, D., Grenthe, I., Hietanen, S., Néher-Neumann, E., Salvatore, F., Studies on metal carbonate equilibria: 12. Zinc(II) carbonate complexes in acid solution, *Acta Chem. Scand.*, **A39**, (1985), 347-353. Cited on pages: 35, 40.

[1985SPA]   Spahiu, K., Studies on metal carbonate equilibria: 11. Yttrium(III) carbonate complex formation in aqueous perchlorate media of various ionic strengths, *Acta Chem. Scand.*, **A39**, (1985), 33-45. Cited on page: 30.

[1986BRU]   Bruno, J., Stoichiometric and structural studies on the Be^{2+}-H_2O-CO_2(g) system, Ph. D. Thesis, The Royal Institute of Technology, (1986), Stockholm, Sweden. Cited on pages: 45, 49.

[1987RIG/VIT]   Riglet, C., Vitorge, P., Grenthe, I., Standard potentials of the (MO_2^{2+}/MO_2^+) systems for uranium and other actinides, *Inorg. Chim. Acta*, **133**, (1987), 323-329. Cited on page: 38.

[1988CIA]   Ciavatta, L., (1988), Università di Napoli, Naples, Italy, Private communication, (from the citation in [92GRE/FUG]). Cited on pages: 34, 35, 52, 53, 56, 61, 64.

[1988HED]   Hedlund, T., Studies of complexation and precipitation equilibria in some aqueous aluminium(III) systems, Ph. D. Thesis, University of Umeå , (1988), Sweden. Cited on pages: 40, 49, 50.

[1989RIG/ROB]   Riglet, C., Robouch, P., Vitorge, P., Standard potentials of the (MO_2^{2+} / MO_2^+) and (M^{4+} / M^{3+}) redox systems for neptunium and plutonium, *Radiochim. Acta*, **46**, (1989), 85-94. Cited on pages: 37, 38, 39, 49, 50.

[1989ROB]   Robouch, P., Contribution à la prévision du comportement de l'américium, du plutonium et du neptunium dans la géosphère; données chimiques, Commissariat à l'Energie Atomique, Report CEA-R-5473, (1989). Cited on pages: 37, 49, 50.

[1990ARC/WAN]   Archer, D. G., Wang, P., The dielectric constant of water and Debye-Hückel limiting law slopes, *J. Phys. Chem. Ref. Data*, **19**, (1990), 371-411. Cited on page: 22.

[1990CIA]   Ciavatta, L., The specific interaction theory in equilibrium analysis: Some empirical rules for estimating interaction coefficients of metal ion complexes, *Ann. Chim. (Rome)*, **80**, (1990), 255-263. Cited on page: 14.

[1990OEL/HEL]   Oelkers, E. H., Helgeson, H. C., Triple-ion anions and polynuclear complexing in supercritical electrolyte solutions, *Geochim. Cosmochim. Acta*, **54**, (1990), 727-738. Cited on page: 22.

[1990RIG]   Riglet, C., Chimie du neptunium et autres actinides en milieu carbonate, Commissariat à l'Energie Atomique, Report CEA-R-5535, (1990), 267 pp. Cited on pages: 37, 38, 49, 50.

[1991GRE/LAG]   Grenthe, I., Lagerman, B., Studies on the metal carbonate
                     equilibria: 22. A coulometric study of the uranium(VI)-
                     carbonate system, the composition of the mixed hydroxide
                     carbonate species, *Acta Chem. Scand.*, **45**, (1991), 122-
                     128. Cited on page: 25.

[1991PIT]   Pitzer, K. S., Ion interaction approach: theory and data
                     correlation, *in Activity coefficients in electrolyte solutions*,
                     Pitzer, K. S., Ed., pp.75-153, CRC Press, Boca Raton,
                     Florida, (1991). Cited on pages: 19, 20.

[1992BAN/BLI]   Bányai, I., Blixt, J., Glaser, J., Tóth, I., On the dissociation
                     of hydrogen cyanide in aqueous solutions containing
                     different ionic media. A combined potentiometric and
                     carbon-13 NMR study, *Acta Chem. Scand.*, **46**, (1992),
                     138-141. Cited on page: 53.

[1992BRU/WER]   Bruno, J., Wersin, P., Stumm, W., On the influence of
                     carbonate in mineral dissolution: II. The solubility of
                     $FeCO_3$(s) at 25°C and 1 atm total pressure, *Geochim.
                     Cosmochim. Acta*, **56**, (1992), 1149-1155. Cited on page:
                     57.

[1992CAP]   Capdevila, H., Données thermodynamiques sur
                     l'oxydoréduction du plutonium en milieux acide et
                     carbonate. Stabilité de Pu(V), Ph. D. Thesis, Université de
                     Paris-Sud, Orsay, France, (1992), in French. Also
                     published as CEA-R-5643 Commissariat à l'Energie
                     Atomique, France, (1993). Cited on pages: 37, 49.

[1992GRE/FUG]   Grenthe, I., Fuger, J., Konings, R. J. M., Lemire, R. J.,
                     Muller, A. B., Nguyen-Trung, C., Wanner, H., *Chemical
                     thermodynamics of uranium*, Wanner, H., Forest, I.,
                     Nuclear Energy Agency, Organisation for Economic Co-
                     operation and Development, Eds., vol. 1, *Chemical
                     Thermodynamics*, North Holland Elsevier Science
                     Publishers B. V., Amsterdam, The Netherlands, (1992),
                     715 pp. Cited on pages: 13, 25, 37, 38, 39, 42, 43, 44, 46,
                     47, 49, 50, 52, 53, 54, 56, 57, 58, 60, 61, 62.

[1993GIF/VIT2]   Giffaut, E., Vitorge, P., Capdevila, H., Corrections de température sur les coefficients d'activité calculés selon la TIS, Commissariat à l'Energie Atomique, Report CEA-N-2737, (1993), 29 pp. Cited on page: 22.

[1994CAP/VIT]   Capdevila, H., Vitorge, P., Potentiels redox des couples PuO_2^{2+}/PuO_2^+ et Pu^{4+}/Pu^{3+} à force ionique et température variables. Entropie et capacité calorifique, Commissariat à l'Energie Atomique, Report CEA-N-2762, (1994), 73 pp. Cited on pages: 37, 49.

[1994GIF]   Giffaut, E., Influence des ions chlorure sur la chimie des actinides, Ph. D. Thesis, Université de Paris-Sud, Orsay, France, (1994), 259 pp., in French. Cited on page: 37.

[1995CAP/VIT]   Capdevila, H., Vitorge, P., Redox potentials of PuO_2^{2+}/PuO_2^+ and Pu^{4+}/Pu^{3+} at different ionic strengths and temperatures. Entropy and heat capacity, *Radiochim. Acta*, **68**, (1995), 51-62. Cited on pages: 37, 49.

[1995GRE/PUI]   Grenthe, I., Puigdomènech, I., Rand, M. H., Sandino, M. C. A., *Corrections to the Uranium NEA-TDB review, Appendix D, in: Chemical Thermodynamics of Americium (authored by Silva, R. J., Bidoglio, G., Rand, M. H. and Robouch, P. B., Wanner, H., Puigdomènech, I.)*, Nuclear Energy Agency, Organisation for Economic Co-operation and Development, Ed., pp.347-374, North Holland Elsevier Science Publishers B. V., Amsterdam, The Netherlands, (1995). Cited on pages: 53, 57, 58, 61, 62.

[1995SIL/BID]   Silva, R. J., Bidoglio, G., Rand, M. H., Robouch, P. B., Wanner, H., Puigdomènech, I., *Chemical thermodynamics of americium*, Nuclear Energy Agency, Organisation for Economic Co-operation, Development, Ed., vol. 2, *Chemical Thermodynamics*, North Holland Elsevier Science Publishers B. V., Amsterdam, The Netherlands, (1995), 374 pp. Cited on pages: 37, 42, 46, 55.

[1997ALL/BAN]   Allard, B., Banwart, S. A., Bruno, J., Ephraim, J. H., Grauer, R., Grenthe, I., Hadermann, J., Hummel, W., Jakob, A., Karapiperis, T., Plyasunov, A. V., Puigdomènech, I., Rard, J. A., Saxena, S., Spahiu, K., *Modelling in Aquatic Chemistry*, Grenthe, I., Puigdomènech, I., Eds., Nuclear Energy Agency, Organisation for Economic Co-operation and Development, Paris, France, (1997), 724 pp. Cited on pages: 7, 12, 13, 14, 15, 17, 22, 29.

[1997GRE/PLY]   Grenthe, I., Plyasunov, A., On the use of semiempirical electrolyte theories for the modeling of solution chemical data, *Pure Appl. Chem.*, **69**, 5, (1997), 951-958. Cited on pages: 22, 23, 28, 29.

[1997KON/FAN]   Könnecke, T., Fanghänel, T., Kim, J. I., Thermodynamics of trivalent actinides in concentrated electrolyte solutions. Modelling the chloride complexation of Cm(III), *Radiochim. Acta*, **76**, 3, (1997), 131-135. Cited on page: 46.

[1998ALM/NOV]   Al Mahamid, I., Novak, C. F., Becraft, K. A., Carpenter, S. A., Hakem, N., Solubility of Np(V) in K-Cl-CO_3 and Na-K-Cl-CO_3 solutions to high concentrations: measurements and thermodynamic model predictions, *Radiochim. Acta*, **81**, (1998), 93-101. Cited on page: 62.

[1998RAI/FEL]   Rai, D., Felmy, A. R., Hess, N. J., Moore, D. A., Yui, M., A thermodynamic model for the solubility of UO_2(am) in the aqueous K^+-Na^+-HCO_3^--CO_3^{2-}-OH^--H_2O system, *Radiochim. Acta*, **82**, (1998), 17-25. Cited on pages: 53, 62.

[1999NEA]   TDB-0-TDB-6, TDB project guidelines, NEA Web site PDF documents, (1999). Cited on page: 24.

[2000WAN/OST2]   Wanner, H., Östhols, E., TDB-5: Standards and conventions for TDB publications, Nuclear Energy Agency Data Bank, Organisation for Economic Co-operation and Development, Report , (2000), 40 pp. Cited on pages: 6, 33.

[2001LEM/FUG]   Lemire, R. J., Fuger, J., Nitsche, H., Potter, P. E., Rand, M. H., Rydberg, J., Spahiu, K., Sullivan, J. C., Ullman, W. J., Vitorge, P., Wanner, H., *Chemical thermodynamics of neptunium and plutonium*, Nuclear Energy Agency Data Bank, Organisation for Economic Co-operation and Development, Ed., vol. 4, *Chemical Thermodynamics*, North Holland Elsevier Science Publishers B. V., Amsterdam, The Netherlands, (2001). Cited on pages: 32, 37, 38, 42, 43, 46, 47, 49, 50, 53, 55, 56, 58, 60, 61, 62.

[2003GUI/FAN]   Guillaumont, R., Fanghänel, T., Fuger, J., Grenthe, I., Neck, V., Palmer, D. A., Rand, M. H., *Update on the chemical thermodynamics of uranium, neptunium, plutonium, americium and technetium*, Nuclear Energy Agency Data Bank, Organisation for Economic Co-operation and Development, Ed., vol. 5, *Chemical Thermodynamics*, North Holland Elsevier Science Publishers B. V., Amsterdam, The Netherlands, (2003). Cited on pages: 37, 39, 42, 47, 55, 56, 58, 59, 60, 61, 62, 63.

[2005GAM/BUG]   Gamsjäger, H., Bugajski, J., Gajda, T., Lemire, R. J., Preis, W., *Chemical thermodynamics of nickel*, Nuclear Energy Agency Data Bank, Organisation for Economic Co-operation and Development, Ed., vol. 6, *Chemical Thermodynamics*, North Holland Elsevier Science Publishers B. V., Amsterdam, The Netherlands, (2005). Cited on pages: 35, 36, 41, 45, 49, 54, 57, 60, 65.

[2005GRI]   Grivé i Solé, M., The linkage between uranium, iron and carbon cycling. Processes at interfaces: evidences from combined solution chemical and spectroscopic studies, Ph. D. Thesis, Universitat Politècnica de Catalunya, (2005), Barcelona, Spain, 341 pp. Cited on page: 60.

[2005HUM/AND]   Hummel, W., Anderegg, G., Puigdomènech, I., Rao, L., Tochiyama, O., *Chemical thermodynamics of compounds and complexes of U, Np, Pu, Am, Tc, Se, Ni and Zr with selected organic ligands*, Nuclear Energy Agency Data Bank, Organisation for Economic Co-operation and Development, Ed., vol. 9, *Chemical Thermodynamics*, North Holland Elsevier Science Publishers B. V., Amsterdam, The Netherlands, (2005). Cited on pages: 31, 34, 36, 37, 40, 53, 54, 55, 56, 57, 58, 59, 60, 61, 64, 65.

[2008RAN/FUG]   Rand, M. H., Fuger, J., Grenthe, I., Neck, V., Rai, D., *Chemical thermodynamics of thorium*, Nuclear Energy Agency Data Bank, Organisation for Economic Co-operation and Development, Ed., vol. 11, *Chemical Thermodynamics*, OECD Publications, (2008). Cited on pages: 40, 44, 45, 48, 49, 50, 51, 53, 56, 59, 62, 63.

[2012GAM/GAJ]   Gamsjäger, H., Gajda, T., Sangster, J., Saxena, S. K., Voigt, W., *Chemical thermodynamics of tin*, Nuclear Energy Agency Data Bank, Organisation for Economic Co-operation and Development, Ed., vol. 12, *Chemical Thermodynamics*, OECD Publications, (2012). Cited on pages: 34, 54.

[2013LEM/BER]   Lemire, R. J., Berner, U., Musikas, C., Palmer, D. A., Taylor, P., Tochiyama, O., *Chemical thermodynamics of iron. Part 1*, Nuclear Energy Agency Data Bank, Organisation for Economic Co-operation and Development, Ed., vol. 13a, *Chemical Thermodynamics*, OECD Publications, (2013). Cited on pages: 36, 40, 41, 45, 49, 54, 64.