Appendix B

Ionic strength corrections[1]

Thermodynamic data always refer to a selected standard state. The definition given by IUPAC [1982LAF] is adopted in this review as outlined in Section II.3.1. According to this definition, the standard state for a solute B in a solution is a hypothetical solution, at the standard state pressure, in which $m_B = m^\circ = 1\ \mathrm{mol \cdot kg^{-1}}$, and in which the activity coefficient γ_B is unity. However, 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. This is invariably the case for reactions involving ions of high charge. Precise thermodynamic information for these systems can only be obtained in the presence of an inert electrolyte of sufficiently high concentration that ensures activity factors are reasonably constant throughout the measurements. This appendix describes and illustrates the method used in this review for the extrapolation of experimental equilibrium data to zero ionic strength.

The activity factors of all the species participating in reactions in high ionic strength media must be estimated in order to reduce the thermodynamic data obtained from the experiment to the state $I = 0$. Two alternative methods can be used to describe the ionic medium dependence of equilibrium constants:

- One method takes into account the individual characteristics of the ionic media by using a medium dependent expression for the activity coefficients of the species involved in the equilibrium reactions. The medium dependence is described by virial or ion interaction coefficients as used in the Pitzer equations [1973PIT] and in the specific ion interaction theory.
- The other method uses an extended Debye-Hückel expression in which the activity coefficients of reactants and products depend only on the ionic charge and the ionic strength, but it accounts for the medium specific properties by

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[1] This Appendix contains much of the text of the TDB-2 Guideline written by Grenthe and Wanner [2000GRE/WAN], earlier versions of which have been printed in the previous NEA TDB reviews. The equations presented here are an essential part of the review procedure and are required to use the selected thermodynamic values. Parts of Section B.1.1 and the contents of Tables B-4, B-5, B-6 and B-7 have been revised.

introducing ion pairing between the medium ions and the species involved in the equilibrium reactions. Earlier, this approach has been used extensively in marine chemistry, *cf.* Refs. [1979JOH/PYT], [1979MIL], [1979PYT], [1979WHI2].

The activity factor estimates are thus based on the use of Debye-Hückel type equations. The "extended" Debye-Hückel equations are either in the form of specific ion interaction methods or the Davies equation [1962DAV]. However, the Davies equation should in general not be used at ionic strengths larger than 0.1 $\text{mol}\cdot\text{kg}^{-1}$. The method preferred in the NEA Thermochemical Data Base review is a medium-dependent expression for the activity coefficients, which is the specific ion interaction theory in the form of the Brønsted-Guggenheim-Scatchard approach. Other forms of specific ion interaction methods (the Pitzer and Brewer "B-method" [1961LEW/RAN] and the Pitzer virial coefficient method [1979PIT]) are described in the NEA Guidelines for the extrapolation to zero ionic strength [2000GRE/WAN].

The specific ion interaction methods are reliable for intercomparison of experimental data in a given concentration range. In many cases this includes data at rather low ionic strengths, I = 0.01 to 0.1 M, *cf.* Figure B-1, while in other cases, notably for cations of high charge ($\geq +4$ and ≤ -4), the lowest available ionic strength is often 0.2 M or higher, see for example Figures V.12 and V.13 in [1992GRE/FUG]. It is reasonable to assume that the extrapolated equilibrium constants at $I = 0$ are more precise in the former than in the latter cases. The extrapolation error is composed of two parts, one due to experimental errors, and the other due to model errors. The model errors seem to be rather small for many systems, less than 0.1 units in $\log_{10} K^{\circ}$. For reactions involving ions of high charge, which may be extensively hydrolysed, one cannot perform experiments at low ionic strengths. Hence, it is impossible to estimate the extrapolation error. This is true for all methods used to estimate activity corrections. Systematic model errors of this type are not included in the uncertainties assigned to the selected data in this review.

B.1 The specific ion interaction equations

B.1.1 Background

The Debye-Hückel term, which is the dominant term in the expression for the activity coefficients in dilute solution, accounts for electrostatic, non-specific long-range interactions. At higher concentrations, short range, non-electrostatic interactions have to be taken into account. This is usually done by adding ionic strength dependent terms to the Debye-Hückel expression. This method was first outlined by Brønsted [1922BRO], [1922BRO2] and elaborated by Scatchard [1936SCA] and Guggenheim [1966GUG]. Biedermann [1975BIE] highlighted its practical value, especially for the estimation of ionic medium effects on equilibrium constants. The two basic assumptions in the specific ion interaction theory are described below.

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

$$\log_{10}\gamma_j = -z_j^2 D + \sum_k \varepsilon(j,k,I_m)\, m_k \tag{B.1}$$

D is the Debye-Hückel term:

$$D = \frac{A\sqrt{I_m}}{1 + B a_j \sqrt{I_m}} \tag{B.2}$$

where I_m is the molal ionic strength:

$$I_m = \frac{1}{2}\sum_i m_i z_i^2$$

A and B are constants which are temperature and pressure dependent, and a_j is an ion size parameter ("distance of closest approach") for the hydrated ion j. The Debye-Hückel limiting slope, A, has a value of $(0.509 \pm 0.001)\ \text{kg}^{\frac{1}{2}} \cdot \text{mol}^{-\frac{1}{2}}$ at 25°C and 1 bar, (*cf.* Section B.1.2). The term Ba_j in the denominator of the Debye-Hückel term has been assigned a value of $Ba_j = 1.5\ \text{kg}^{\frac{1}{2}} \cdot \text{mol}^{-\frac{1}{2}}$ at 25°C and 1 bar, as proposed by Scatchard [1976SCA] and accepted by Ciavatta [1980CIA]. This value has been found to minimise, for several species, the ionic strength dependence of $\varepsilon(j,k,I_m)$ between I_m = 0.5 m and I_m = 3.5 m. It should be mentioned that some authors have proposed different values for Ba_j ranging from Ba_j = 1.0 [1935GUG] to Ba_j = 1.6 [1962VAS]. However, the parameter Ba_j is empirical and as such is correlated to the value of $\varepsilon(j,k,I_m)$. Hence, this variety of values for Ba_j does not represent an uncertainty range, but rather indicates that several different sets of Ba_j and $\varepsilon(j,k,I_m)$ may describe equally well the experimental mean activity coefficients of a given electrolyte. The ion interaction coefficients at 25°C listed in Table B-4, Table B-5, Table B-6 and Table B-7 have thus to be used with $Ba_j = 1.5\ \text{kg}^{\frac{1}{2}} \cdot \text{mol}^{-\frac{1}{2}}$.

The summation in Eq. (B.1) extends over all ions k present in solution. Their molality is denoted by m_k, and the specific ion interaction parameters, $\varepsilon(j,k,I_m)$, in general depend only slightly on the ionic strength. The concentrations of the ions of the ionic medium are often very much larger than 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 participating ionic species and the ionic medium ions are included, as shown in Eqs. (B.5) to (B.9).

- **Assumption 2:** The ion interaction coefficients, $\varepsilon(j,k,I_m)$ are zero for ions of the same charge sign and for uncharged species. The rationale behind this is that ε, which describes specific short-range interactions, must be small for ions of the same charge since they are usually far from one another due to electrostatic repulsion. This holds to a lesser extent also for uncharged species, but in some cases the experimental data allow determination of interaction coefficients for uncharged species with electroneutral combinations of ions, *cf.* Table B-7.

Eq. (B.1) will 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.

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 m. The concentration dependence of the ion interaction coefficients can thus often be neglected. This point was emphasised by Guggenheim [1966GUG], who has presented a considerable amount of experimental material supporting this approach. The concentration dependence is larger for electrolytes of higher charge. In order to reproduce accurately their activity coefficient data, concentration dependent ion interaction coefficients have to be used, *cf.* Lewis *et al.* [1961LEW/RAN], Baes and Mesmer [1976BAE/MES], or Ciavatta [1980CIA].

For cases where the uncertainties in the epsilon values collected in Table B-4 and Table B-5 are ± 0.03 $\text{kg}\cdot\text{mol}^{-1}$ or greater, Ciavatta [1980CIA] proposed the use of Equation (B.3)

$$\varepsilon = \varepsilon_1 + \varepsilon_2 \log_{10} I_m \qquad \text{(B.3)}$$

However, even if the value of ε calculated in this way describes the variation with ionic strength slightly better than a constant value, this equation has no theoretical basis; ε_2 is a fitting parameter and the term $\varepsilon_2 \log_{10} I_\text{m}$ goes to minus infinity at the limiting value $I_\text{m} = 0$. This expression for the concentration dependence of ε should be avoided, even though the term $\varepsilon \cdot m = (\varepsilon_1 + \varepsilon_2 \log_{10} I_\text{m}) \cdot m$ (in the calculation of activity coefficients) is zero at $I_\text{m} = 0$. There may be cases where reviewers will still want to use Eq.(B.3) to describe the ionic strength variation of the interaction parameters, but the rationale behind this should then be described. This conclusion was reached at a time when the present review, wherein we have used the two-epsilon model for a few systems, was nearly complete. However, it is expected that the one- and two-epsilon models will provide similar calculated results for the $\log_{10} K^\circ$. To confirm this, we remodelled a few important cases (solubility of solids containing $Th(SO_4)_2$) as a function of Li_2SO_4 or Na_2SO_4 concentrations (*cf.* Section IX.1.3.3) using a one-epsilon model. Our results show, as expected, that the calculated values of $\log_{10} K^\circ$ using the one- and two-epsilon models differ insignificantly (identical in the Li system and less than 0.028 $\log_{10}$ units for the Na system, far less than the overall uncertainty in the $\log_{10} K^\circ$). As the two-epsilon model has been used in the current and previous volumes, the relevant parameters have been retained in Table B-6.

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 managed to describe measured activity coefficients of a large number of electrolytes with high precision over a large concentration range. Pitzer's model generally contains three parameters as compared to one in the specific ion interaction theory. The use of the theory requires the knowledge of all these parameters. The derivation of Pitzer coefficients for many complexes, such as those of the actinides would require a very large amount of additional experimental work, since few data of this type are currently available.

The way in which the activity coefficient corrections are performed in this review according to the specific ion interaction theory is illustrated below for a general case of a complex formation reaction. Charges on all species except the hydrogen ions are omitted for brevity.

$$m\mathrm{M} + q\mathrm{L} + n\mathrm{H_2O(l)} \rightleftharpoons \mathrm{M}_m\mathrm{L}_q(\mathrm{OH})_n + n\mathrm{H}^+$$

The formation constant of $\mathrm{M}_m\mathrm{L}_q(\mathrm{OH})_n$, ${}^*\beta_{q,n,m}$, determined in an ionic medium (1:1 salt NX) of the ionic strength I_m, is related to the corresponding value at zero ionic strength, ${}^*\beta^\circ_{q,n,m}$ by Eq.(B.4).

$$\begin{aligned}\log_{10}{}^*\beta_{q,n,m} = \log_{10}{}^*\beta^\circ_{q,n,m} + m\log_{10}\gamma_\mathrm{M} + q\log_{10}\gamma_\mathrm{L} + n\log_{10}a_{\mathrm{H_2O}} \\ -\log_{10}\gamma_{q,n,m} - n\log_{10}\gamma_{\mathrm{H}^+}\end{aligned} \qquad \text{(B.4)}$$

The subscript (*q,n,m*) denotes the complex ion, $\mathrm{M}_m\mathrm{L}_q(\mathrm{OH})_n$. If the concentrations of N and X are much greater than the concentrations of M, L, $\mathrm{M}_m\mathrm{L}_q(\mathrm{OH})_n$ and H^+, only the molalities m_N and m_X have to be taken into account for the calculation of the term, $\sum_k \varepsilon(j,k,I_m)m_k$ in Eq. (B.1). For example, for the activity coefficient of the metal cation M, γ_M, Eq. (B.5) is obtained at 25°C and 1 bar.

$$\log_{10}\gamma_\mathrm{M} = \frac{-z_\mathrm{M}^2\,0.509\sqrt{I_m}}{1+1.5\sqrt{I_m}} + \varepsilon(\mathrm{M,X},I_m)m_\mathrm{X} \qquad \text{(B.5)}$$

Under these conditions, $I_m \approx m_\mathrm{X} = m_\mathrm{N}$ Substituting the $\log_{10}\gamma_j$ values in Eq. (B.4) with the corresponding forms of Eq. (B.5) and rearranging leads to:

$$\log_{10}{}^*\beta_{q,n,m} - \Delta z^2 D - n\log_{10}a_{\mathrm{H_2O}} = \log_{10}{}^*\beta^\circ_{q,n,m} - \Delta\varepsilon I_m \qquad \text{(B.6)}$$

where, at 25°C and 1 bar:

$$\Delta z^2 = (m z_\mathrm{M} - q z_\mathrm{L} - n)^2 + n - m z_\mathrm{M}^2 - q z_\mathrm{L}^2 \qquad \text{(B.7)}$$

$$D = \frac{0.509\sqrt{I_m}}{1+1.5\sqrt{I_m}} \qquad \text{(B.8)}$$

$$\Delta\varepsilon = \varepsilon(q,n,m,\mathrm{N\ or\ X}) + n\varepsilon(\mathrm{H,X}) - q\varepsilon(\mathrm{N,L}) - m\varepsilon(\mathrm{M,X}) \qquad \text{(B.9)}$$

Here $(m z_{\mathrm{M}} - q z_{\mathrm{L}} - n)$, z_{M} and z_{L} are the charges of the complex, $\mathrm{M}_m\mathrm{L}_q(\mathrm{OH})_n$, the metal ion M and the ligand L, respectively.

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

$$\log_{10} a_{\mathrm{H_2O}} = \frac{-\phi_m \sum_k m_k}{\ln(10)\cdot 55.508} \tag{B.10}$$

where ϕ_m is the osmotic coefficient of the mixture, 55.508 ($\mathrm{mol\cdot kg^{-1}}$) is the molality of pure water, and the summation extends over all solute species k with molality m_k present in the solution. In the presence of an ionic medium NX as the dominant species, Eq. (B.10) 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 $I_m \approx m_{\mathrm{NX}}$, Eq. (B.10) becomes:

$$\log_{10} a_{\mathrm{H_2O}} = \frac{-2\, m_{\mathrm{NX}}\, \phi_m}{\ln(10)\times 55.508} \tag{B.11}$$

Alternatively, water activities can be taken from Table B-1. These have been calculated for the most common ionic media at various concentrations applying Pitzer's ion interaction model 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.

Values of osmotic coefficients for single electrolytes have been compiled by various authors, *e.g.*, Robinson and Stokes [1959ROB/STO]. The activity of water can also be calculated from the known activity coefficients of the dissolved species. In the presence of an ionic medium, $\mathrm{N}_{\nu_+}\mathrm{X}_{\nu_-}$, of a concentration much larger than those of the reacting ions, the osmotic coefficient can be calculated according to Eq. (B.12) (*cf.* Eqs. (23-39), (23-40) and (A4-2) in [1961LEW/RAN]).

$$\begin{aligned} 1-\phi_m = {} & \frac{A\ln(10)|z_+z_-|}{I_m(B\,a_j)^3}\left[1+B\,a_j\sqrt{I_m} - 2\ln(1+B\,a_j\sqrt{I_m}) - \frac{1}{1+B\,a_j\sqrt{I_m}}\right] \\ & -\ln(10)\ \varepsilon(\mathrm{N,X})\, m_{\mathrm{NX}}\left(\frac{\nu_+\nu_-}{\nu_+ + \nu_-}\right) \end{aligned} \tag{B.12}$$

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

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

Table B-1: Water activities a_{H_2O} for the most common ionic media at various concentrations applying 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*

(Continued on next page)

Table B-1: (continued)

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*

The activity of water is obtained by inserting Eq. (B.12) into Eq. (B.11). It should be mentioned that in mixed electrolytes with several components at high concentrations, it might be necessary to use Pitzer's equation to calculate the activity of water. On the other hand, a_{H_2O} is nearly constant in most experimental studies of equilibria in dilute aqueous solutions, where an ionic medium is used in large excess with respect to the reactants. The medium electrolyte thus determines the osmotic coefficient of the solvent.

In natural waters the situation is similar; 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 equation (*cf.* [2000GRE/WAN]) may be used to estimate the osmotic coefficient; the necessary interaction coefficients are known for most systems of geochemical interest.

Note that in all ion interaction approaches, the equation for the mean activity coefficients can be split up to give equations for conventional single ion activity coefficients in mixtures, *e.g.*, Eq. (B.1). 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, $H^+ + e^- \rightleftharpoons \frac{1}{2}H_2(g)$, is necessary (*cf.* Example B.3).

B.1.2 Ionic strength corrections at temperatures other than 298.15 K

Values of the Debye-Hückel parameters A and B in Eqs. (B.2) and (B.12) are listed in Table B-2 for a few temperatures at a pressure of 1 bar below 100°C and at the steam saturated pressure for $t \geq 100°C$. The values in Table B-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/KIR], [1979BRA/PIT], [1981HEL/KIR], [1984ANA/ATK], [1990ARC/WAN].

The term, Ba_j, in the denominator of the Debye-Hückel term, D, *cf.* Eq. (B.2), has been assigned in this review a value of 1.5 $\text{kg}^{½} \cdot \text{mol}^{-½}$ at 25°C and 1 bar, *cf.* Section B.1.1 At temperatures and pressures other than the reference and standard state, the following possibilities exist:

- The value of Ba_j is calculated at each temperature assuming that ion sizes are independent of temperature and using the values of B listed in Table B-2.
- The value Ba_j is kept constant at 1.5 $\text{kg}^{½} \cdot \text{mol}^{-½}$. Due the variation of B with temperature, *cf.* Table B-2, this implies a temperature dependence for ion size parameters. Assuming for the ion size is in reality constant, then it is seen that this simplification introduces an error in D, which increases with temperature and ionic strength (this error is less than $\pm$ 0.01 at $t \leq 100°C$ and $I < 6$ m, and less than $\pm$ 0.006 at $t \leq 50°C$ and $I \leq 4$ m).
- The value of Ba_j is calculated at each temperature assuming a given temperature variation for a_j and using the values of B listed in Table B-2. For example, in the aqueous ionic model of Helgeson and co-workers ([1988TAN/HEL], [1988SHO/HEL], [1989SHO/HEL], [1989SHO/HEL2]) ionic sizes follow the relation: $a_j(T) = a_j(298.15\text{ K, 1 bar}) + |z_j| g(T, p)$ [1990OEL/HEL], where $g(T, p)$ is a temperature and pressure function which is tabulated in [1988TAN/HEL], [1992SHO/OEL], and is approximately zero at temperatures below 175°C.

The values of $\varepsilon(j,k,I_m)$, obtained with the methods described in Section B.1.3 at temperatures other than 25°C, will depend on the value adopted for Ba_j. As long as a consistent approach is followed, values of $\varepsilon(j,k,I_m)$ absorb the choice of Ba_j, and for moderate temperature intervals (between 0 and 200°C) the choice $Ba_j = 1.5\ \text{kg}^{½} \cdot \text{mol}^{-½}$ is the simplest one and is recommended by this review.

The variation of $\varepsilon(j,k,I_m)$ with temperature is discussed by Lewis *et al.* [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 $\leq 0.005\ \text{kg} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ for temperatures below 200°C. Therefore, if values of $\varepsilon(j,k,I_m)$ obtained at 25°C are used in the temperature range 0 to 50°C to perform ionic strength corrections, the error in $\log_{10}\gamma_j / I_m$ will be ≤ 0.13. It is clear that in order to reduce the uncertainties in solubility calculations at $t \neq 25$°C, studies on the variation of $\varepsilon(j,k,I_m)$ values with temperature should be undertaken.

Table B-2: Debye-Hückel constants as a function of temperature at a pressure of 1 bar below 100°C and at the steam saturated pressure for $t \geq 100$°C. The uncertainty in the A parameter is estimated by this review to be ± 0.001 at 25°C, and ± 0.006 at 300°C, while for the B parameter the estimated uncertainty ranges from ± 0.0003 at 25°C to ± 0.001 at 300°C.

t(°C)	p(bar)	A ($\mathrm{kg}^{1/2}\cdot\mathrm{mol}^{-1/2}$)	$B \times 10^{-10}$ ($\mathrm{kg}^{1/2}\cdot\mathrm{mol}^{-1/2}\cdot\mathrm{m}^{-1}$)
0	1.00	0.491	0.3246
5	1.00	0.494	0.3254
10	1.00	0.498	0.3261
15	1.00	0.501	0.3268
20	1.00	0.505	0.3277
25	1.00	0.509	0.3284
30	1.00	0.513	0.3292
35	1.00	0.518	0.3300
40	1.00	0.525	0.3312
50	1.00	0.534	0.3326
75	1.00	0.564	0.3371
100	1.013	0.600	0.3422
125	2.32	0.642	0.3476
150	4.76	0.690	0.3533
175	8.92	0.746	0.3593
200	15.5	0.810	0.365
250	29.7	0.980	0.379
300	85.8	1.252	0.396

B.1.3 Estimation of ion interaction coefficients

B.1.3.1 Estimation from mean activity coefficient data

Example B.1:

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

$$\begin{aligned}
2\log_{10}\gamma_{\pm,\,\mathrm{HCl}} &= \log_{10}\gamma_{\mathrm{H}^+} + \log_{10}\gamma_{\mathrm{Cl}^-} \\
&= -D + \varepsilon(\mathrm{H}^+,\mathrm{Cl}^-)\,m_{\mathrm{Cl}^-} - D + \varepsilon(\mathrm{Cl}^-,\mathrm{H}^+)\,m_{\mathrm{H}^+} \\
\log_{10}\gamma_{\pm,\,\mathrm{HCl}} &= -D + \varepsilon(\mathrm{H}^+,\mathrm{Cl}^-)\,m_{\mathrm{HCl}}
\end{aligned}$$

By plotting $(\log_{10}\gamma_{\pm,\mathrm{HCl}} + D)$ *versus* m_{HCl} a straight line with the slope $\varepsilon(\mathrm{H}^+,\mathrm{Cl}^-)$ 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.

B.1.3.2 Estimations based on experimental values of equilibrium constants at different ionic strengths

Example B.2:

Equilibrium constants are given in Table B-3 for the reaction:

$$\mathrm{UO}_2^{2+} + \mathrm{Cl}^- \rightleftharpoons \mathrm{UO}_2\mathrm{Cl}^+ \qquad \text{(B.13)}$$

Table B-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 (B.13). The linear regression of this set of data is shown in Figure B-1.

I_m	$\log_{10}\beta_1$ (exp) [(a)]	$\log_{10}\beta_{1,m}$ [(b)]	$\log_{10}\beta_{1,m} + 4D$
0.10	-0.17 ± 0.10	-0.174	0.264 ± 0.100
0.20	-0.25 ± 0.10	-0.254	0.292 ± 0.100
0.26	-0.35 ± 0.04	-0.357	0.230 ± 0.040
0.31	-0.39 ± 0.04	-0.397	0.220 ± 0.040
0.41	-0.41 ± 0.04	-0.420	0.246 ± 0.040
0.51	-0.32 ± 0.10	-0.331	0.371 ± 0.100
0.57	-0.42 ± 0.04	-0.432	0.288 ± 0.040
0.67	-0.34 ± 0.04	-0.354	0.395 ± 0.040
0.89	-0.42 ± 0.04	-0.438	0.357 ± 0.040
1.05	-0.31 ± 0.10	-0.331	0.491 ± 0.100
1.05	-0.277 ± 0.260	-0.298	0.525 ± 0.260
1.61	-0.24 ± 0.10	-0.272	0.618 ± 0.100
2.21	-0.15 ± 0.10	-0.193	0.744 ± 0.100
2.21	-0.12 ± 0.10	-0.163	0.774 ± 0.100
2.82	-0.06 ± 0.10	-0.112	0.860 ± 0.100
3.50	0.04 ± 0.10	-0.027	0.974 ± 0.100

(a) Equilibrium constants for Reaction (B.13) in aqueous $\mathrm{NaClO_4}$ solutions, with assigned uncertainties, corrected to 25°C where necessary. For details of the data, see Section V.4.2.1.2 of [1992GRE/FUG].

(b) Equilibrium constants, corrected from molarity to molality units as described in Section II.2

The following formula is deduced from Eq. (B.6) for the extrapolation to $I = 0$:

$$\log_{10} \beta_1 + 4D = \log_{10} \beta_1^{\circ} - \Delta\varepsilon\, I_m \qquad \text{(B.14)}$$

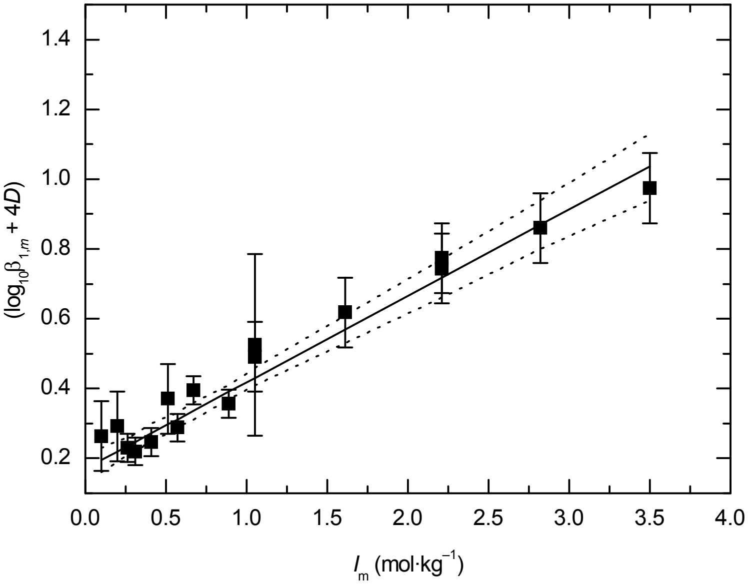
The linear regression is done as described in Appendix C. The following results are obtained:

$$\log_{10} \beta_1^{\circ} = (0.170 \pm 0.021)$$

$$\Delta\varepsilon(\text{B.13}) = -\,(0.248 \pm 0.022)\ \text{kg·mol}^{-1}.$$

The experimental data are depicted in Figure B-1, where the area enclosed by the dotted lines represents the uncertainty range that is obtained by using the results in $\log_{10} \beta_1^{\circ}$ and $\Delta\varepsilon$ and correcting back to $I \neq 0$.

Figure B-1: Plot of $\log_{10} \beta_1 + 4D$ *versus* I_m for Reaction (B.13), at 25°C and 1 bar. The straight line shows the result of the weighted linear regression, and the dotted lines represent the uncertainty range obtained by propagating the resulting uncertainties at $I = 0$ back to $I = 4$ m.



Example B.3:

When using the specific ion interaction theory, the relationship between the redox potential of the couple, PuO_2^{2+}/Pu^{4+}, in a medium of ionic strength, I_m, and the corresponding quantity at $I = 0$ should be calculated in the following way. The reaction in the galvanic cell:

$$\mathrm{Pt} \left| \mathrm{H_2(g, r)} \right| \mathrm{H^+(r)} \left\| \mathrm{PuO_2^{2+}, Pu^{4+}, H^+, H_2O(l)} \right| \mathrm{Pt}$$

is:

$$\mathrm{PuO_2^{2+} + H_2(g, r) + 4H^+ - 2H^+(r) \rightleftharpoons Pu^{4+} + 2H_2O(l)} \qquad \text{(B.15)}$$

where "r" is used to indicate that $H_2(g)$ and H^+ are at the chemical conditions in the reference electrode compartment, *i.e.*, standard conditions when the reference electrode is the SHE. However, activities of H^+, $H_2O(l)$ and the ratio of activity of PuO_2^{2+} to Pu^{4+} depend on the conditions of the experimental measurements (*i.e.*, non-standard conditions, usually high ionic strength to improve the accuracy of the measurement).

For Reaction (B.15):

$$\log_{10} K^\circ = \log_{10}\left(\frac{a_{\mathrm{Pu^{4+}}} \cdot a^2_{\mathrm{H_2O}} \cdot a_{\mathrm{H^+(r)}}}{a_{\mathrm{PuO_2^{2+}}} \cdot a^4_{\mathrm{H^+}} \cdot f_{\mathrm{H_2(r)}}}\right).$$

Since by definition of the SHE, $f_{\mathrm{H_2(r)}} = 1$ and $\gamma_{\mathrm{H^+(r)}} = 1$,

$$\log_{10} K^\circ = \log_{10} K + \log_{10}\gamma_{\mathrm{Pu^{4+}}} - \log_{10}\gamma_{\mathrm{PuO_2^{2+}}} - 4\log_{10}\gamma_{\mathrm{H^+}} + 2\log_{10} a_{\mathrm{H_2O}},$$

and

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

$$\log_{10}\gamma_{\mathrm{PuO_2^{2+}}} = -4D + \varepsilon(\mathrm{PuO_2^{2+}, ClO_4^-})\, m_{\mathrm{ClO_4^-}}$$

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

Hence,

$$\begin{aligned}\log_{10} K^\circ = \log_{10} K - 8D + (\varepsilon(\mathrm{Pu^{4+}, ClO_4^-}) - \varepsilon(\mathrm{PuO_2^{2+}, ClO_4^-}) \\ - 4\varepsilon(\mathrm{H^+, ClO_4^-}))\, m_{\mathrm{ClO_4^-}} + 2\log_{10} a_{\mathrm{H_2O}}\end{aligned} \qquad \text{(B.16)}$$

The relationship between the equilibrium constant and the redox potential is:

$$\ln K = \frac{nF}{\mathrm{R}T} E^{\circ\prime} \qquad \text{(B.17)}$$

$$\ln K^\circ = \frac{nF}{\mathrm{R}T} E^\circ. \qquad \text{(B.18)}$$

$E^{\circ\prime}$ is the redox potential in a medium of ionic strength I, E° is the corresponding standard potential at $I = 0$, and n is the number of transferred electrons in the reaction considered. Combining Eqs. (B.16), (B.17) and (B.18) and rearranging them leads to Eq.(B.19):

$$E^{\mathrm{o}\prime} - (8D - 2\log_{10} a_{\mathrm{H_2O}})\left(\frac{\mathrm{R}T\ln(10)}{nF}\right) = E^{\mathrm{o}} - \Delta\varepsilon\; m_{\mathrm{ClO_4^-}}\left(\frac{\mathrm{R}T\ln(10)}{nF}\right) \qquad \text{(B.19)}$$

For $n = 2$ in the present example and $T = 298.15$ K, Eq.(B.19) becomes:

$$E^{\mathrm{o}\prime}[\mathrm{mV}] - 236.6\; D + 59.16\log_{10} a_{\mathrm{H_2O}} = E^{\mathrm{o}}[\mathrm{mV}] - 29.58\,\Delta\varepsilon\; m_{\mathrm{ClO_4^-}}$$

where

$$\Delta\varepsilon = \varepsilon(\mathrm{Pu^{4+}},\ \mathrm{ClO_4^-})\ - \varepsilon(\mathrm{PuO_2^{2+}},\ \mathrm{ClO_4^-})\ - 4\,\varepsilon(\mathrm{H^+},\ \mathrm{ClO_4^-})\,.$$

The value of $a_{\mathrm{H_2O}}$ can be taken from experimental data or calculated from equations (B.11) and (B.12).

In general, formal potentials are reported with reference to the standard hydrogen electrode, *cf.* Section II.1.6.5, as exemplified in Tables V.2 and V.3 of the uranium NEA review [1992GRE/FUG]. In that case, the H^+ appearing in the reduction reaction is already at standard conditions. For example, experimental data are available on the formal potentials for reactions:

$$\mathrm{PuO_2^{2+}} + 4\mathrm{H^+} + 2\mathrm{e^-} \rightleftharpoons \mathrm{Pu^{4+}} + 2\mathrm{H_2O(l)} \qquad \text{(B.20)}$$

and

$$\mathrm{PuO_2^{2+}} + \mathrm{e^-} \rightleftharpoons \mathrm{PuO_2^+}\,. \qquad \text{(B.21)}$$

While Reaction (B.20) corresponds to (B.15), Reaction (B.21) is equivalent to:

$$\mathrm{PuO_2^{2+}} + \frac{1}{2}\mathrm{H_2(g)} \rightleftharpoons \mathrm{PuO_2^+} + \mathrm{H^+} \qquad \text{(B.22)}$$

where the designator "(r)" has been omitted, since in these equations only the H^+ in the reference compartment is relevant.

The cations in Reaction (B.15) represent aqueous species in the ionic media used during the experiments. In Reaction (B.22) H^+ represents the cation in the standard hydrogen electrode, and therefore it is already in standard conditions, and its activity coefficient must not be included in any extrapolation to $I = 0$ of experimental values for Reaction (B.21). Reactions (B.21) and (B.22) are equivalent, as are Reactions (B.15) and (B.20), as can be seen if any of these equations are combined with Reaction (II.27). Hence Eq. (B.19) can be obtained more simply by using Eq. (II.34) for Reaction (B.20).

B.1.4 On the magnitude of ion interaction coefficients

Ciavatta [1980CIA] made a compilation of ion interaction coefficients for a large number of electrolytes. Similar data for complex formation reactions of various kinds were reported by Spahiu [1983SPA] and Ferri *et al.* [1983FER/GRE]. These and some other data for 25°C and 1 bar have been collected and are listed in Section B.3.

It is obvious from the data in these tables that the charge of an ion is of great importance for determining the magnitude of the ion interaction coefficient. Ions of the same charge type have similar ion interaction coefficients with a given counter-ion. Based on the tabulated data, Grenthe *et al.* [1992GRE/FUG] proposed that it is possible to estimate, with an error of at most ± 0.1 kg · mol^{-1} in ε, ion interaction coefficients for cases where there are insufficient experimental data for an extrapolation to $I = 0$. The error that is made by this approximation is estimated to be ± 0.1 kg · mol^{-1} in Δε in most cases, based on comparison with Δε values of various reactions of the same charge type.

B.2 Ion interaction coefficients *versus* equilibrium constants for ion pairs

It can be shown that the virial type of activity coefficient equations and the ionic pairing model are equivalent provided that the ionic pairing is weak. In these cases the distinction between complex formation and activity coefficient variations is difficult or even arbitrary unless independent experimental evidence for complex formation is available, *e.g.*, from spectroscopic data, as is the case for the weak uranium(VI) chloride complexes. It should be noted that the ion interaction coefficients evaluated and tabulated by Ciavatta [1980CIA] were obtained from experimental mean activity coefficient data without taking into account complex formation. However, it is known that many of the metal ions listed by Ciavatta form weak complexes with chloride and nitrate ion. This fact is reflected by ion interaction coefficients that are smaller than those for the non-complexing perchlorate ion, *cf.* Table B-4. This review takes chloride and nitrate complex formation into account when these ions are part of the ionic medium and uses the value of the ion interaction coefficient, $\varepsilon(\mathrm{M}^{n+},\mathrm{ClO}_4^-)$, as a substitute for $\varepsilon(\mathrm{M}^{n+},\mathrm{Cl}^-)$ and $\varepsilon(\mathrm{M}^{n+},\mathrm{NO}_3^-)$. In this way, the medium dependence of the activity coefficients is described with a combination of a specific ion interaction model and an ion pairing model. It is evident that the use of NEA recommended data with ionic strength correction models that differ from those used in the evaluation procedure can lead to inconsistencies in the results of the speciation calculations.

It should be mentioned that complex formation may also occur between highly charged complexes and the counterion of the ionic medium. An example is the stabilisation of the complex ion, $\mathrm{UO}_2(\mathrm{CO}_3)_3^{5-}$, at high ionic strength, see for example Section V.7.1.2.1.d (p. 322) in the uranium review [1992GRE/FUG].

B.3 Tables of ion interaction coefficients

Table B-4, Table B-5, Table B-6 and Table B-7 contain the selected specific ion interaction coefficients used in this review, according to the specific ion interaction theory described. Table B-4 contains cation interaction coefficients with Cl^-, ClO_4^- and NO_3^-, Table B-5 anion interaction coefficients with Li^+, Na^+ (or NH_4^+) and K^+, and Table B-7 neutral species – electroneutral combination of ions. The coefficients have the units of kg·mol^{-1} and are valid for 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 II.1.8.

It should be noted that ion interaction coefficients tabulated in Table B-4, Table B-5 and Table B-6 may also involve ion pairing effects, as described in Section B.3. In direct comparisons of ion interaction coefficients, or when estimates are made by analogy, this aspect must be taken into account.

Table B-4: Ion interaction coefficients $\varepsilon(j,k)$ (kg·mol^{-1}) for cations j with k = Cl$^-$, ClO_4^- and NO_3^-. The uncertainties represent the 95% confidence level. The ion interaction coefficients marked with † can be described more accurately with an ionic strength dependent function, listed in Table B-6. The coefficients $\varepsilon(M^{n+}, Cl^-)$ and $\varepsilon(M^{n+}, NO_3^-)$ reported by Ciavatta [1980CIA] were evaluated without taking chloride and nitrate complexation into account, as discussed in Section B.2.

j	k	$\varepsilon(j,\kappa)$	Comments
H^+	Cl^-	0.12 ± 0.01	Reported by Ciavatta [1980CIA].
	ClO_4^-	0.14 ± 0.02	
	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	See Section VIII.3.7 of [2005HUM/AND].
	ClO_4^-	-0.23 ± 0.15	
	NO_3^-	-0.23 ± 0.15	
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^-	—	

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Table B-4: (continued)

j	k	$\varepsilon(j,\kappa)$	Comments
$CdSCN^+$	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 $Ni^{2+} + H_2O \rightleftharpoons NiOH^+ + H^+$ from $\Delta\varepsilon$ in chloride media/perchlorate media.
	ClO_4^-	0.14 ± 0.07	
	NO_3^-	—	
NiF^+	Cl^-	—	
	ClO_4^-	0.34 ± 0.08	Derived from $\Delta\varepsilon = \varepsilon(NiF^+,ClO_4^-) - \varepsilon(Ni^{2+},ClO_4^-) - \varepsilon(Na^+,F^-) = -(0.049 ((0.060)$ 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^-	—	
$NiNO_3^+$	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 ± 0.5	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^-	—	

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Table B-4: (continued)

j	k	$\varepsilon(j,\kappa)$	Comments
$NiHS^+$	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 $\Delta\varepsilon = \varepsilon(NiSCN^-, Na^+) - \varepsilon(SCN^-, Na^+) - \varepsilon(Ni^{2+}, ClO_4^-) = -(0.109 \pm 0.025)$ kg·mol^{-1} (see [2005GAM/BUG], Section V.7.1.3.1).
	NO_3^-	—	
YCO_3^+	Cl^-	—	
	ClO_4^-	0.17 ± 0.04	Taken from Spahiu [1983SPA].
	NO_3^-	—	
$Am(OH)_2^+$	Cl^-	-0.27 ± 0.20	Evaluated in [2003GUI/FAN] (*cf.* Section 12.3.1.1) from Δε (in NaCl solution) for the reactions $An^{3+} + nH_2O(l) \rightleftharpoons An(OH)_n^{(3-n)} + n\,H^+$.
	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 Δε (in NaCl solution) for the reactions $An^{3+} + n\,CO_3^{2-} \rightleftharpoons An(CO_3)_n^{(3-n)}$ (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^-	—	

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Table B-4: (continued)

j	k	$\varepsilon(j,\kappa)$	Comments
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 Δε of the corresponding Np(IV) reaction.
	NO_3^-	—	
PuO_2Cl^+	Cl^-	—	
	ClO_4^-	0.50 ± 0.09	From Δε evaluated by Giffaut [1994GIF].
	NO_3^-	—	
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·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 Δε of the corresponding U(IV) reaction.
	NO_3^-	—	
NpO_2Cl^+	Cl^-	—	
	ClO_4^-	0.50 ± 0.14	Estimated in [2001LEM/FUG] by analogy with Δε 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^-	—	

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Table B-4: (continued)

j	*k*	ε(*j*,*κ*)	Comments
$\mathrm{Np(SCN)_3^+}$	$\mathrm{Cl^-}$	—	
	$\mathrm{ClO_4^-}$	0.17 ± 0.04	Estimated in [2001LEM/FUG] by assuming $\varepsilon(\mathrm{Np(SCN)_3^+},\mathrm{ClO_4^-}) \approx \varepsilon(\mathrm{AmF_2^+},\mathrm{ClO_4^-})$.
	$\mathrm{NO_3^-}$	—	
$\mathrm{UO_2^+}$	$\mathrm{Cl^-}$	—	
	$\mathrm{ClO_4^-}$	0.26 ± 0.03	Evaluated in [1992GRE/FUG], using $\varepsilon(\mathrm{UO_2^{2+}},\mathrm{ClO_4^-}) = (0.46 \pm 0.03)$ kg·mol^{-1}.
	$\mathrm{NO_3^-}$	—	
$\mathrm{UO_2OH^+}$	$\mathrm{Cl^-}$	—	
	$\mathrm{ClO_4^-}$	− 0.06 ± 0.40	Evaluated in [1992GRE/FUG], using $\varepsilon(\mathrm{UO_2^{2+}},\mathrm{X}) = (0.46 \pm 0.03)$ kg·mol^{-1}, where X = $\mathrm{Cl^-}$, $\mathrm{ClO_4^-}$ and $\mathrm{NO_3^-}$.
	$\mathrm{NO_3^-}$	0.51 ± 1.4	
$\mathrm{(UO_2)_3(OH)_5^+}$	$\mathrm{Cl^-}$	0.81 ± 0.17	Evaluated in [1992GRE/FUG], using $\varepsilon(\mathrm{UO_2^{2+}},\mathrm{X}) = (0.46 \pm 0.03)$ kg·mol^{-1}, where X = $\mathrm{Cl^-}$, $\mathrm{ClO_4^-}$ and $\mathrm{NO_3^-}$.
	$\mathrm{ClO_4^-}$	0.45 ± 0.15	
	$\mathrm{NO_3^-}$	0.41 ± 0.22	
$\mathrm{UF_3^+}$	$\mathrm{Cl^-}$	0.1 ± 0.1	Estimated in [1992GRE/FUG].
	$\mathrm{ClO_4^-}$	0.1 ± 0.1	
	$\mathrm{NO_3^-}$	—	
$\mathrm{UO_2F^+}$	$\mathrm{Cl^-}$	0.04 ± 0.07	Taken from Riglet *et al.* [1989RIG/ROB], where the following assumptions were made: $\varepsilon(\mathrm{Np^{3+}},\mathrm{ClO_4^-}) \approx \varepsilon(\mathrm{Pu^{3+}},\mathrm{ClO_4^-}) = 0.49$ kg·mol^{-1} as for other $(\mathrm{M^{3+}},\mathrm{ClO_4^-})$ interactions, and $\varepsilon(\mathrm{NpO_2^{2+}},\mathrm{ClO_4^-}) \approx \varepsilon(\mathrm{PuO_2^{2+}},\mathrm{ClO_4^-}) \approx \varepsilon(\mathrm{UO_2^{2+}},\mathrm{ClO_4^-}) = 0.46$ kg·mol^{-1}.
	$\mathrm{ClO_4^-}$	0.28 ± 0.04	See Section 9.4.2.2.1 of [2003GUI/FAN].
	$\mathrm{NO_3^-}$	—	
$\mathrm{UO_2Cl^+}$	$\mathrm{Cl^-}$	—	
	$\mathrm{ClO_4^-}$	0.33 ± 0.04	Evaluated in [1992GRE/FUG], using $\varepsilon(\mathrm{UO_2^{2+}},\mathrm{X}) = (0.46 \pm 0.03)$ kg·mol^{-1}, where X = $\mathrm{Cl^-}$, $\mathrm{ClO_4^-}$ and $\mathrm{NO_3^-}$.
	$\mathrm{NO_3^-}$	—	
$\mathrm{UO_2ClO_3^+}$	$\mathrm{Cl^-}$	—	
	$\mathrm{ClO_4^-}$	0.33 ± 0.04	Estimated in [1992GRE/FUG].
	$\mathrm{NO_3^-}$	—	
$\mathrm{UO_2Br^+}$	$\mathrm{Cl^-}$	—	
	$\mathrm{ClO_4^-}$	0.24 ± 0.04	Estimated in [1992GRE/FUG].
	$\mathrm{NO_3^-}$	—	
$\mathrm{UO_2BrO_3^+}$	$\mathrm{Cl^-}$	—	
	$\mathrm{ClO_4^-}$	0.33 ± 0.04	Estimated in [1992GRE/FUG].
	$\mathrm{NO_3^-}$	—	

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Table B-4: (continued)

j	k	$\varepsilon(j,\kappa)$	Comments
$UO_2IO_3^+$	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^-	—	
$Th(OH)_3^+$	Cl^-	0.06 ± 0.05	See Table VII-16 in Section VII.3.6.1 of this review.
	ClO_4^-	0.15 ± 0.10	
	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 this review.
	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 this review, using $\varepsilon(Th^{4+}, X)$ = (0.70 ± 0.10) kg·mol^{-1} where X = ClO_4^- and NO_3^-.
	NO_3^-	0.25 ± 0.15	
H_6edta^{2+}	Cl^-	−0.20 ± 0.16	Evaluated in [2005HUM/AND] (Section VIII.3.7).
	ClO_4^-	−0.20 ± 0.16	
	NO_3^-	−0.20 ± 0.16	
Pb^{2+}	Cl^-	—	
	ClO_4^-	0.15 ± 0.02	Reported by Ciavatta [1980CIA].
	NO_3^-	− 0.20 ± 0.12†	
$AlOH^{2+}$	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	

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Table B-4: (continued)

j	k	$\varepsilon(j,\kappa)$	Comments
$ZnCO_3^{2+}$	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].
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	Reported by Ciavatta [1980CIA].
	ClO_4^-	0.32 ± 0.02	
	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	Reported by Ciavatta [1980CIA].
	ClO_4^-	0.34 ± 0.03	
	NO_3^-	0.14 ± 0.01	
$FeOH^{2+}$	Cl^-	—	
	ClO_4^-	0.38	Taken from Spahiu [1983SPA].
	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^-	—	

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Table B-4: (continued)

j	k	$\varepsilon(j,\kappa)$	Comments
$YHCO_3^{2+}$	Cl^-	—	
	ClO_4^-	0.39 ± 0.04	Taken from Spahiu [1983SPA].
	NO_3^-	—	
$AmOH^{2+}$	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^-	—	

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Table B-4: (continued)

j	*k*	$\varepsilon(j,\kappa)$	Comments
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^-	—	
$PuCl^{2+}$	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 $\varepsilon(I^-,NH_4^+) \approx \varepsilon(SCN^-,Na^+)$.
	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^-	—	

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Table B-4: (continued)

j	k	$\varepsilon(j,\kappa)$	Comments
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^-.
$(UO_2)_2(OH)_2^{2+}$	Cl^-	0.69 ± 0.07	Evaluated in [1992GRE/FUG], using $\varepsilon(UO_2^{2+},X) = (0.46 \pm 0.03)$ kg·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·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 $\varepsilon(U^{4+},X) = (0.76 \pm 0.06)$ kg·mol^{-1}.
	NO_3^-	—	
$Th(OH)_2^{2+}$	Cl^-	0.13 ± 0.05	Calculated in Section VII.3.6.1 of this review.
	ClO_4^-	0.33 ± 0.10	
	NO_3^-	0.10 ± 0.15	
ThF_2^{2+}	Cl^-	—	
	ClO_4^-	0.3 ± 0.1	See Table VIII-8 in Section VIII.1.2.1 of this review.
	NO_3^-	0.15 ± 0.20	
$ThSO_4^{2+}$	Cl^-	0.14 ± 0.15	See Section IX.1.3.2 of this review.
	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 this review.
	NO_3^-	—	

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Table B-4: (continued)

j	k	$\varepsilon(j,\kappa)$	Comments
$\mathrm{Th(NO_3)_2^{2+}}$	$\mathrm{Cl^-}$	—	
	$\mathrm{ClO_4^-}$	0.43 ± 0.18	Estimated in Section X.1.3.3 of this review, using $\varepsilon(\mathrm{Th^{4+}}, \mathrm{X})$ = (0.70 ± 0.10) $\mathrm{kg{\cdot}mol^{-1}}$ for X = $\mathrm{ClO_4^-}$ and $\mathrm{NO_3^-}$.
	$\mathrm{NO_3^-}$	0.43 ± 0.18	
$\mathrm{Th(H_2PO_4)_2^{2+}}$	$\mathrm{Cl^-}$	—	
	$\mathrm{ClO_4^-}$	0.4 ± 0.1	Estimated in Section X.2.3.2 of this review.
	$\mathrm{NO_3^-}$	—	
$\mathrm{Th(SCN)_2^{2+}}$	$\mathrm{Cl^-}$	—	
	$\mathrm{ClO_4^-}$	0.38 ± 0.20	See Section XI.1.3.6.1 of this review.
	$\mathrm{NO_3^-}$	—	
$\mathrm{Mg^{2+}}$	$\mathrm{Cl^-}$	0.19 ± 0.02	Reported by Ciavatta [1980CIA].
	$\mathrm{ClO_4^-}$	0.33 ± 0.03	
	$\mathrm{NO_3^-}$	0.17 ± 0.01	
$\mathrm{Ca^{2+}}$	$\mathrm{Cl^-}$	0.14 ± 0.01	Reported by Ciavatta [1980CIA].
	$\mathrm{ClO_4^-}$	0.27 ± 0.03	
	$\mathrm{NO_3^-}$	0.02 ± 0.01	
$\mathrm{Ba^{2+}}$	$\mathrm{Cl^-}$	0.07 ± 0.01	Reported by Ciavatta [1980CIA].
	$\mathrm{ClO_4^-}$	0.15 ± 0.02	
	$\mathrm{NO_3^-}$	−0.28 ± 0.03	
$\mathrm{Al^{3+}}$	$\mathrm{Cl^-}$	0.33 ± 0.02	Reported by Ciavatta [1980CIA].
	$\mathrm{ClO_4^-}$	—	
	$\mathrm{NO_3^-}$	—	
$\mathrm{Ni_2OH^{3+}}$	$\mathrm{Cl^-}$	—	
	$\mathrm{ClO_4^-}$	0.59 ± 0.15	By assuming $\varepsilon(\mathrm{Ni_2OH^{3+}},\mathrm{ClO_4^-}) \approx \varepsilon(\mathrm{Be_2OH^{3+}},\mathrm{ClO_4^-})$, see Section V.3.1.1 in [2005GAM/BUG].
	$\mathrm{NO_3^-}$	—	
$\mathrm{Fe^{3+}}$	$\mathrm{Cl^-}$	—	
	$\mathrm{ClO_4^-}$	0.56 ± 0.03	Reported by Ciavatta [1980CIA].
	$\mathrm{NO_3^-}$	0.42 ± 0.08	
$\mathrm{Cr^{3+}}$	$\mathrm{Cl^-}$	0.30 ± 0.03	Reported by Ciavatta [1980CIA].
	$\mathrm{ClO_4^-}$	—	
	$\mathrm{NO_3^-}$	0.27 ± 0.02	Reported by Ciavatta [1980CIA].
$\mathrm{La^{3+}}$	$\mathrm{Cl^-}$	0.22 ± 0.02	Reported by Ciavatta [1980CIA].
	$\mathrm{ClO_4^-}$	0.47 ± 0.03	
	$\mathrm{NO_3^-}$	—	

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Table B-4: (continued)

j	k	$\varepsilon(j,k)$	Comments
$La^{3+} \rightarrow Lu^{3+}$	Cl^-	—	
	ClO_4^-	0.47 → 0.52	Taken from Spahiu [1983SPA].
	NO_3^-	—	
Am^{3+}	Cl^-	0.23 ± 0.02	The $\varepsilon(An^{3+},Cl^-)$ for An = Am and Cm is assumed to 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 ion interaction Pitzer 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 $\varepsilon(Br^-,H^+) \approx \varepsilon(Br^-,Na^+)$.
	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^-	—	

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Table B-4: (continued)

j	k	$\varepsilon(j,\kappa)$	Comments
NpF^{3+}	Cl^-	—	
	ClO_4^-	0.58 ± 0.07	Evaluated in [2001LEM/FUG].
	NO_3^-	—	
$NpCl^{3+}$	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 $\varepsilon(I^-,H^+) \approx \varepsilon(I^-,Na^+)$.
	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 [2001LEM/FUG] by analogy with $\Delta\varepsilon$ of the corresponding Pu(VI) reaction and using $\varepsilon(U^{4+},X) = (0.76 \pm 0.06)$ kg·mol^{-1} for X = Cl^- and ClO_4^-.
	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^-	—	
	NO_3^-	0.56 ± 0.14	

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Table B-4: (continued)

j	*k*	ε(*j*,κ)	Comments
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^-	—	
$Th(OH)^{3+}$	Cl^-	0.19 ± 0.05	See Table VII-18 in Section VII.3.6.1 of this review.
	ClO_4^-	0.48 ± 0.08	
	NO_3^-	0.20 ± 0.15	
ThF^{3+}	Cl^-	—	
	ClO_4^-	0.48 ± 0.08	Estimated in Section VIII.1.2.1 of this review (Table VIII-8).
	NO_3^-	0.25 ± 0.20	
$ThCl^{3+}$	Cl^-	0.62 ± 0.11	Calculated in Section VIII.2.2.1.2 of this review using $\varepsilon(Th^{4+},X) = (0.70 \pm 0.10)$ kg·mol^{-1}, for X = Cl^- and ClO_4^-
	ClO_4^-	0.62 ± 0.11	
	NO_3^-	—	
$ThClO_3^{3+}$	Cl^-	—	
	ClO_4^-	0.62 ± 0.11	Calculated in Section VIII.2.2.2 of this review 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 this review 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 this review 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 this review.
	NO_3^-	—	
$Th(NO_3)^{3+}$	Cl^-	—	
	ClO_4^-	0.56 ± 0.14	Calculated in Section X.1.3.3 of this review using $\varepsilon(Th^{4+},X) = (0.70 \pm 0.10)$ kg·mol^{-1}, for X = ClO_4^- and NO_3^-.
	NO_3^-	0.56 ± 0.14	
$Th(H_2PO_4)^{3+}$	Cl^-	—	
	ClO_4^-	0.5 ± 0.1	Estimated in Section X.2.3.2 of this review.
	NO_3^-	—	

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Table B-4: (continued)

j	k	$\varepsilon(j,\kappa)$	Comments
$Th(H_2PO_4)(H_3PO_4)^{3+}$	Cl^-	—	
	ClO_4^-	0.5 ± 0.1	Estimated in Section X.2.3.2 of this review.
	NO_3^-	—	
$Th(SCN)^{3+}$	Cl^-	—	
	ClO_4^-	0.50 ± 0.10	See Section XI.1.3.6.1 of this review.
	NO_3^-	—	
Be_2OH^{3+}	Cl^-	—	
	ClO_4^-	0.50 ± 0.05	Taken from [1986BRU], where the following assumptions were made: $\varepsilon(Be^{2+},ClO_4^-) = 0.30$ kg·mol^{-1} as for other $\varepsilon(M^{2+},ClO_4^-)$; $\varepsilon(Be^{2+},Cl^-) = 0.17$ kg·mol^{-1} as for other $\varepsilon(M^{2+},Cl^-)$ and $\varepsilon(Be^{2+},NO_3^-) = 0.17$ kg·mol^{-1} as for other $\varepsilon(M^{2+},NO_3^-)$.
	NO_3^-	—	
$Be_3(OH)_3^{3+}$	Cl^-	0.30 ± 0.05	Taken from [1986BRU], where the following assumptions were made: $\varepsilon(Be^{2+},ClO_4^-) = 0.30$ kg·mol^{-1} as for other $\varepsilon(M^{2+},ClO_4^-)$; $\varepsilon(Be^{2+},Cl^-) = 0.17$ kg·mol^{-1} as for other $\varepsilon(M^{2+},Cl^-)$ and $\varepsilon(Be^{2+},NO_3^-) = 0.17$ kg·mol^{-1} as for other $\varepsilon(M^{2+},NO_3^-)$.
	ClO_4^-	0.51 ± 0.05	Evaluated in [1992GRE/FUG] using $\varepsilon(U^{4+},X) = (0.76 \pm 0.06)$ kg·mol^{-1}.
	NO_3^-	0.29 ± 0.05	Taken from [1986BRU], where the following assumptions were made: $\varepsilon(Be^{2+},ClO_4^-) = 0.30$ kg·mol^{-1} as for other $\varepsilon(M^{2+},ClO_4^-)$; $\varepsilon(Be^{2+},Cl^-) = 0.17$ kg·mol^{-1} as for other $\varepsilon(M^{2+},Cl^-)$ and $\varepsilon(Be^{2+},NO_3^-) = 0.17$ kg·mol^{-1} as for other $\varepsilon(M^{2+},NO_3^-)$
$Al_3HCO_3(OH)_4^{4+}$	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^-	0.82	Taken from Spahiu [1983SPA].
	NO_3^-	—	

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Table B-4: (continued)

j	*k*	ε(*j*,*κ*)	Comments
$Y_2CO_3^{4+}$	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 this review.
	ClO_4^-	0.82 ± 0.07	Derived from $\Delta\varepsilon = \varepsilon(Pu^{4+},ClO_4^-) - \varepsilon(Pu^{3+},ClO_4^-) =$ (0.33 ± 0.035) kg·mol^{-1} [1995CAP/VIT]. Uncertainty estimated in [2001LEM/FUG]. In the [1992GRE/FUG], $\varepsilon(Pu^{3+},ClO_4^-) =$ (1.03 ± 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^-	—	
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 ± 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 ± 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 ± 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 ± 0.06) kg·mol^{-1} is consistent with that tabulated $\varepsilon(U^{4+},ClO_4^-) =$ (0.76 ± 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 this review.
	NO_3^-	0.31 ± 0.12	Evaluated in Section VI.3.1 of this review.

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Table B-4: (continued)

j	k	$\varepsilon(j,\kappa)$	Comments
$Th_4(OH)_{12}^{4+}$	Cl^-	0.25 ± 0.20	See Section VII.3.4.1.3 of this review.
	ClO_4^-	0.56 ± 0.42	
	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 this review.
	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	Calculated in Section VII.3.4.1.1 of this review.
	ClO_4^-	0.91 ± 0.21	
	NO_3^-	0.69 ± 0.25	
$Th_2(OH)_2^{6+}$	Cl^-	0.40 ± 0.16	Evaluated in Section VII.3.4.1.1 of this review.
	ClO_4^-	1.22 ± 0.24	
	NO_3^-	0.69 ± 0.26	
$Th_4(OH)_8^{8+}$	Cl^-	0.70 ± 0.20	Evaluated in Section VII.3.4.1.3 of this review.
	ClO_4^-	1.69 ± 0.42	
	NO_3^-	1.59 ± 0.51	
$Th_6(OH)_{15}^{9+}$	Cl^-	0.72 ± 0.30	See details in Section VII.3.4.1.4 of this review.
	ClO_4^-	1.85 ± 0.74	
	NO_3^-	2.20 ± 0.77	
$Th_6(OH)_{14}^{10+}$	Cl^-	0.83 ± 0.30	Estimated in Section VII.3.4.1.4 of this review.
	ClO_4^-	2.2 ± 0.3	
	NO_3^-	2.9 ± 0.5	

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

j	*k*	ε(*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	Reported by Ciavatta [1980CIA].
	Na^+	0.03 ± 0.01	
	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	Reported by Ciavatta [1980CIA].
	Na^+	0.01 ± 0.01	
	K^+	—	
Br^-	Li^+	0.13 ± 0.02	Reported by Ciavatta [1980CIA].
	Na^+	0.05 ± 0.01	
	K^+	0.01 ± 0.02	
BrO_3^-	Li^+	—	
	Na^+	−0.06 ± 0.02	Reported by Ciavatta [1980CIA].
	K^+	—	
I^-	Li^+	0.16 ± 0.01	Reported by Ciavatta [1980CIA].
	Na^+	0.08 ± 0.02	
	K^+	0.02 ± 0.01	
IO_3^-	Li^+	—	
	Na^+	−0.06 ± 0.02	Estimated in [1992GRE/FUG].
	K^+	—	
HSO_4^-	Li^+	—	
	Na^+	−0.01 ± 0.02	Reported by Ciavatta [1980CIA].
	K^+	—	

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Table B-5: (continued)

j	*k*	ε(*j*,*k*)	Comments
N_3^-	Li^+	—	
	Na^+	0.015 ± 0.020	See Section X.1.2 of this review.
	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	Evaluated in Section VI.3.5 of [2005HUM/AND].
	Na^+	−0.07 ± 0.01	
	K^+	−0.01 ± 0.08	
H_2cit^-	Li^+	−0.11 ± 0.03	Evaluated in Section VII.3.6 of [2005HUM/AND].
	Na^+	−0.05 ± 0.01	
	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	
$HCOO^-$	Li^+	—	
	Na^+	0.03 ± 0.01	Reported by Ciavatta [1980CIA].
	K^+	—	
CH_3COO^-	Li^+	0.05 ± 0.01	Reported by Ciavatta [1980CIA].
	Na^+	0.08 ± 0.01	
	K^+	0.09 ± 0.01	

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Table B-5: (continued)

j	k	$\varepsilon(j,k)$	Comments
H_3edta^-	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^+	—	
$Si_2O_2(OH)_5^-$	Li^+	—	
	Na^+	-0.08 ± 0.04	Estimated in [1992GRE/FUG].
	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 ± 0.5	Evaluated in Section VII.7 of [2005HUM/AND].
	K^+	—	
$Am(SO_4)_2^-$	Li^+	—	
	Na^+	-0.05 ± 0.05	Estimated in [1995SIL/BID].
	K^+	—	
$Am(CO_3)_2^-$	Li^+	—	
	Na^+	-0.14 ± 0.06	Evaluated Section 12.6.1.1.1 [2003GUI/FAN], from $\Delta\varepsilon_n$ in NaCl solution for the reactions $An^{3+} + n\,CO_3^{2-} \rightleftharpoons An(CO_3)_n^{(3-n)}$ based on $\varepsilon(Am^{3+},Cl^-) = (0.23 \pm 0.02)\,kg \cdot mol^{-1}$ and $\varepsilon(Na^+, CO_3^{2-}) = -(0.08 \pm 0.03)\,kg \cdot mol^{-1}$.
	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 $\varepsilon(Am(edta)^-, K^+) \approx \varepsilon(Am(edta)^-, Na^+)$.

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Table B-5: (continued)

j	k	$\varepsilon(j,k)$	Comments
$PuO_2CO_3^-$	Li^+	—	
	Na^+	-0.18 ± 0.18	Estimated in [2001LEM/FUG] by analogy with $\varepsilon(NpO_2CO_3^-, Na^+)$.
	K^+	—	
$Pu(edta)^-$	Li^+	—	
	Na^+	—	
	K^+	0.01 ± 0.16	Estimated in [2005HUM/AND], Section VIII.12.2.1 by assuming $\varepsilon(Pu(edta)^-, K^+) \approx \varepsilon(Am(edta)^-, Na^+)$.
$NpO_2(OH)_2^-$	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^+	—	
$(NpO_2)_2CO_3(OH)_3^-$	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^+	—	

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Table B-5: (continued)

j	*k*	ε(*j*,*k*)	Comments
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 this review.
	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].
$S_2O_3^{2-}$	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	Evaluated in Section VI.3.5 of [2005HUM/AND].
	Na^+	−0.08 ± 0.01	
	K^+	0.07 ± 0.08	
$Hcit^{2-}$	Li^+	−0.17 ± 0.04	Evaluated in Section VII.3.6 of [2005HUM/AND].
	Na^+	−0.04 ± 0.02	
	K^+	−0.01 ± 0.02	

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Table B-5: (continued)

j	k	$\varepsilon(j,k)$	Comments
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^+	—	
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_2cit^{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^+	—	

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Table B-5: (continued)

j	*k*	ε(*j*,*k*)	Comments
$UO_2(N_3)_4^{2-}$	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_2edta^{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^+	—	
$(UO_2)_2(OH)_2(SO_4)_2^{2-}$	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 this review.
	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 this review.
	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 this review.
	K^+	—	
$Th(OH)_4(CO_3)^{2-}$	Li^+	—	
	Na^+	-0.1 ± 0.2	See Section XI.1.3.2 of this review.
	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 $\varepsilon(Mg(ox)_2^{2-}, K^+) \approx \varepsilon(Mg(ox)_2^{2-}, Na^+)$.
$Mg(edta)^{2-}$	Li^+	—	
	Na^+	-0.01 ± 0.15	Evaluated in Section VIII.5.2 of [2005HUM/AND].
	K^+	—	

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Table B-5: (continued)

j	*k*	ε(*j*,*k*)	Comments
$Ca(ox)_2^{2-}$	Li^+	—	
	Na^+	-0.15 ± 0.10	Estimated in [2005HUM/AND], Section VI.5.2 by assuming $\varepsilon(Ca(ox)_2^{2-}, Na^+) \approx \varepsilon(Mg(ox)_2^{2-}, Na^+)$.
	K^+	-0.15 ± 0.10	Estimated in [2005HUM/AND], Section VI.5.2 by assuming $\varepsilon(Ca(ox)_2^{2-}, K^+) \approx \varepsilon(Mg(ox)_2^{2-}, Na^+)$.
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].
$Si_3O_6(OH)_3^{3-}$	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^+	—	
$Am(CO_3)_3^{3-}$	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 $An^{3+} + n\,CO_3^{2-} \rightleftharpoons An(CO_3)_n^{(3-n)}$ 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 $\varepsilon(Am(ox)_3^{3-}, Na^+) \approx \varepsilon(Am(CO_3)_3^{3-}, Na^+)$.
	K^+	—	

(Continued on next page)

Table B-5: (continued)

j	*k*	ε(*j*,*k*)	Comments
$Np(CO_3)_3^{3-}$	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^+	—	
$NpO_2(ox)_2^{3-}$	Li^+	—	
	Na^+	-0.3 ± 0.2	Evaluated in Section VI.11.2.3 of [2005HUM/AND].
	K^+	—	
NpO_2edta^{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	$\varepsilon(NpO_2(CO_3)_3^{4-}, NH_4^+) = -(0.78 \pm 0.25)$ kg · mol^{-1} is calculated in [2001LEM/FUG] (Section 12.1.2.2.1).
$NpO_2(CO_3)_2OH^{4-}$	Li^+	—	
	Na^+	-0.40 ± 0.19	Estimated in [2001LEM/FUG] by analogy with $NpO_2(CO_3)_3^{4-}$.
	K^+	—	
$U(CO_3)_4^{4-}$	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^+	—	

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Table B-5: (continued)

j	*k*	ε(*j*,*k*)	Comments
$\mathrm{UO_2(CO_3)_3^{4-}}$	$\mathrm{Li^+}$	—	
	$\mathrm{Na^+}$	-0.01 ± 0.11	These values differ from those reported in [1992GRE/FUG]. See the discussion in [1995GRE/PUI]. Values for $\mathrm{CO_3^{2-}}$ and $\mathrm{HCO_3^-}$ are based on [1980CIA].
	$\mathrm{K^+}$	—	
$\mathrm{UO_2(ox)_3^{4-}}$	$\mathrm{Li^+}$	—	
	$\mathrm{Na^+}$	-0.01 ± 0.11	Estimated in [2005HUM/AND], Section VI.10.2.4.1 by assuming $\varepsilon(\mathrm{UO_2(ox)_3^{4-}, Na^+}) \approx \varepsilon(\mathrm{UO_2(CO_3)_3^{4-}, Na^+})$.
	$\mathrm{K^+}$	—	
$\mathrm{(UO_2)_3(OH)_4(SO_4)_3^{4-}}$	$\mathrm{Li^+}$	—	
	$\mathrm{Na^+}$	0.6 ± 0.6	Estimated in Section 9.5.1.1.2 of [2003GUI/FAN].
	$\mathrm{K^+}$	—	
$\mathrm{NpO_2(CO_3)_3^{5-}}$	$\mathrm{Li^+}$	—	
	$\mathrm{Na^+}$	-0.53 ± 0.19	Calculated in [2001LEM/FUG] (Section 12.1.2.1.3).
	$\mathrm{K^+}$	-0.22 ± 0.03	Evaluated in [2003GUI/FAN] (discussion of [1998ALM/NOV] in Appendix A) from Δε for the reactions $\mathrm{KNpO_2CO_3(s) + 2\,CO_3^{2-} \rightleftharpoons NpO_2(CO_3)_3^{5-} + K^+}$ (in $\mathrm{K_2CO_3}$–KCl solution) and $\mathrm{K_3NpO_2(CO_3)_2(s) + CO_3^{2-} \rightleftharpoons NpO_2(CO_3)_3^{5-} + 3\,K^+}$ (in $\mathrm{K_2CO_3}$ solution) (based on $\varepsilon(\mathrm{K^+, CO_3^{2-}}) = (0.02 \pm 0.01)\ \mathrm{kg \cdot mol^{-1}}$).
$\mathrm{UO_2(CO_3)_3^{5-}}$	$\mathrm{Li^+}$	—	
	$\mathrm{Na^+}$	-0.62 ± 0.15	These values differ from those reported in [1992GRE/FUG]. See the discussion in [1995GRE/PUI]. Values for $\mathrm{CO_3^{2-}}$ and $\mathrm{HCO_3^-}$ are based on [1980CIA].
	$\mathrm{K^+}$	—	
$\mathrm{Th(OH)(CO_3)_4^{5-}}$	$\mathrm{Li^+}$	—	
	$\mathrm{Na^+}$	-0.22 ± 0.13	Evaluated in Section XI.1.3.2.1 of this review.
	$\mathrm{K^+}$	—	
$\mathrm{Np(CO_3)_5^{6-}}$	$\mathrm{Li^+}$	—	
	$\mathrm{Na^+}$	—	
	$\mathrm{K^+}$	-0.73 ± 0.68	Calculated in [2001LEM/FUG] (Section 12.1.2.1.4).
$\mathrm{(NpO_2)_3(CO_3)_6^{6-}}$	$\mathrm{Li^+}$	—	
	$\mathrm{Na^+}$	-0.46 ± 0.73	Calculated in [2001LEM/FUG] (Section 12.1.2.1.2).
	$\mathrm{K^+}$	—	

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Table B-5: (continued)

j	*k*	ε(*j*,*k*)	Comments
$U(CO_3)_5^{6-}$	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^+	—	
$Th(CO_3)_5^{6-}$	Li^+	—	
	Na^+	-0.30 ± 0.15	Estimated in Section XI.1.3.2.1 of this review.
	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 B-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 $k \rightarrow$	Cl^-		ClO_4^-		NO_3^-	
$\downarrow$	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		
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

j $k \rightarrow$	Li^+		Na^+		K^+	
$\downarrow$	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].

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

j *k*→ ↓	$Na^+ + ClO_4^-$	$Na^+ + Cl^-$	$K^+ + NO_3^-$
H_2ox(aq)	0.00 ± 0.01 [b]	0.00 ± 0.01 [b]	0.00 ± 0.01 [b]
H_3cit(aq)	0.00 ± 0.01 [b]	0.00 ± 0.01 [b]	0.00 ± 0.01 [b]
H_4edta(aq)	– 0.29 ± 0.14	– 0.29 ± 0.14	– 0.29 ± 0.14
Ni(ox)(aq)	– 0.07 ± 0.03	– 0.07 ± 0.03	
Ni(Hcit)(aq)	– 0.07 ± 0.05		
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_2ox(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 of this review, see Sections VI.3.5 and VII.3.6 for discussions.

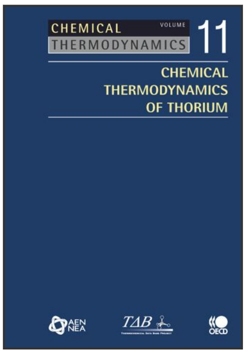
(c): Estimated in Section VI.5.2 of [2005HUM/AND] by assuming ε(Mg(ox)(aq), KNO_3) ≈ ε(Mg(ox)(aq), NaCl).

(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), $NaClO_4$).



Please cite this chapter as:

OECD/Nuclear Energy Agency (2008), “Appendix B: Ionic strength corrections”, in *Chemical Thermodynamics of Thorium, Volume 11*, OECD Publishing, Paris.

DOI: https://doi.org/10.1787/9789264056688-15-en