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TDB-2

GUIDELINES FOR THE EXTRAPOLATION TO ZERO IONIC STRENGTH

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Guidelines for the Extrapolation to Zero Ionic Strength

Thermodynamic data always refer to a selected standard state. The definition given by IUPAC [82LAF] is adopted in the NEA-TDB project as outlined in the TDB-5 guideline [99NEA]. 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 $m_B = m^\circ = 1 \text{ mol} \cdot \text{kg}^{-1}$, 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, ensuring that activity factors are reasonably constant throughout the measurements. The objectives of this guideline are to describe and illustrate various methods of extrapolation to zero ionic strength and to indicate the methods preferred in the NEA TDB reviews along with recommended values of the auxiliary parameters. By following these guidelines, the members of the NEA TDB specialist teams performing the review will be assured of using the same theory consistently for the extrapolation 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 standard state ($I = 0$). Two alternative types of methods can be used to describe the ionic medium dependence of equilibrium constants:

- One type of 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 [73PIT] and in the specific ion interaction theory.
- The other type of 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 introducing ionic 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. [79JOH/PYT, 79MIL, 79PYT, 79WHI].

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. However, the Davies equation (see Section 2.3) should in general not be used at ionic strengths larger than $0.1 \text{ mol} \cdot \text{kg}^{-1}$.

The following forms of specific ion interaction methods have been described in the literature:

1. The Brønsted-Guggenheim-Scatchard approach (abbreviated “B-G-S equation” in this document), *cf.* Section 1.
2. The Pitzer and Brewer “B-method” (abbreviated “P-B” in this document) *cf.* Section 2.1.
3. The Pitzer virial coefficient method, *cf.* Section 2.2.

Methods 1 and 2 are equivalent and differ only in the form of the denominator in the Debye-Hückel term. Method 3 requires more parameters for the description of the activity factors. These parameters are not available in many cases. This is generally the case for complex formation reactions.

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 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 [92GRE/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, 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 the NEA TDB reviews.

The method used in the NEA Thermochemical Data Base review is the specific ion interaction theory in the form of the Brønsted-Guggenheim-Scatchard approach. It should be emphasised that the specific ion interaction model is *approximate*. Modifying it, for example by introducing the equations suggested by Ciavatta [90CIA, Eqs. (8–10)] (*cf.* Section 1.4), would result in slightly different ion interaction coefficients and equilibrium constants. Both methods provide an internally consistent set of values. However, their absolute values may differ somewhat. Grenthe *et al.* [92GRE/FUG] estimate that these differences in general are less than 0.2 units in $\log_{10} K^\circ$, *i.e.*, approximately $1 \text{ kJ} \cdot \text{mol}^{-1}$ in derived $\Delta_f G_m^\circ$ values.

One may sometimes have access to the parameters required for the Pitzer approaches, *e.g.*, for some hydrolysis equilibria and possibly for some solubility product data, *cf.* Baes and Mesmer [76BAE/MES] and Pitzer [79PIT]. In this case, the reviewer should perform a calculation using the B-G-S equation, the P-B equation and the full virial coefficient methods and compare the results. If the results differ more than the experimental uncertainty, this should be brought to the attention of the advisory group for ionic strength corrections.

1 The specific ion interaction model (SIT)

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 [22BRØ2, 22BRØ], and elaborated by Scatchard [36SCA] and Guggenheim [66GUG]. 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. (1).

$$\log_{10} \gamma_j = -z_j^2 D + \sum_k \varepsilon_{(j,k,I_m)} m_k \quad (1)$$

D is the Debye-Hückel term:

$$D = \frac{A\sqrt{I_m}}{1 + Ba_j\sqrt{I_m}} \quad (2)$$

A and B are constants which are temperature dependent, and a_j is the effective diameter of the hydrated ion j . The values of A and B as a function of temperature are listed in Table 1.

The term Ba_j in the denominator of the Debye-Hückel term has been assigned a value of $Ba_j = 1.5 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$, as proposed by Scatchard [76SCA] and accepted by Ciavatta [80CIA]. This value has been found to minimize, for several species, the ionic strength dependence of $\varepsilon_{(j,k,I_m)}$ between $I_m = 0.5 \text{ m}$ and $I_m = 3.5 \text{ m}$. It should be mentioned that some authors have proposed different values for Ba_j , ranging from $Ba_j = 1.0$ [35GUG] to $Ba_j = 1.6$ [62VAS]. However,

the parameter Ba_j is empirical and as such 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 listed in Tables 3 through 5 have thus to be used with $Ba_j = 1.5 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$.

The summation in Eq. (1) extends over all ions k present in solution. Their molality is denoted m_k . The concentrations of the ions of the ionic medium is 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. (5) to (9).

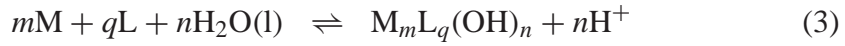
Assumption 2: The ion interaction coefficients $\varepsilon_{(j,k,I_m)}$ are zero for ions of the same charge sign and for uncharged species. The rationale behind this is that ε , which describes specific short-range interactions, must be small for ions of the same charge since they are usually far from one another due to electrostatic repulsion. This holds to a lesser extent also for uncharged species.

Eq. (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 emphasized by Guggenheim [66GUG], 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 accurately reproduce their activity coefficient data, concentration dependent ion interaction coefficients have to be used, *cf.* Pitzer and Brewer [61LEW/RAN], Baes and Mesmer [76BAE/MES], or Ciavatta [80CIA]. By using a more elaborate virial expansion, Pitzer and co-workers [73PIT, 73PIT/MAY, 74PIT/KIM, 74PIT/MAY, 75PIT, 76PIT/SIL, 78PIT/PET, 79PIT] 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 the NEA-TDB reviews according to the specific ion interaction theory is illustrated below for a general case of a complex formation reaction. Charges are omitted for brevity.



The formation constant of $M_mL_q(OH)_n$, ${}^*\beta_{q,n,m}$, 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, ${}^*\beta_{q,n,m}^\circ$, by Eq. (4).

$$\log_{10} {}^*\beta_{q,n,m} = \log_{10} {}^*\beta_{q,n,m}^\circ + m \log_{10} \gamma_M + q \log_{10} \gamma_L + n \log_{10} a_{H_2O} - \log_{10} \gamma_{q,n,m} - n \log_{10} \gamma_H \quad (4)$$

The subscript (q,n,m) denotes the complex ion $M_mL_q(OH)_n$. If the concentrations of N and X are much greater than the concentrations of M, L, $M_mL_q(OH)_n$ 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. (1). For example, for the activity coefficient of the metal cation M, γ_M , Eq. (5) is obtained.

$$\log_{10} \gamma_M = \frac{-z_M^2 0.509 \sqrt{I_m}}{1 + 1.5 \sqrt{I_m}} + \varepsilon_{(M,X,I_m)} m_X \quad (5)$$

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

$$\log_{10} {}^*\beta_{n,p,m} - \Delta z^2 D - p \log_{10} a_{H_2O} = \log_{10} {}^*\beta_{n,p,m}^\circ - \Delta \varepsilon I_m \quad (6)$$

where

$$\Delta z^2 = (mz_M - nz_L - p)^2 + p - mz_M^2 - nz_L^2 \quad (7)$$

$$D = \frac{0.5091 \sqrt{I_m}}{1 + 1.5 \sqrt{I_m}} \quad (8)$$

$$\Delta \varepsilon = \varepsilon_{(n,p,m,N \text{ or } X)} + p\varepsilon_{(H,X)} - n\varepsilon_{(N,L)} - m\varepsilon_{(M,X)} \quad (9)$$

Here $(mz_M - nz_L - p)$, z_M and z_L are the charges of the complex $M_mL_n(OH)_p$, 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, $a_{\text{H}_2\text{O}}$. The activity of water in an electrolyte mixture can be calculated as

$$\log_{10} a_{\text{H}_2\text{O}} = \frac{-\Phi \sum_k m_k}{\ln(10) \times 55.51} \quad (10)$$

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. (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 $I_m \approx m_{\text{NX}}$, Eq. (10) becomes

$$\log_{10} a_{\text{H}_2\text{O}} = \frac{-2m_{\text{NX}}\Phi}{\ln(10) \times 55.51}. \quad (11)$$

Values of osmotic coefficients for single electrolytes have been compiled by various authors, *e.g.*, Robinson and Stokes [59ROB/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 $\text{N}_{\nu_+}\text{X}_{\nu_-}$ of a concentration much larger than those of the reacting ions, the osmotic coefficient can be calculated according to Eq. (12) (*cf.* Eqs. (23-39), (23-40) and (A4-2) in [61LEW/RAN]).

$$1 - \phi = \frac{A \ln(10) |z_+ z_-|}{I_m (B a_j)^3} \left[1 + B a_j \sqrt{I_m} - 2 \log_{10}(1 + B a_j \sqrt{I_m}) - \frac{1}{1 + B a_j \sqrt{I_m}} \right] - \ln(10) \varepsilon_{(\text{N},\text{X})} m_{\text{NX}} \left(\frac{\nu_+ \nu_-}{\nu_+ + \nu_-} \right) \quad (12)$$

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

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

The activity of water is obtained by inserting Eq. (12) into Eq. (11). 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. On the other hand, $a_{\text{H}_2\text{O}}$ is near constant (and equal to 1) 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 $\text{H}_2\text{O}(\text{l})$ 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.*, $(\text{Na}^+, \text{Mg}^{2+}, \text{Ca}^{2+})(\text{Cl}^-, \text{SO}_4^{2-})$, Pitzer's equation 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 mean activity coefficients can be split up to give equations for conventional single ion activity coefficients in mixtures, *e.g.*, Eq. (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 $\text{H}^+ + \text{e}^- \rightleftharpoons \frac{1}{2}\text{H}_2(\text{g})$ is necessary (*cf.* Example 3).

1.2 Ionic strength corrections at temperatures other than 298.15 K

Values of the Debye-Hückel parameters A and B in Eqs. (2) and (12) are listed in Table 1 for a few temperatures at a pressure of 1 bar below 100°C and at the steam saturated pressure for $t \geq 100^\circ\text{C}$. The values in Table 1 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. [74HEL/KIR, 79BRA/PIT, 81HEL/KIR, 84ANA/ATK, 90ARC/WAN]. The value of A is normally treated as temperature dependent, although the correction is usually small. The values of $\varepsilon_{(j,k,I_m)}$ obtained with the methods described in Section 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 temperature intervals between 0 and 200°C the choice $Ba_j = 1.5 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$ is the simplest one and is recommended by this review.

The variation of $\varepsilon_{(j,k,I_m)}$ with temperature is discussed by Lewis, Randall, Pitzer and Brewer [61LEW/RAN], Millero [79MIL], Helgeson *et al.* [81HEL/KIR, 90OEL/HEL], Giffaut *et al.* [93GIF/VIT] and Grenthe and Plyasunov [97GRE/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 on solubility calculations at $t \neq 25^\circ$, studies on the variation of $\varepsilon_{(j,k,I_m)}$ -values with temperature should be undertaken.

Table 1: Debye-Hückel constants as a function of temperature at a pressure of 1 bar below 100°C and at the steam saturated pressure for $t \geq 100^\circ\text{C}$. 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 ($\text{kg} \cdot \text{mol}^{-1}$) $^{\frac{1}{2}}$	$B \times 10^{-10}$ ($\text{kg}^{\frac{1}{2}} \cdot \text{mol}^{-\frac{1}{2}} \cdot \text{m}^{-1}$)
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

1.3 Estimation of ion interaction coefficients

1.3.1 Estimation from mean activity coefficient data

Example 1:

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

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

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

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

Example 2:

Equilibrium constants are given in Table 2 for the reaction



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

Table 2: 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 (13). The linear regression of this set of data is shown in Figure 1.

I_m	$\log_{10} \beta_1(\text{exp})^{(a)}$	$\log_{10} \beta_{1,m}^{(b)}$	$\log_{10} \beta_{1,m} + 4D$
0.1	-0.17±0.10	-0.174	0.264 ± 0.100
0.2	-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	-0.021	0.860 ± 0.100
3.5	0.04±0.10	-0.021	0.974 ± 0.100

(a) Equilibrium constants for Reaction (13) with assigned uncertainties, corrected to 25°C where necessary.

(b) Equilibrium constants corrected from molarity to molality units, as described in the TDB-5 guideline [99NEA].

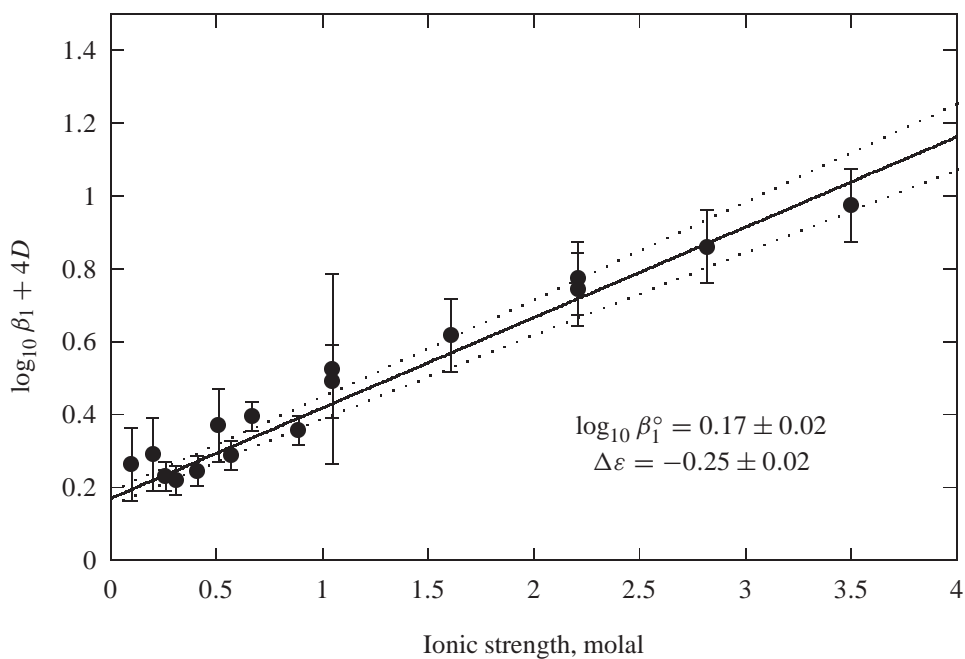
$$\log_{10} \beta_1 + 4D = \log_{10} \beta_1^\circ - \Delta\varepsilon I_m \quad (14)$$

The linear regression is done as described in the NEA Guidelines for the Assignment of Uncertainties [99NEA]. The following results are obtained:

$$\begin{aligned}\log_{10} \beta_1^\circ &= 0.170 \pm 0.021 \\ \Delta\varepsilon(13) &= 0.248 \pm 0.022 \text{ kg} \cdot \text{mol}^{-1}\end{aligned}$$

The experimental data are depicted in Figure 1, where the area between the dashed 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 1: Plot of $\log_{10} \beta_1 + 4D$ vs. I_m for Reaction (13). 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 3:

When using the specific ion interaction theory, the relationship between the normal potential of the redox couple $\text{UO}_2^{2+}/\text{U}^{4+}$ 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



is



For this reaction

$$\begin{aligned} \log_{10} K^\circ &= \log_{10} \left(\frac{a_{\text{U}^{4+}} \times a_{\text{H}_2\text{O}}^2}{a_{\text{UO}_2^{2+}} \times a_{\text{H}^+}^2 \times f_{\text{H}_2}} \right), \\ \log_{10} K^\circ &= \log_{10} K + \log_{10} \gamma_{\text{U}^{4+}} - \log_{10} \gamma_{\text{UO}_2^{2+}} - 2 \log_{10} \gamma_{\text{H}^+} \\ &\quad - \log_{10} \gamma_{f, \text{H}_2} + 2 \log_{10} a_{\text{H}_2\text{O}}, \end{aligned}$$

$f_{\text{H}_2} \approx p_{\text{H}_2}$ at reasonably low partial pressure of $\text{H}_2(\text{g})$, $a_{\text{H}_2\text{O}} \approx 1$, and

$$\begin{aligned} \log_{10} \gamma_{\text{U}^{4+}} &= -16D + \varepsilon_{(\text{U}^{4+}, \text{ClO}_4^-)} m_{\text{ClO}_4^-} \\ \log_{10} \gamma_{\text{UO}_2^{2+}} &= -4D + \varepsilon_{(\text{UO}_2^{2+}, \text{ClO}_4^-)} m_{\text{ClO}_4^-} \\ \log_{10} \gamma_{\text{H}^+} &= -D + \varepsilon_{(\text{H}^+, \text{ClO}_4^-)} m_{\text{ClO}_4^-}. \end{aligned}$$

Hence,

$$\begin{aligned} \log_{10} K^\circ &= \log_{10} K - 10D \\ &\quad + \left(\varepsilon_{(\text{U}^{4+}, \text{ClO}_4^-)} - \varepsilon_{(\text{UO}_2^{2+}, \text{ClO}_4^-)} - 2\varepsilon_{(\text{H}^+, \text{ClO}_4^-)} \right) m_{\text{ClO}_4^-}. \quad (17) \end{aligned}$$

The relationship between the equilibrium constant and the standard potential is

$$\ln K = \frac{nF}{RT} E \quad (18)$$

$$\ln K^\circ = \frac{nF}{RT} E^\circ. \quad (19)$$

E is the standard potential in a medium of ionic strength I , E° is the corresponding quantity at $I = 0$, and n is the number of transferred electrons in the reaction considered. Combining Eqs. (17), (18) and (19) and rearranging them leads to Eq. (20).

$$E - 10D \left(\frac{RT \ln(10)}{nF} \right) = E^\circ - \Delta \varepsilon m_{\text{ClO}_4^-} \left(\frac{RT \ln(10)}{nF} \right) \quad (20)$$

For $n = 2$ in the present example and $T = 298.15$ K, Eq. (20) becomes

$$E[\text{mV}] - 295.8D = E^\circ[\text{mV}] - 29.58 \Delta \varepsilon m_{\text{ClO}_4^-} \quad (21)$$

where

$$\Delta \varepsilon = \left(\varepsilon_{(\text{U}^{4+}, \text{ClO}_4^-)} - \varepsilon_{(\text{UO}_2^{2+}, \text{ClO}_4^-)} - 2\varepsilon_{(\text{H}^+, \text{ClO}_4^-)} \right). \quad (22)$$

1.4 On the magnitude of ion interaction coefficients

Ciavatta [80CIA] made a compilation of ion interaction coefficients for a large number of electrolytes. Similar data for complexations of various kinds were reported by Spahiu [83SPA] and Ferri, Grenthe and Salvatore [83FER/GRE]. These and some other data have been collected and are listed in Tables 3 to 5. It is obvious from the data in these tables that the charge of an ion is of great importance for 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.* [92GRE/FUG] proposed that it is possible to estimate, with an error of at most ± 0.1 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 ± 0.1 in $\Delta\varepsilon$ in most cases, based on comparison with $\Delta\varepsilon$ values of various reactions of the same charge type.

Ciavatta [90CIA] has proposed an alternative method to estimate values of ε for a first or second complex, ML or ML_2 , in an ionic media NX , according to the following relationships,

$$\varepsilon(\text{ML}, \text{N or X}) \approx (\varepsilon(\text{M,X}) + \varepsilon(\text{L,N}))/2 \quad (23)$$

$$\varepsilon(\text{ML}_2, \text{N, or X}) \approx (\varepsilon(\text{M,X}) + 2\varepsilon(\text{L,N}))/3 \quad (24)$$

Ciavatta obtained [90CIA] an average deviation of $\pm 0.05 \text{ kg} \cdot \text{mol}^{-1}$ between ε -estimates according to Eqs. (23) and (24) and the ε -values at 25°C obtained from ionic strength dependency of equilibrium constants.

2 Other methods for ionic strength corrections

2.1 The Pitzer and Brewer equation

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

$$\log_{10} \gamma_i = \frac{-z_i^2 0.5107 \sqrt{I_m}}{1 + \sqrt{I_m}} + \sum_j B(i, j) m_j \quad (25)$$

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 [61LEW/RAN] and by Baes and Mesmer [76BAE/MES]. The Debye-Hückel term, *cf.* Eq. (2), is different from that in the B-G-S equation. Apart from a slightly different value for A , the factor Ba_j has been chosen equal to 1.0 in the P-B equation compared to 1.5 in the B-G-S equation. The B-G-S equation is preferred to the P-B equation in the critical evaluations of the NEA-TDB Project for the reasons given in Section 1.1.

2.2 The Pitzer equations

The following text is only intended to provide the reader with a brief outline of the Pitzer method. This approach consists in the development of an explicit function relating the ion interaction coefficient to the ionic strength and the addition of a third virial coefficient to Eq. (1). For the solution of a single electrolyte MX the activity coefficient may be expressed by Eq. (26) [73PIT].

$$\ln \gamma = |z_M z_X| f^\gamma + m \frac{(2\nu_M \nu_X)}{\nu} B_{MX}^\gamma + m^2 \left(\frac{2(\nu_M \nu_X)^{3/2}}{\nu} \right) C_{MX}^\gamma \quad (26)$$

where ν_M and ν_X are the numbers of M and X ions in the formula unit and z_M and z_X their charges. m is the molality of the solution and $\nu = \nu_M + \nu_X$. In aqueous solutions at 25°C and 10⁵ Pa the following relations are given [73PIT/MAY]:

$$f^\gamma = -0.392 \left(\frac{\sqrt{I_m}}{1 + 1.2\sqrt{I_m}} + 1.667 \ln(1 + 1.2\sqrt{I_m}) \right) \quad (27)$$

$$B_{MX}^\gamma = 2\beta_{MX}^{(0)} + \frac{\beta_{MX}^{(1)}}{2I_m} \left(1 - (1 + 2\sqrt{I_m} - 2I_m)e^{-2\sqrt{I_m}} \right) \quad (28)$$

$$C_{MX}^\gamma = \frac{3}{2} C_{MX}^\phi \quad (29)$$

where f^γ is the Debye-Hückel term extended to include osmotic effects, the parameters $\beta_{MX}^{(0)}$ and $\beta_{MX}^{(1)}$ define the second virial coefficient (corresponding to ε in the B-G-S equation), and C_{MX}^ϕ defines the third virial coefficient. $I_m = \frac{1}{2} \sum m_i z_i^2$ is the ionic strength in molal units. In the case of 2:2 electrolytes one could add to the second virial coefficient terms of the same form. Pitzer's equations have been extended to cover electrolyte mixtures [74PIT/KIM], including terms allowing for the interactions of ions of the same charge sign. Eq. (30) is an extension of Eq. (26) for a anions and c cations [79PIT]. Here a and a' cover all anions, c and c' cover all cations, and $(\sum m z) = \sum_c m_c z_c = \sum_a m_a |z_a|$.

$$\begin{aligned} \ln \gamma_{MX} = & |z_M z_X| f^\gamma + \frac{2\nu_M}{\nu} \sum_a m_a \left(B_{Ma} + (\sum m z) C_{Ma} + \frac{\nu_X}{\nu_M} \theta_{Xa} \right) \\ & + \frac{2\nu_X}{\nu} \sum_c m_c \left(B_{cX} + (\sum m z) C_{cX} + \frac{\nu_M}{\nu_X} \theta_{Mc} \right) \\ & + \sum_c \sum_a m_c m_a \left(|z_M z_X| B'_{ca} + \frac{1}{\nu} (2\nu_M z_M C_{ca} + \nu_M \psi_{Mca} + \nu_X \psi_{caX}) \right) \\ & + \frac{1}{2} \sum_c \sum_{c'} m_c m_{c'} \left(\frac{\nu_X}{\nu} \psi_{cc'X} + |z_M z_X| \theta'_{cc'} \right) \\ & + \frac{1}{2} \sum_a \sum_{a'} m_a m_{a'} \left(\frac{\nu_M}{\nu} \psi_{Maa'} + |z_M z_X| \theta'_{aa'} \right) \end{aligned} \quad (30)$$

In Eq. (30) f^γ is the same as in Eq. (26), C_{MX} , B_{MX} and its derivative with ionic strength, B'_{MX} , have the forms

$$B_{MX} = \beta_{MX}^{(0)} + \frac{\beta_{MX}^{(1)}}{2I_m} \left(1 - (1 + 2\sqrt{I_m})e^{-2\sqrt{I_m}} \right) \quad (31)$$

$$B'_{MX} = \frac{\beta_{MX}^{(1)}}{2I_m^2} \left(-1 + (1 + 2\sqrt{I_m} + 2I_m)e^{-2\sqrt{I_m}} \right) \quad (32)$$

$$C_{MX} = \frac{C_{MX}^\phi}{2\sqrt{|z_M z_X|}} \quad (33)$$

where $\beta^{(0)}$, $\beta^{(1)}$, C^ϕ are the same as for pure electrolytes. In Eq. (30) the θ terms summarise the interactions between ions of the same charge sign that are independent of the common ion in a ternary mixture, and the ψ terms account for the modifying influence of the common ion on these interactions. Pitzer [79PIT] points out that higher order electrostatic terms (beyond the Debye-Hückel approximation) become important in cases of unsymmetrical mixing, especially if one of the ions has a charge of three or higher. Higher order electrostatic effects on the other hand were found to be unimportant for cases of symmetrical mixing and for pure unsymmetrical electrolytes.

Based on the cluster integral method [62FRI], Pitzer [75PIT] divided the difference terms θ_{MN} into two parts

$$\theta_{MN} = {}^s\theta_{MN} + {}^E\theta_{MN} \quad (34)$$

The ${}^E\theta_{MN}$ terms may be expressed as:

$${}^E\theta_{MN} = \frac{z_M z_N}{4I_m} \left(J(x_{MN}) - \frac{1}{2}J(x_{MM}) - \frac{1}{2}J(x_{NN}) \right) \quad (35)$$

$${}^E\theta'_{MN} = -\frac{{}^E\theta}{I_m} + \frac{z_M z_N}{8I_m^2} \left(x_{MN}J'(x_{MN}) - \frac{1}{2}x_{MM}J'(x_{MM}) - \frac{1}{2}x_{NN}J'(x_{NN}) \right) \quad (36)$$

where $x_{ij} = 6z_i z_j 0.392\sqrt{I_m}$ at 25°C and 10⁵Pa and $J(x)$ is an integral which can be approximated as

$$J(x) = -\frac{1}{6}x^2(\ln x)e^{-10x^2} + \left(\sum_{k=1}^6 C_k x^{-k} \right)^{-1}. \quad (37)$$

The first term is in fact important only at very low ionic strengths, thus for cases used in equilibrium analysis one has

$$J(x) = \left(\frac{4.118}{x} + \frac{7.247}{x^2} + \frac{4.408}{x^3} + \frac{1.837}{x^4} + \frac{0.251}{x^5} + \frac{0.0164}{x^6} \right)^{-1}. \quad (38)$$

The ${}^s\theta_{MN}$ parameters can be evaluated from data on mixtures of electrolytes by calculating the differences between the experimental value of γ^{exp} and the value calculated with the appropriate values for all pure electrolyte terms and ${}^E\theta$ terms but zero values for ${}^s\theta$ and ψ terms. For the activity coefficient of MX in a MX-NX mixture one has Eq. (39) and equivalent expressions for other cases.

$$\frac{\nu}{2\nu_M m_N} \Delta \ln \gamma = \left({}^s\theta_{MN} + \frac{1}{2} \left(m_X + \left| \frac{z_M}{z_X} \right| m_M \right) \psi_{MNX} \right) \quad (39)$$

This is the equation of a straight line with intercept ${}^s\theta_{MN}$ and slope ψ_{MNX} , when the left side of Eq. (39) is plotted against a function of the composition $\frac{1}{2} \left(m_X + \left| \frac{z_M}{z_X} \right| m_M \right)$.

The Pitzer equation for single electrolytes with the value of parameters collected in several publications, may be used as a compact source of activity coefficient data. From the values $\gamma_{\pm,jk}^\circ$ thus obtained, one may calculate, for example, $\varepsilon_{(j,k,l_m)}$ values using Eq. (1).

For the estimation of medium effects on solubility equilibria in mixtures of electrolytes involving ions of charge less than 3 units, one may neglect the θ and ψ terms in Eq. (30).

In equilibrium analysis studies carried out in the presence of an inert salt (medium salt NX) and small (“trace”) concentrations of the reactants, only the terms involving m_{NX} have to be considered in Eq. (30), while those involving m_i^{trace} can be neglected. Nevertheless, as the main difficulty there still remains the accurate estimation of the parameters of single electrolyte $\beta^{(0)}$, $\beta^{(1)}$, C^ϕ for species such as metal ion complexes.

Equations for single ion activity coefficients [79PIT], osmotic coefficients [74PIT/KIM] and other thermodynamic quantities [77SIL/PIT], as well as applications in different cases (*e.g.*, H₂SO₄ and H₃PO₄ solutions) have been given by Pitzer and co-workers [79PIT, 76PIT/SIL].

From Tables 3 and 4 it seems that the size and charge correlations can be extended to complex ions. This observation is very important because it indicates a possibility to estimate the ion interaction coefficients for complexes by using such correlations. It is, of course, always preferable to use experimental ion interaction coefficient data. However, the efforts needed to obtain these data for complexes will be so great that it is unlikely that they will be available for more than a few complex species. It is even less likely that one will have data for the Pitzer parameters for these species. Hence, the specific ion interaction approach may have a practical advantage over the inherently more precise Pitzer approach.

2.3 The equations used by Baes and Mesmer

Baes and Mesmer [76BAE/MES] use 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

$$\log_{10} \gamma_{\pm MX}^{\circ} = -|z_M z_X| \frac{0.511\sqrt{I_m}}{1 + \sqrt{I_m}} + \frac{2\nu_M \nu_X}{\nu} B_{MX} m_{MX} \quad (40)$$

where

$$B_{MX} = B_{MX}^{\infty} + (B_{MX}^{\circ} - B_{MX}^{\infty})F(I_m) \quad (41)$$

$$F(I_m) = \frac{1 - (1 + 2\sqrt{I_m} - 2I_m)e^{-2\sqrt{I_m}}}{4I_m}, \quad F(0) = 1, \quad F(\infty) = 0. \quad (42)$$

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. (1), are not obtained at high ionic strengths. The parameters B_{MX}° and B_{MX}^{∞} can be determined from a single electrolyte activity coefficient datum by calculating first B_{MX} . (Note that $B_{MX} \neq \varepsilon_{(j,k)}$, since the Debye-Hückel term in Eq. (40) does not have the factor 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}° is obtained from the slope of the straight line, *cf.* Eq. (41). The equation for a mixture is similar to Eq. (40) 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. (6).

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

$$\log_{10} \beta(I_{m,n}) - \Delta z_i^2 \frac{0.511\sqrt{I_{m,n}}}{1 + \sqrt{I_{m,n}}} - r \log_{10}(a_{H_2O})_n = \log_{10} \beta^{\circ} + \Delta B^{\infty} [1 - F(I_{m,n})] I_{m,n} + \Delta B^{\circ} F(I_{m,n}) I_{m,n} \quad (43)$$

where $\beta(I_{m,n})$ and $(a_{H_2O})_n$ refer to the values of β and a_{H_2O} at ionic strength $I_{m,n}$. From the values obtained for ΔB° and ΔB^{∞} and equations similar to Eq. (9), one may estimate the unknown B_{MX}° and B_{MX}^{∞} values.

2.3 The Davies equation

The Davies equation [62DAV] has been used extensively to calculate activity coefficients of electrolytes at fairly low ionic strengths.

The Davies equation for the activity coefficient of an ion i of charge z_i is, at 25°C:

$$\log_{10} \gamma_i = -0.5102z_i^2 \left(\frac{\sqrt{I_m}}{1 + \sqrt{I_m}} - 0.3I_m \right). \quad (44)$$

The equation has no theoretical foundation but is found to work fairly well up to ionic strengths of $0.1 \text{ mol} \cdot \text{kg}^{-1}$. It should not be used at higher ionic strengths. The Davies equation has a form similar to the B-G-S equation but with “ion interaction coefficients” equal to $0.153z_i^2$, *i.e.*, 0.15, 0.61 and 1.38 for ions of charge 1, 2 and 3, respectively. These values do not agree very well with the tabulated ϵ values.

3 Conclusions

The specific ion interaction approach is simple to use and gives a fairly good estimate of activity factors. 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 Data Base review for the extrapolation and correction of equilibrium data to the infinite dilution standard state.

Tables of ion interaction coefficients

Tables 3 through 5 contain the selected specific ion interaction coefficients used in this review, according to the specific ion interaction theory described in Section 1. Table 3 contains cation interaction coefficients with Cl^- , ClO_4^- and NO_3^- , Table 4 anion interaction coefficients with Li^+ , with Na^+ or NH_4^+ and with K^+ . The coefficients have the units of $\text{kg} \cdot \text{mol}^{-1}$ and are valid for 298.15 K. The species are ordered by charge and appear, within each charge class, in standard order of arrangement, *cf.* Ref. [82WAG/EVA].

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 [80CIA] proposed the use of Eq. (45) for cases where the uncertainties in Tables 3 and 4 are ± 0.03 or greater.

$$\varepsilon = \varepsilon_1 + \varepsilon_2 \log_{10} I_m \quad (45)$$

For these cases, and when the uncertainty can be improved with respect to the use of a constant value of ε , the values ε_1 and ε_2 given in Table 5 should be used.

It should be noted that ion interaction coefficients tabulated in Tables 3 through 5 may also involve ion pairing effects. In direct comparisons of ion interaction coefficients, or when estimates are made by analogy, this aspect must be taken into account.

Table 3: Ion interaction coefficients $\varepsilon_{j,k}$ for cations j with $k = \text{Cl}^-$, ClO_4^- and NO_3^- , taken from Ciavatta [80CIA, 88CIA] unless indicated otherwise. 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 5. The coefficients $\varepsilon_{(\text{M}^{n+}, \text{Cl}^-)}$ and $\varepsilon_{(\text{M}^{n+}, \text{NO}_3^-)}$ reported by Ciavatta [80CIA] were evaluated without taking chloride and nitrate complexation into account.

$j \quad k \rightarrow$ ↓	Cl^-	ClO_4^-	NO_3^-
H^+	0.12 ± 0.01	0.14 ± 0.02	0.07 ± 0.01
NH_4^+	-0.01 ± 0.01	$-0.08 \pm 0.04^\dagger$	$-0.06 \pm 0.03^\dagger$
H_2gly^+	-0.06 ± 0.02		
Tl^+		$-0.21 \pm 0.06^\dagger$	
ZnHCO_3^+	$0.2^{(a)}$		
CdCl^+		0.25 ± 0.02	

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^(a)Taken from Ferri *et al.* [85FER/GRE].

Table 3: (continued)

$j \quad k \rightarrow$ \downarrow	Cl^-	ClO_4^-	NO_3^-
CdI^+		0.27 ± 0.02	
CdSCN^+		0.31 ± 0.02	
HgCl^+		0.19 ± 0.02	
Cu^+		0.11 ± 0.01	
Ag^+		0.00 ± 0.01	$-0.12 \pm 0.05^\dagger$
YCO_3^+		$0.17 \pm 0.04^{(b)}$	
UO_2^+		$0.26 \pm 0.03^{(c)}$	
UO_2OH^+		$-0.06 \pm 0.40^{(c)}$	$0.51 \pm 1.4^{(c)}$
$(\text{UO}_2)_3(\text{OH})_5^+$	$0.81 \pm 0.17^{(c)}$	$0.45 \pm 0.15^{(c)}$	$0.41 \pm 0.22^{(c)}$
UF_3^+	$0.1 \pm 0.1^{(d)}$	$0.1 \pm 0.1^{(d)}$	
UO_2F^+	$0.04 \pm 0.07^{(e)}$	$0.29 \pm 0.05^{(c)}$	
UO_2Cl^+		$0.33 \pm 0.04^{(c)}$	
$\text{UO}_2\text{ClO}_3^+$		$0.33 \pm 0.04^{(d)}$	
UO_2Br^+		$0.24 \pm 0.04^{(d)}$	
$\text{UO}_2\text{BrO}_3^+$		$0.33 \pm 0.04^{(d)}$	
UO_2IO_3^+		$0.33 \pm 0.04^{(d)}$	
UO_2N_3^+		$0.3 \pm 0.1^{(d)}$	
UO_2NO_3^+		$0.33 \pm 0.04^{(d)}$	
UO_2SCN^+		$0.22 \pm 0.04^{(d)}$	
PuO_2^+		$0.24 \pm 0.05^{(f)}$	
NpO_2^+		$0.25 \pm 0.05^{(g)}$	

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(b) Taken from Spahiu [83SPA].

(c) Evaluated in the uranium review [92GRE/FUG], using $\varepsilon_{(\text{UO}_2^+, X)} = (0.46 \pm 0.03) \text{ kg} \cdot \text{mol}^{-1}$, where $X = \text{Cl}^-$, ClO_4^- and NO_3^- .

(d) Estimated in the uranium review [92GRE/FUG].

(e) Taken from Riglet, Robouch and Vitorge [89RIG/ROB], where the following assumptions were made: $\varepsilon_{(\text{Np}^{3+}, \text{ClO}_4^-)} \approx \varepsilon_{(\text{Pu}^{3+}, \text{ClO}_4^-)} = 0.49 \text{ kg} \cdot \text{mol}^{-1}$ as for other (M^{3+} , ClO_4^-) interactions, and $\varepsilon_{(\text{NpO}_2^+, \text{ClO}_4^-)} \approx \varepsilon_{(\text{PuO}_2^+, \text{ClO}_4^-)} \approx \varepsilon_{(\text{UO}_2^+, \text{ClO}_4^-)} = 0.46 \text{ kg} \cdot \text{mol}^{-1}$.(f) Derived from $\Delta\varepsilon = \varepsilon_{(\text{PuO}_2^+, \text{ClO}_4^-)} - \varepsilon_{(\text{PuO}_2^+, \text{ClO}_3^-)} = (0.22 \pm 0.03) \text{ kg} \cdot \text{mol}^{-1}$ [95CAP/VIT]. In [92GRE/FUG] $\varepsilon = \varepsilon_{(\text{PuO}_2^+, \text{ClO}_4^-)} = (0.17 \pm 0.05) \text{ kg} \cdot \text{mol}^{-1}$ was tabulated based on [89ROB, 89RIG/ROB, 90RIG]. Capdevila and Vitorge's data [92CAP, 94CAP/VIT, 95CAP/VIT] were

Table 3: (continued)

$j \quad k \rightarrow$ \downarrow	Cl^-	ClO_4^-	NO_3^-
NpO_2OH^+		$-(0.06 \pm 0.40)^{(o)}$	
$(\text{NpO}_2)_3(\text{OH})_5^+$		$-(0.45 \pm 0.20)^{(o)}$	
$\text{Am}(\text{OH})_2^+$		$0.17 \pm 0.04^{(h)}$	
AmF_2^+		$0.17 \pm 0.04^{(h)}$	
AmSO_4^+		$0.22 \pm 0.08^{(i)}$	
AmCO_3^+		$0.17 \pm 0.04^{(h)}$	
AlOH^{2+}	$0.09^{(j)}$	$0.31^{(j)}$	
$\text{Al}_2\text{CO}_3(\text{OH})_2^{2+}$	$0.26^{(j)}$		
Pb^{2+}		0.15 ± 0.02	$-0.20 \pm 0.12^\dagger$
Zn^{2+}		0.33 ± 0.03	0.16 ± 0.02
ZnCO_3^{2+}	$0.35 \pm 0.05^{(a)}$		
Cd^{2+}			0.09 ± 0.02
Hg^{2+}		0.34 ± 0.03	$-0.1 \pm 0.1^\dagger$
Hg_2^{2+}		0.09 ± 0.02	$-0.2 \pm 0.1^\dagger$
Cu^{2+}	0.08 ± 0.01	0.32 ± 0.02	0.11 ± 0.01
Ni^{2+}	0.17 ± 0.02		
Co^{2+}	0.16 ± 0.02	0.34 ± 0.03	0.14 ± 0.01
FeOH^{2+}		$0.38^{(b)}$	
FeSCN^{2+}		$0.45^{(b)}$	
Mn^{2+}	0.13 ± 0.01		
YHCO_3^{2+}		$0.39 \pm 0.04^{(b)}$	
PuO_2^{2+}		$0.46 \pm 0.05^{(k)}$	
NpO_2^{2+}		$0.46 \pm 0.05^{(k)}$	

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 not available at that time.

^(e) As in [92GRE/FUG], derived from $\Delta\varepsilon = \varepsilon_{(\text{NpO}_2^{2+}, \text{ClO}_4^-)} - \varepsilon_{(\text{NpO}_2^+, \text{ClO}_4^-)} = (0.21 \pm 0.03)$ $\text{kg}\cdot\text{mol}^{-1}$ [87RIG/VIT, 89RIG/ROB, 90RIG].

^(h) Estimated in the NEA-TDB review on americium thermodynamics [95SIL/BID].

⁽ⁱ⁾ Evaluated in the NEA-TDB review on americium thermodynamics [95SIL/BID].

^(j) Taken from Hedlund [88HED].

Table 3: (continued)

$j \quad k \rightarrow$ \downarrow	Cl^-	ClO_4^-	NO_3^-
$(\text{NpO}_2)_2(\text{OH})_2^{2+}$		$-(0.57 \pm 0.10)^{(o)}$	
NpSO_4^{2+}		(0.48 ± 0.10)	
UO_2^{2+}	$0.21 \pm 0.02^{(l)}$	0.46 ± 0.03	$0.24 \pm 0.03^{(l)}$
$(\text{UO}_2)_2(\text{OH})_2^{2+}$	$0.69 \pm 0.07^{(c)}$	$0.57 \pm 0.07^{(c)}$	$0.49 \pm 0.09^{(c)}$
$(\text{UO}_2)_3(\text{OH})_4^{2+}$	$0.50 \pm 0.18^{(c)}$	$0.89 \pm 0.23^{(c)}$	$0.72 \pm 1.0^{(c)}$
UF_2^{2+}		$0.3 \pm 0.1^{(d)}$	
USO_4^{2+}		$0.3 \pm 0.1^{(d)}$	
$\text{U}(\text{NO}_3)_2^{2+}$		$0.49 \pm 0.14^{(m)}$	
AmOH^{2+}		$0.39 \pm 0.04^{(h)}$	
AmF^{2+}		$0.39 \pm 0.04^{(h)}$	
AmCl^{2+}		$0.39 \pm 0.04^{(h)}$	
AmN_3^{2+}		$0.39 \pm 0.04^{(h)}$	
AmNO_2^{2+}		$0.39 \pm 0.04^{(h)}$	
AmNO_3^{2+}		$0.39 \pm 0.04^{(h)}$	
$\text{AmH}_2\text{PO}_4^{2+}$		$0.39 \pm 0.04^{(h)}$	
AmSCN^{2+}		$0.39 \pm 0.04^{(h)}$	
Mg^{2+}	0.19 ± 0.02	0.33 ± 0.03	0.17 ± 0.01
Ca^{2+}	0.14 ± 0.01	0.27 ± 0.03	0.02 ± 0.01
Ba^{2+}	0.07 ± 0.01	0.15 ± 0.02	-0.28 ± 0.03
Al^{3+}	0.33 ± 0.02		
Fe^{3+}		0.56 ± 0.03	0.42 ± 0.08
Cr^{3+}	0.30 ± 0.03		0.27 ± 0.02
La^{3+}	0.22 ± 0.02	0.47 ± 0.03	

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^(k) By analogy with $\varepsilon_{(\text{UO}_2^{2+}, \text{ClO}_4^-)}$ as derived from isopiestic measurements in [92GRE/FUG]. The uncertainty is increased because the value is estimated by analogy.

^(l) These coefficients were not used in the NEA-TDB uranium review [92GRE/FUG] because they were evaluated by Ciavatta [80CIA] without taking chloride and nitrate complexation into account. Instead, Grenthe *et al.* used $\varepsilon_{(\text{UO}_2^{2+}, X)} = (0.46 \pm 0.03) \text{ kg} \cdot \text{mol}^{-1}$, for $X = \text{Cl}^-$, ClO_4^- and NO_3^- .

^(m) Evaluated in the uranium review [92GRE/FUG] using $\varepsilon_{(\text{U}^{4+}, \text{ClO}_4^-)} = (0.76 \pm 0.06) \text{ kg} \cdot \text{mol}^{-1}$.

Table 3: (continued)

$j \quad k \rightarrow$ \downarrow	Cl^-	ClO_4^-	NO_3^-
$\text{La}^{3+} \rightarrow \text{Lu}^{3+}$		$0.47 \rightarrow 0.52^{(b)}$	
Pu^{3+}		$0.49 \pm 0.05^{(n)}$	
PuOH^{3+}		$0.50 \pm 0.05^{(o)}$	
Np^{3+}		$0.49 \pm 0.05^{(n)}$	
NpOH^{3+}		$0.50 \pm 0.05^{(o)}$	
U^{3+}		$0.49 \pm 0.05^{(m)}$	
UOH^{3+}		$0.48 \pm 0.08^{(m)}$	
UF^{3+}		$0.48 \pm 0.08^{(d)}$	
UCl^{3+}		$0.59 \pm 0.10^{(m)}$	
UBr^{3+}		$0.52 \pm 0.10^{(d)}$	
UI^{3+}		$0.55 \pm 0.10^{(d)}$	
UNO_3^{3+}		$0.62 \pm 0.08^{(m)}$	
Am^{3+}		$0.49 \pm 0.03^{(h)}$	
$\text{Be}_2\text{OH}^{3+}$		$0.50 \pm 0.05^{(p)}$	
$\text{Be}_3(\text{OH})_3^{3+}$	$0.30 \pm 0.05^{(p)}$	$0.51 \pm 0.05^{(p)}$	$0.29 \pm 0.05^{(p)}$
$\text{Al}_3\text{CO}_3(\text{OH})_4^{4+}$	$0.41^{(j)}$		
$\text{Fe}_2(\text{OH})_2^{4+}$		$0.82^{(b)}$	
$\text{Y}_2\text{CO}_3^{4+}$		$0.80 \pm 0.04^{(b)}$	
Pu^{4+}		$0.82 \pm 0.06^{(q)}$	
Np^{4+}		$0.84 \pm 0.06^{(r)}$	

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⁽ⁿ⁾ Estimated by analogy with $\varepsilon_{(\text{Ho}^{3+}, \text{ClO}_4^-)}$ [83SPA] as in previous books in this series [92GRE/FUG, 95SIL/BID]. The uncertainty is increased because the value is estimated by analogy.

^(o) Estimated in the TDB Np/Pu review [2000LEM/FUG]

^(p) Taken from Bruno [86BRU], where the following assumptions were made: $\varepsilon_{(\text{Be}^{2+}, \text{ClO}_4^-)} = 0.30 \text{ kg} \cdot \text{mol}^{-1}$ as for other $\varepsilon_{(\text{M}^{2+}, \text{ClO}_4^-)}$, $\varepsilon_{(\text{Be}^{2+}, \text{Cl}^-)} = 0.17 \text{ kg} \cdot \text{mol}^{-1}$ as for other $\varepsilon_{(\text{M}^{2+}, \text{Cl}^-)}$, and $\varepsilon_{(\text{Be}^{2+}, \text{NO}_3^-)} = 0.17 \text{ kg} \cdot \text{mol}^{-1}$ as for other $\varepsilon_{(\text{M}^{2+}, \text{NO}_3^-)}$.

^(q) Derived from $\Delta\varepsilon = \varepsilon_{(\text{Pu}^{4+}, \text{ClO}_4^-)} - \varepsilon_{(\text{Pu}^{3+}, \text{ClO}_4^-)} = (0.33 \pm 0.035) \text{ kg} \cdot \text{mol}^{-1}$ [95CAP/VIT]. Uncertainty estimated in the Np/Pu review [2000LEM/FUG]. In the first book of this series [92GRE/FUG], $\varepsilon_{(\text{Pu}^{3+}, \text{ClO}_4^-)} = (1.03 \pm 0.05) \text{ kg} \cdot \text{mol}^{-1}$ was tabulated based on refer-

Table 3: (continued)

$j \quad k \rightarrow$ \downarrow	Cl^-	ClO_4^-	NO_3^-
U^{4+} Th^{4+}	0.25 ± 0.03	$0.76 \pm 0.06^{(d)(s)}$	0.11 ± 0.02
$\text{Al}_3(\text{OH})_4^{5+}$	$0.66^{(j)}$	$1.30^{(j)}$	

ences [89ROB, 89RIG/ROB, 90RIG]. Capdevila and Vitorge's data [92CAP, 94CAP/VIT, 95CAP/VIT] were not available at that time.

^(r) Derived from $\Delta\varepsilon = \varepsilon_{(\text{Np}^{4+}, \text{ClO}_4^-)} - \varepsilon_{(\text{Np}^{3+}, \text{ClO}_4^-)} = (0.35 \pm 0.03) \text{ kg}\cdot\text{mol}^{-1}$ [89ROB, 89RIG/ROB, 90RIG].

^(s) Using the measured value of $\Delta\varepsilon = \varepsilon_{(\text{U}^{4+}, \text{ClO}_4^-)} - \varepsilon_{(\text{U}^{3+}, \text{ClO}_4^-)} = (0.35 \pm 0.06) \text{ kg}\cdot\text{mol}^{-1}$ page 89 [90RIG], where the uncertainty is recalculated in the TDB Np/Pu review [2000LEM/FUG] from the data given in this thesis, and $\varepsilon_{(\text{U}^{3+}, \text{ClO}_4^-)} = (0.49 \pm 0.05) \text{ kg}\cdot\text{mol}^{-1}$ (see footnote (m)), a value for $\varepsilon_{(\text{U}^{4+}, \text{ClO}_4^-)}$ can be calculated in the same way as is done for $\varepsilon_{(\text{Np}^{4+}, \text{ClO}_4^-)}$ and $\varepsilon_{(\text{Pu}^{4+}, \text{ClO}_4^-)}$. This value, $\varepsilon_{(\text{U}^{4+}, \text{ClO}_4^-)} = (0.84 \pm 0.06) \text{ kg}\cdot\text{mol}^{-1}$, is consistent with the tabulated $\varepsilon_{(\text{U}^{4+}, \text{ClO}_4^-)} = (0.76 \pm 0.06)$ since the uncertainties overlap. The authors of the present work do not believe that a change in the previously selected value for $\varepsilon_{(\text{U}^{4+}, \text{ClO}_4^-)}$ is justified at present.

Table 4: Ion interaction coefficients $\varepsilon_{j,k}$ for anions j with $k = \text{Li}^+, \text{Na}^+$ and K^+ , taken from Ciavatta [80CIA, 88CIA] unless indicated otherwise. 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 5.

$j \quad k \rightarrow$ ↓	Li^+	Na^+	K^+
OH^-	$-0.02 \pm 0.03^\dagger$	0.04 ± 0.01	0.09 ± 0.01
F^-		$0.02 \pm 0.02^{(a)}$	0.03 ± 0.02
HF_2^-		$-0.11 \pm 0.06^{(a)}$	
Cl^-	0.10 ± 0.01	0.03 ± 0.01	0.00 ± 0.01
ClO_3^-		-0.01 ± 0.02	
ClO_4^-	0.15 ± 0.01	0.01 ± 0.01	
Br^-	0.13 ± 0.02	0.05 ± 0.01	0.01 ± 0.02
BrO_3^-		-0.06 ± 0.02	
I^-	0.16 ± 0.01	0.08 ± 0.02	0.02 ± 0.01
IO_3^-		$-0.06 \pm 0.02^{(b)}$	
HSO_4^-		-0.01 ± 0.02	
N_3^-		$0.0 \pm 0.1^{(b)}$	
NO_2^-	$0.06 \pm 0.04^\dagger$	0.00 ± 0.02	-0.04 ± 0.02
NO_3^-	0.08 ± 0.01	$-0.04 \pm 0.03^\dagger$	$-0.11 \pm 0.04^\dagger$
H_2PO_4^-		$-0.08 \pm 0.04^\dagger$	$-0.14 \pm 0.04^\dagger$
HCO_3^-		$0.00 \pm 0.02^{(d)}$	$-0.06 \pm 0.05^{(i)}$
SCN^-		0.05 ± 0.01	-0.01 ± 0.01
HCOO^-		0.03 ± 0.01	
CH_3COO^-	0.05 ± 0.01	0.08 ± 0.01	0.09 ± 0.01
$\text{SiO}(\text{OH})_3^-$		$-0.08 \pm 0.03^{(a)}$	
$\text{Si}_2\text{O}_2(\text{OH})_5^-$		$-0.08 \pm 0.04^{(b)}$	
$\text{B}(\text{OH})_4^-$		$-0.07 \pm 0.05^\dagger$	
$\text{UO}_2(\text{OH})_3^-$		$-0.09 \pm 0.05^{(b)}$	
UO_2F_3^-		$0.00 \pm 0.05^{(b)}$	
$\text{UO}_2(\text{N}_3)_3^-$		$0.0 \pm 0.1^{(b)}$	
$(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$		$0.00 \pm 0.05^{(b)}$	
$\text{Am}(\text{SO}_4)_2^-$		$-0.05 \pm 0.05^{(c)}$	
$\text{Am}(\text{CO}_3)_2^-$		$-0.05 \pm 0.05^{(c)}$	

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Table 4: (continued)

$j \quad k \rightarrow$ \downarrow	Li^+	Na^+	K^+
$\text{NpO}_2(\text{OH})_2^-$		$-(0.01 \pm 0.07)$	
$\text{NpO}_2\text{CO}_3^-$		$-0.18 \pm 0.15^{(f)}$	
$(\text{NpO}_2)_2\text{CO}_3(\text{OH})_3^-$		(0.00 ± 0.05)	
SO_3^{2-}		$-0.08 \pm 0.05^\dagger$	
SO_4^{2-}	$-0.03 \pm 0.04^\dagger$	$-0.12 \pm 0.06^\dagger$	-0.06 ± 0.02
$\text{S}_2\text{O}_3^{2-}$		$-0.08 \pm 0.05^\dagger$	
HPO_4^{2-}		$-0.15 \pm 0.06^\dagger$	$-0.10 \pm 0.06^\dagger$
CO_3^{2-}		$-0.08 \pm 0.03^{(d)}$	0.02 ± 0.01
$\text{SiO}_2(\text{OH})_2^{2-}$		$-0.10 \pm 0.07^{(a)}$	
$\text{Si}_2\text{O}_3(\text{OH})_4^{2-}$		$-0.15 \pm 0.06^{(b)}$	
CrO_4^{2-}		$-0.06 \pm 0.04^\dagger$	$-0.08 \pm 0.04^\dagger$
$\text{UO}_2\text{F}_4^{2-}$		$-0.08 \pm 0.06^{(b)}$	
$\text{UO}_2(\text{SO}_4)_2^{2-}$		$-0.12 \pm 0.06^{(b)}$	
$\text{UO}_2(\text{N}_3)_4^{2-}$		$-0.1 \pm 0.1^{(b)}$	
$\text{UO}_2(\text{CO}_3)_2^{2-}$		$-0.02 \pm 0.09^{(d)}$	
$\text{NpO}_2(\text{CO}_3)_2^{2-}$		$-0.02 \pm 0.14^{(k)}$	
PO_4^{3-}		$-0.25 \pm 0.03^\dagger$	-0.09 ± 0.02
$\text{Si}_3\text{O}_6(\text{OH})_3^{3-}$		$-0.25 \pm 0.03^{(b)}$	
$\text{Si}_3\text{O}_5(\text{OH})_5^{3-}$		$-0.25 \pm 0.03^{(b)}$	
$\text{Si}_4\text{O}_7(\text{OH})_5^{3-}$		$-0.25 \pm 0.03^{(b)}$	
$\text{Am}(\text{CO}_3)_3^{3-}$		$-0.15 \pm 0.05^{(c)}$	
$\text{NpO}_2(\text{CO}_3)_2^{3-}$		$-0.33 \pm 0.17^{(f)}$	
$\text{P}_2\text{O}_7^{4-}$		-0.26 ± 0.05	-0.15 ± 0.05
$\text{Fe}(\text{CN})_6^{4-}$			-0.17 ± 0.03
$\text{U}(\text{CO}_3)_4^{4-}$		$-0.09 \pm 0.10^{(b)(d)}$	
$\text{UO}_2(\text{CO}_3)_3^{4-}$		$-0.01 \pm 0.11^{(d)}$	
$\text{NpO}_2(\text{CO}_3)_3^{4-}$		$-0.40 \pm 0.19^{(e)}$	$-0.62 \pm 0.42^{(g)(h)}$
$\text{NpO}_2(\text{CO}_3)_2\text{OH}^{4-}$		$-(0.40 \pm 0.19)^{(m)}$	

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Table 4: (continued)

$j \quad k \rightarrow$ \downarrow	Li^+	Na^+	K^+
$\text{UO}_2(\text{CO}_3)_3^{5-}$ $\text{NpO}_2(\text{CO}_3)_3^{5-}$		$-0.62 \pm 0.15^{(d)}$ $-0.53 \pm 0.19^{(f)}$	
$\text{U}(\text{CO}_3)_5^{6-}$ $(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$ $(\text{NpO}_2)_3(\text{CO}_3)_6^{6-}$ $(\text{UO}_2)_2\text{NpO}_2(\text{CO}_3)_6^{6-}$ $\text{Np}(\text{CO}_3)_5^{6-}$		$-0.30 \pm 0.15^{(d)}$ $0.37 \pm 0.11^{(d)}$ $-0.46 \pm 0.73^{(e)}$ $0.09 \pm 0.71^{(l)}$	$0.70 \pm 0.31^{(i)}$ $-0.73 \pm 0.68^{(j)}$

^(a)Evaluated in the NEA-TDB uranium review [92GRE/FUG].

^(b)Estimated in the NEA-TDB uranium review [92GRE/FUG].

^(c)Estimated in the NEA-TDB americium review [95SIL/BID].

^(d)These values differ from those reported in the NEA-TDB uranium review. See the discussion in [95GRE/PUI]. Values for CO_3^{2-} and HCO_3^- are based on [80CIA].

^(e)Calculated in the Np/Pu review [2000LEM/FUG].

^(f)Calculated in the Np/Pu review [2000LEM/FUG].

^(g)Calculated in the Np/Pu review [2000LEM/FUG].

^(h) $\varepsilon_{(\text{NpO}_2(\text{CO}_3)_3^{4-}, \text{NH}_4^+)} = -(0.78 \pm 0.25) \text{ kg}\cdot\text{mol}^{-1}$ is calculated in the Np/Pu review [2000LEM/FUG].

⁽ⁱ⁾Calculated in the Np/Pu review [2000LEM/FUG].

^(j)Calculated in the Np/Pu review [2000LEM/FUG].

^(k)Estimated by analogy in the Np/Pu review [2000LEM/FUG].

^(l)Estimated by analogy in the Np/Pu review [2000LEM/FUG].

^(m)Estimated in the Np/Pu review [2000LEM/FUG] by analogy with $\text{NpO}_2(\text{CO}_3)_3^{4-}$.

Table 5: Ion interaction coefficients $\varepsilon_{(1,j,k)}$ and $\varepsilon_{(2,j,k)}$ for cations j with $k = \text{Cl}^-$, ClO_4^- and NO_3^- (first part), and for anions j with $k = \text{Li}^+$, Na^+ and K^+ (second part), according to the relationship $\varepsilon = \varepsilon_1 + \varepsilon_2 \log_{10} I_m$. The data are taken from Ciavatta [80CIA, 88CIA]. The uncertainties represent the 95% confidence level.

$j \quad k \rightarrow$ \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
Ag^+					-0.1432 ± 0.0002	0.0971 ± 0.0009
Tl^+			-0.18 ± 0.02	0.09 ± 0.02		
Hg_2^{2+}					-0.2300 ± 0.0004	0.194 ± 0.002
Hg^{2+}					-0.145 ± 0.001	0.194 ± 0.002
Pb^{2+}					-0.329 ± 0.007	0.288 ± 0.018
$j \quad k \rightarrow$ \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
$\text{B}(\text{OH})_4^-$			-0.092 ± 0.002	0.103 ± 0.005		
H_2PO_4^-			-0.109 ± 0.001	0.095 ± 0.003	-0.1473 ± 0.0008	0.121 ± 0.004
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		
$\text{S}_2\text{O}_3^{2-}$			-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
PO_4^{3-}			-0.29 ± 0.02	0.10 ± 0.01		

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