Chapter IX

Estimations of Medium Effects on Thermodynamic Data

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IX.1. Introduction

This chapter describes methods for the estimation of deviations from ideality, e.g., the activity coefficients of reactants and products (usually ions) of chemical reactions in solution, usually complex formation, redox and acid/base equilibria. The typical feature of these reactions is that they involve strong interactions between the components of the system, where often many different species (complexes) are present simultaneously in comparable concentrations. This is a situation that is very different from mixtures of strong electrolytes, and these differences will be reflected in the methods used to describe the deviations from ideality.

1 This Chapter originates from an internal NEA technical report (TDB-2), and from Appendices B in the published NEA reviews on the thermochemistry of uranium and americium [92GRE/FUG, 95SIL/BID]. However, the text has undergone a complete revision and it has been substantially expanded.

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Compilations of thermodynamic data always contain information referring to standard state conditions, defined according to IUPAC [82AF] in Chapter II, Section II.3.1. Users of thermodynamic data must therefore recalculate these data to the conditions present in the system they are studying. Thermodynamics in combination with physico-chemical theories provides the framework for such calculations and we will briefly review the theories on which these methods are based, and their relative merits. We will discuss two types of calculations:

- Those using equilibrium constant data determined in the laboratory, usually in an ionic medium, to determine the corresponding constant at zero ionic strength (the usual standard state in compilations of thermodynamic data). However, there is no "standard" ionic medium, or ionic strength, preferred in the experimental determinations of equilibrium constants. Hence, there is a need to recalculate the data to a common standard state in order to allow a comparison of them. The standard state preferred in compilations of thermodynamic data is the infinite dilute solution, with pure water as the solvent. The experimental data are usually available at a few ionic strengths, typically from 0.1 up to 4 mol \( \cdot \) kg\(^{-1}\).

- Those using tabulated standard state data to calculate equilibrium constants and properties of single strong electrolytes and their mixtures over a large ionic strength range.

An important aspect of activity coefficient estimations is related to the possibility of measuring precise thermodynamic data in the laboratory, particularly data for complex formation and other reactions involving ionic species in solution. In order to deduce the stoichiometry and equilibrium constants in such systems, it is always necessary to vary the concentrations of reactants and products over fairly large concentration ranges under conditions where the activity coefficients of the species are either known, or constant. Only in this way is it possible to use the mass balance equations for the various components, together with the measurement of one or more free concentrations to obtain the information desired [61ROS/ROS, 90BEC/NAG]. Activity coefficients may be estimated at very low total concentrations of reactants/products (where they approach unity). However, under these conditions it is not possible to perform the variation in concentrations required to establish a proper chemical model.

The activity coefficient of a species \( i \), denoted \( \gamma_i \), in an electrolyte mixture composed of different ionic species depends on the concentrations of all these species and their chemical characteristics (e.g., size and charge), on temperature, pressure and solvent properties. If one component of the electrolyte mixture is present in a much larger concentration than the others, this component will determine the activity coefficients of the minor components, which are then called "trace" activity coefficients.

For this reason most experimental studies of solution chemical equilibria are performed in the presence of an ionic medium, using an inert electrolyte (a strong electrolyte, usually \( \text{NaClO}_4 \)), the ions of which do not react with the reactants/products of the reactions studied. The concentration of inert electrolyte is usually 10 - 100 times larger than the
On the estimation of activity coefficients in electrolyte systems

concentration of the reactants. More details about the use of the ionic medium method may be found in [53BIE/SIL, 61ROS/ROS, Chapter 1, 90BEC/NAG, Chapter 2]. By using an ionic medium one ensures that the (trace) activity coefficients of reactants and products are nearly constant over a large concentration range, and that activities and concentrations are proportional to one another. It is customary to define the proportionality constant as unity in the ionic medium used. This is equivalent to assuming that the activity coefficients of reactants and products approach unity when their concentrations are much lower than the total concentration of the ionic medium. The most important difference between the ionic medium solvent and the pure water solvent is that the concentration range where the activity coefficients are constant is much larger in the former case.

The equilibrium constants deduced from measurements in ionic media are conditional equilibrium constants, because the activity coefficients may be defined as unity in any ionic medium. In order to compare the magnitude of equilibrium constants obtained in different ionic media it is necessary to have a method for estimating activity coefficients of ionic species in mixed electrolyte systems by using one common standard state. The “infinite dilution” state is the one generally used. This will also be the standard state in the following discussion.

IX.2. On the estimation of activity coefficients in electrolyte systems

Ionic solutions depart strongly from ideality due to the long-range electrostatic interactions. The interaction energy between neutral molecules falls off as \( r^{-6} \), while Coulomb interactions between ions falls off as \( r^{-1} \) (\( r \) is the distance between the interacting particles).

In most cases it is experimentally straightforward to measure deviations from ideality in pure electrolyte and other systems [58HAR/OWE, Chapters 9 and 10, 59ROB/STO, 90ATK, Chapter 10]. The interpretation of these deviations in terms of theoretical models, is less simple. There exists a number of alternative semi-empirical methods for the estimation of activity coefficients, each with its own advantages and draw-backs. The following figure shows the variation of the mean-activity coefficient for some 1:1 electrolytes as a function of the square-root of the ionic strength \( I_m \) \( (I_m = \frac{1}{2} \sum m_i Z_i^2 ) \), where \( m_i \) and \( Z_i \) stand for molality and charge of species \( i \).

There are four main observations to be made:

- There are large changes in the mean activity coefficients with concentration.

- The slopes of \( \log_{10} \gamma_{\pm} \) vs. \( \sqrt{I_m} \) are identical within the experimental error at very low ionic strengths for a particular valence type. Any theory must be able to explain this limiting behavior.

- The variations are not the same for different electrolytes. Any theory must be able to describe their individual characteristics.
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Figure IX.1: The variation of $\log_{10} \gamma_\pm$ for some 1:1 electrolytes as a function of the square-root of the ionic strength at 298.15 K and 1 atm. The source of $\log_{10} \gamma_\pm$ is Ref. [91PIT].

- At intermediate high ionic strengths $\log_{10} \gamma_\pm$ is a linear function of the ionic strength over fairly large molality ranges, cf. Figure IX.2.

All electrolyte models are based on microscopic physico-chemical descriptions of the interactions between dissolved ions, and sometimes the interactions between ions and solvent. The reader should be aware that a self-consistent theory of ionic solutions is still to be awaited. Until such a theory is available we have to rely on provisional models. The ones described in this chapter are all based on the Debye-Hückel theory [90ATK, Chapter 10] and extensions thereof.

The classical Debye-Hückel model takes only into account electrostatic interactions between ions of opposite charge, and is able to give a quantitative description of the variation of $\log_{10} \gamma_\pm$ vs. $\sqrt{I_m}$, as the ionic strength approaches zero.

The Debye-Hückel limiting law is

$$\log_{10} \gamma_\pm = -|Z_M Z_X| A \sqrt{I_m} \quad \text{(IX.1)}$$

where $Z_M$ and $Z_X$ are the ionic charges for the particular electrolyte, $I_m$ the ionic strength, and $A$ a constant with the value 0.5100 mol$^{-1/2}$·kg$^{1/2}$ at 298.15 K and 1 atm [90ARC/WAN]. $\gamma_\pm$ is used here for the molal mean-activity coefficient. The range of validity of the limiting law varies with the electrolyte, typically up to $I_m = 0.01$ mol·kg$^{-1}$ for 1:1 electrolytes, and 0.001 for 3:1 electrolytes. Various empirical attempts to “extend” the
Figure IX.2: The variation of function \( \log_{10} \gamma_{\pm} + [Z_M Z_X D] \) vs. ionic strength for a number of electrolytes at 298.15 K and 1 atm. The source of \( \log_{10} \gamma_{\pm} \) is Ref. [91PIT].

range of application of the Debye-Hückel limiting law have been made, typically to ionic strengths of about 0.03 mol·kg\(^{-1}\) for 1:1 electrolytes, by the introduction of an electrolyte dependent “effective” diameter of the hydrated ions, which results in a Debye-Hückel term of the type:

\[
D = \frac{A \sqrt{T_m}}{1 + B_{aMX} \sqrt{T_m}} \tag{IX.2}
\]

where \(a_{MX}\) stands for an “effective” distance, and \(B\) is a Debye-Hückel parameter, defined by temperature, pressure (the density of pure water), and the dielectric constant of water, (see [81HEL/KIR] for further details). In order to extend the equations for activity coefficient estimations to higher ionic strength, and to take the individual characteristics of different electrolytes into account, various techniques have been used:

- Non-electrostatic short range interactions, with terms proportional to the concentration of ions or to the ionic strength are included in addition to the Debye-Hückel term. In Figure IX.2 we have illustrated the deviations from the simple Debye-Hückel theory by plotting \( \log_{10} \gamma_{\pm} + [Z_M Z_X D] \) vs. \( I_m \), where \( D \) has been calculated using Eq. (IX.2) with \( B_{aMX} = 1.5 \).

The best known of this type of models is the Davies’ equation, which describes the
activity coefficient of an ion \( i \) of charge \( Z_i \) at 298.15 K with the expression:

\[
\log_{10} \gamma_i = -0.5100 Z_i^2 \left( \frac{\sqrt{I_m}}{1 + \sqrt{I_m}} - 0.3 I_m \right)
\]  

(IX.3)

Davies’ equation has a formal similarity to the specific ion interaction equations described in the following text, but has no theoretical foundation. It is often found to work fairly well up to ionic strengths of 0.1 mol·kg\(^{-1}\). Davies’ equation takes only the charge of the ions into account, not their individual characteristics. In order to account for these the concept of ionic pairing is introduced, where deviations between measured values of mean-activity coefficients and those calculated using Eq. (IX.3) are assumed to be due to complex formation reactions, \( e.g. \), of the type:

\[
\text{Na}^+ + \text{CO}_3^{2-} \Rightarrow \text{NaCO}_3^-
\]

which are described by equilibrium constants.

Ion association models use the same extended Debye-Hückel expression to describe the electrostatic interactions between all electrolytes, while the electrolyte specific characteristics are described using ion-pair formation between ions of opposite charge. The equations used vary in complexity from Davies’ equation, to the equations developed by Helgeson et al. [8IHEL/KIR]. Davies’ equation is used in some codes for the calculation of thermodynamic properties in geochemical systems, but its use at moderate, or high ionic strengths for the calculation of activity coefficients of species in trace concentrations is not recommended [84HAR/MOL].

- The individual characteristics of electrolytes may also be described using specific ion interaction models. These semiempirical models contain a number of parameters which have a theoretical basis, but must be determined from the experimental data. The precision of the description \( e.g. \), of mean-activity coefficient data, increases with the number of model parameters. These models often describe the activity coefficients and their temperature and pressure derivatives fairly well, especially in binary systems (\textit{vide infra} Section IX.9, p.397).

Specific ion interaction models also use a Debye-Hückel term for the description of long range electrostatic forces and a virial series expansion in powers of the molality of the electrolyte(s) to model short-range interactions [91PIT], with specific interaction terms for each type of pair, or triple interaction.

In the following sections we will outline the basic features of the most important specific ion interaction models, always with the emphasis on their use for the modelling of complex geochemical systems at moderate temperatures and pressures. These models allow the user to:

- extend the equations describing the activity coefficient variations in simple electrolyte systems to more complex systems with many components;
The Brønsted-Guggenheim-Scatchard model (SIT)

- use “single-ion” activity coefficients, provided that comparisons with experimental data are always made on electroneutral combinations of ions.

This chapter is intended to provide a rationale for the selection and use of models for the estimate of the ionic medium/ionic strength dependence of thermodynamic quantities in (multi)electrolyte media. All such methods have a common theoretical basis in the Debye-Hückel theory, which is then extended to include various non-electrostatic interactions. These take the form of phenomenological parameters which have to be determined from experimental data. The various models differ mainly in the number of parameters they contain, and this will influence their predictive capacity. We will concentrate on the Pitzer and the Brønsted-Guggenheim-Scatchard (SIT) models. The main part of the discussion refers to chemical equilibria in ionic medium systems, where the reactants/products are present in low concentration, compared to that of the medium.

The Pitzer method has mainly been applied to strong electrolyte systems, both single and mixtures at high concentrations, while the SIT model has been used by solution coordination chemists for the description of the ionic medium/ionic strength dependence of concentration equilibrium constants. There is some overlap, but fairly small, between these two areas. In order to use all solution chemical information in an efficient way, it is necessary to have a common method for estimating deviations from ideality. Such a method should be based on the most developed theoretical framework, i.e., the Pitzer model. However, when treating equilibrium constant data in this way, it is often necessary to make a number of approximations, or use procedures for estimating unknown interaction coefficients.

By using a number of examples we will demonstrate the characteristics of the models, and how their predictive capacity is influenced by the model parameters and their uncertainty. We will also describe methods to transform interaction coefficients between the two model structures, and to estimate unknown parameters.

IX.3. The Brønsted-Guggenheim-Scatchard model (SIT)†

The Debye-Hückel term, which is the dominant term in the expression for the activity coefficients in dilute solutions, accounts for electrostatic, long-range interactions. At higher concentrations short-range, non-electrostatic interactions have to be taken into account as well. This is usually done by adding terms to the Debye-Hückel expression as outlined by Brønsted [22BRO, 22BRO2] and elaborated by Guggenheim [35GUG, 66GUG] and Scatchard [36SCA]. This approach was successfully used by different groups of solution coordination chemists, mainly for the description of the concentration dependence of complex formation equilibria, including the determination of equilibrium constants for

† Note by the Editors: The abbreviation “SIT” stands for Specific Ion Interaction Theory. Although the name is misleading, the use of this abbreviation is continued because of its wide use in the literature (it apparently originates from Ref. [82BIE/BRU]; see also Refs. [89RIG/ROB, 92CAP/VIT, 92CHO/DU, 94ERT/MOH, 94FAN/KIM, 95CAP/VTT, 95NEC/FAN], etc.).
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reactions at infinite dilution [75BIE, 80CIA, 92GRE/FUG]. The two basic assumptions in the Brønsted-Guggenheim-Scatchard model are described below.

Assumption 1:

The activity coefficient $\gamma_i$ of an ion of charge $Z_i$ in a solution of ionic strength is equal to:

$$\ln \gamma_i = -\frac{Z_i^2 A \gamma \sqrt{T_m}}{1 + 1.5 \sqrt{T_m}} + \sum_k \varepsilon(i, k) m_k$$  \hspace{1cm} (IX.4)

or

$$\log_{10} \gamma_i = -\frac{Z_i^2 A \sqrt{T_m}}{1 + 1.5 \sqrt{T_m}} + \sum_k \varepsilon(i, k) m_k$$

$$= -Z_i^2 D + \sum_k \varepsilon(i, k) m_k$$  \hspace{1cm} (IX.5)

where $D$ is a particular form of Debye-Hückel term used in the SIT model. $A_\gamma$ and $A$ are the limiting Debye-Hückel law slopes for the natural and decadic logarithm of the activity coefficient ($A_\gamma = \ln(10) A$), and $\varepsilon(i, k)$ (or $\varepsilon_\gamma(i, k) = \ln(10) \varepsilon(i, k)$) is an aqueous species interaction coefficient, which describes the specific short-range interactions between aqueous species $i$ and $k$. Values of $\varepsilon(i, k)$ are given in Tables IX.1 and IX.2 (p.335) and Figures IX.6 to IX.12.

In the simplest approximation the ion interaction coefficients are considered to be concentration independent. The summation extends over all species $k$, with molality $m_k$, present in solution. The value of $1.5 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$ in the denominator of the Eqs. (IX.4), (IX.5) is an empirical value of the product $a_j B$ in the Debye-Hückel term (where $a_j$ is an “effective” ion diameter and $B$ is a constant determined by the temperature and the physical properties of pure water, cf. p.329). The value 1.5 was proposed by Scatchard [76SCA] in order to minimise the ionic strength dependence of $\varepsilon(i, k)$ for a number of electrolytes at 298.15 K, cf. Figure IX.3.

It should be mentioned that a small change in the proposed value ($1.5 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$) has very little influence on the quality of the fit of experimental mean-activity coefficients data, presumably due to correlation between $a_j B$ and the fitted value of $\varepsilon(i, k)$. A constant value of $a_j B$ for all ionic species simplifies the modelling of both binary and multicomponent aqueous electrolyte systems and makes it easy to give a consistent description of mean activity coefficients both in binary and multicomponent solutions [59ROB/STO, p.435-441].

The model assumption that the SIT interaction coefficients $\varepsilon(i, k)$ are concentration independent is an oversimplification. There is both theoretical and experimental evidence [91PIT] that they vary at lower molality, cf. Figure IX.3. At high molality the value of $\varepsilon(i, k)$ becomes nearly constant. In principle, it is possible to consider the SIT coefficient to be dependent on concentration, but in this case all required thermodynamic transformations become complex. In the simplest SIT model one does not take this concentration
Figure IX.3: The concentration dependence of the SIT coefficient for a number of electrolytes at 298.15 K and 1 atm. The source of log_{10} \gamma_\pm is Ref. [91PIT]. The units of \varepsilon are kg \cdot mol^{-1}.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>\varepsilon(i, k)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La(ClO_4)_2</td>
<td>1.2</td>
</tr>
<tr>
<td>AlCl_3</td>
<td>1.0</td>
</tr>
<tr>
<td>Sr(ClO_4)_2</td>
<td>0.8</td>
</tr>
<tr>
<td>MgCl_2</td>
<td>0.6</td>
</tr>
<tr>
<td>LiCl</td>
<td>0.4</td>
</tr>
<tr>
<td>KI</td>
<td>0.2</td>
</tr>
<tr>
<td>Molality / mol \cdot kg^{-1}</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1.2</td>
</tr>
<tr>
<td>1</td>
<td>1.0</td>
</tr>
<tr>
<td>2</td>
<td>0.8</td>
</tr>
<tr>
<td>3</td>
<td>0.6</td>
</tr>
<tr>
<td>4</td>
<td>0.4</td>
</tr>
</tbody>
</table>

dependence into account. If the available experimental data permit the determination of more than one interaction parameter the reader is advised to use the Pitzer approach. One should also observe that the variations of \varepsilon(i, k) are largest at low molalities where the second term makes only a small contribution to the total value of the activity coefficient, cf. Eq. (IX.4).

**Note.** This assumption results in the identity \varepsilon(i, k) \equiv \varepsilon(k, i), i.e., log_{10} \gamma_+ \equiv log_{10} \gamma_- for all strong non electrolytes. In the framework of other models these single ion activities could be assumed to be rather different from one another, cf. [70BAT/STA].

**Assumption 2:**

The ion interaction coefficients \varepsilon(i, k) are zero for ions of the same charge sign, according to the Brønsted principle of specific ion interaction [22BRO, 22BRO2]. The rationale behind this is straightforward: the ions of the same charge sign are far from one another due to electrostatic repulsion. Hence, short-range forces between them are small. The ions of opposite charge are close to one other, and they are therefore strongly affected by the short-range forces, which are specific for each pair of co-ions. It is known that the Brønsted principle is not fully in agreement with the best experimental data, but these deviations are usually small (often < 0.01-0.02 in the values of the osmotic coefficient \Phi or
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ln $\gamma_\pm$ [91PIT]). Thus, Assumption 2 (the Brønsted principle of specific ion interaction) is a good approximation with a sound theoretical basis. In order to compare the SIT model with experimental data, one must combine Eq. (IX.4) or (IX.5) for single ion activity coefficients to a measurable quantity, mean-activity coefficients, osmotic coefficients, or equilibrium constants. In [92GRE/FUG] it was assumed that the interaction coefficients for uncharged species were zero. There is no problem (and it is more correct) with including possible interactions between uncharged and ionic species in the SIT model.

For uncharged solutes the SIT model is reduced to one term, which is equivalent to the Setchenow equation [52LON/MCD, 58HAR/OWE], which assumes a linear dependence of ln $\gamma^o$ on electrolyte concentration (where $\gamma^o$ is the activity coefficient of the uncharged molecule in an aqueous electrolyte solution). The Setchenow equation has been shown [52LON/MCD, 58HAR/OWE] to be a good approximation for the concentration dependence of the solubility of many gases (N$_2$O, C$_2$H$_4$, CO$_2$, O$_2$, etc.), liquids (phenol, ethyl acetate, etc.), complexes (CdX$_2$, X = Cl$^-$, Br$^-$, I$^-$) and solids (e.g., SiO$_2$), in electrolyte solutions ("salting-in" or "salting-out" effects). Hence, the SIT equation has the potential to describe the activity coefficients and related properties of neutral species. SIT parameters for the interaction between ions and uncharged species can only be determined for electroneutral combinations of ions and uncharged species. To handle this problem Pitzer [91PIT, p.93] proposed to define an arbitrary zero point for the interaction between single ions and neutral molecules, and suggested that the interactions between H$^+$ and neutral molecules be defined as zero. Other single-ion neutral molecule interactions may then be calculated from experimental data. A number of SIT interaction coefficients for neutral species — electroneutral combination of ions have been tabulated by Cavatta [90CIA]; $\varepsilon$(CdCl$_2^0$, Na$^+$ + ClO$_4^-$) = (0.15 ± 0.02); $\varepsilon$(CdCl$_2^0$, Li$^+$ + ClO$_4^-$) = (0.23 ± 0.05); $\varepsilon$(CdCl$_2^0$, Na$^+$ + ClO$_4^-$) = (0.25 ± 0.05); $\varepsilon$(Hg(OH)$_2^0$, Na$^+$ + ClO$_4^-$) = (0.06 ± 0.05); $\varepsilon$(HgCl$_2^0$, Na$^+$ + ClO$_4^-$) = (0.06 ± 0.03); $\varepsilon$(PbCl$_2^0$, Li$^+$ + ClO$_4^-$) = (0.13 ± 0.02), where all values are given in units of kg·mol$^{-1}$.

Interactions between uncharged species may be far from negligible due to a so-called "self-interaction" contribution. Robinson and Stokes [59ROB/STO] give evidence that the activity coefficients of sucrose and glycerol are larger than 1 in an aqueous solution; other examples are given by Long and McDevit [52LON/MCD]. Interactions of this type may also be described using the SIT model, e.g., the activity coefficients of the non-electrolytes mentioned above are reproduced better than 0.001 log$_{10}$ unit in log$_{10}$ $\gamma$ up to 3 mol·kg$^{-1}$ by using the self-interaction coefficients 0.08 for sucrose ($\varepsilon$(sucrose, sucrose) = 0.08) and 0.01 for glycerol ($\varepsilon$(glycerol, glycerol) = 0.01). However, the deviations from ideality in aqueous solutions of non-electrolytes are in general small.
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Table IX.1: Ion interaction coefficients $\varepsilon_{j,k}$ (kg \cdot mol$^{-1}$) at 25°C and 1 bar for cations $j$ with $k = \text{Cl}^-$, ClO$_4^-$ and NO$_3^-$, taken from Ciavatta [80CIA] unless indicated otherwise. The uncertainties represent the 95% confidence level, most of them were estimated by Ciavatta [88CIA]. Care should be taken when using the coefficients $\varepsilon_{(M^+, \text{Cl}^-)}$ and $\varepsilon_{(M^+, \text{NO}_3^-)}$ reported by Ciavatta [80CIA], which were evaluated without taking chloride and nitrate complexation into account.

<table>
<thead>
<tr>
<th>$j \rightarrow k$</th>
<th>Cl$^-$</th>
<th>ClO$_4^-$</th>
<th>NO$_3^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$^+$</td>
<td>0.12 ± 0.01</td>
<td>0.14 ± 0.02</td>
<td>0.07 ± 0.01</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>−0.01 ± 0.01</td>
<td>−0.08 ± 0.04</td>
<td>−0.06 ± 0.03</td>
</tr>
<tr>
<td>H$_2$gly$^+$</td>
<td>−0.06 ± 0.02</td>
<td>−0.21 ± 0.06</td>
<td></td>
</tr>
<tr>
<td>ZnHCO$_3^+$</td>
<td></td>
<td>0.25 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>CdCl$^+$</td>
<td></td>
<td>0.27 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>Cd$^+$</td>
<td></td>
<td>0.31 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>CdSCN$^+$</td>
<td></td>
<td>0.19 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>HgCl$^+$</td>
<td></td>
<td>0.11 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>Cu$^+$</td>
<td></td>
<td>0.00 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>Ag$^+$</td>
<td></td>
<td>0.17 ± 0.04$^{(d)}$</td>
<td></td>
</tr>
<tr>
<td>YCO$_2^+$</td>
<td></td>
<td>0.26 ± 0.03$^{(c)}$</td>
<td></td>
</tr>
<tr>
<td>UO$^+_2$</td>
<td></td>
<td>−0.06 ± 3.7$^{(c)}$</td>
<td>0.51 ± 1.4$^{(c)}$</td>
</tr>
<tr>
<td>UO$_2$OH$^+$</td>
<td>0.81 ± 0.17$^{(c)}$</td>
<td>0.45 ± 0.15$^{(c)}$</td>
<td>0.41 ± 0.22$^{(c)}$</td>
</tr>
<tr>
<td>(UO$_2$)$_3$(OH)$_2^+$</td>
<td>0.1 ± 0.1$^{(f)}$</td>
<td>0.1 ± 0.1$^{(f)}$</td>
<td></td>
</tr>
<tr>
<td>UF$_3^+$</td>
<td>0.04 ± 0.07$^{(b)}$</td>
<td>0.29 ± 0.05$^{(c)}$</td>
<td></td>
</tr>
<tr>
<td>UO$_2$F$^+$</td>
<td></td>
<td>0.33 ± 0.04$^{(c)}$</td>
<td></td>
</tr>
<tr>
<td>UO$_2$Cl$^+$</td>
<td></td>
<td>0.33 ± 0.04$^{(f)}$</td>
<td></td>
</tr>
<tr>
<td>UO$_2$ClO$_3^+$</td>
<td></td>
<td>0.24 ± 0.04$^{(f)}$</td>
<td></td>
</tr>
<tr>
<td>UO$_2$Br$^+$</td>
<td></td>
<td>0.33 ± 0.04$^{(f)}$</td>
<td></td>
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<tr>
<td>UO$_2$BrO$_3^+$</td>
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<td>0.33 ± 0.04$^{(f)}$</td>
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<td>UO$_2$IO$_3^+$</td>
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<td>0.33 ± 0.04$^{(f)}$</td>
<td></td>
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<tr>
<td>UO$_2$N$_2^+$</td>
<td></td>
<td>0.3 ± 0.1$^{(f)}$</td>
<td></td>
</tr>
<tr>
<td>UO$_2$NO$_3^+$</td>
<td></td>
<td>0.33 ± 0.04$^{(f)}$</td>
<td></td>
</tr>
<tr>
<td>UO$_2$SCN$^+$</td>
<td></td>
<td>0.22 ± 0.04$^{(f)}$</td>
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<td>NpO$_2^+$</td>
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<td>0.25 ± 0.05$^{(b)}$</td>
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<td>PuO$_2^+$</td>
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<td>0.17 ± 0.05$^{(b)}$</td>
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<tr>
<td>Am(OH)$_2^+$</td>
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<td>0.17 ± 0.04$^{(d)}$</td>
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<td>AmF$_2^+$</td>
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<td>0.17 ± 0.04$^{(d)}$</td>
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### Table IX.1 (continued)

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<th>$j$</th>
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<th>$\text{Cl}^-$</th>
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<th>$\text{NO}_3^-$</th>
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<td>$\downarrow$</td>
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<td>0.17 ± 0.04$^{(i)}$</td>
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<tr>
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<td>AmCO$_3^+$</td>
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<td>0.33 ± 0.03</td>
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<td>Zn$^{2+}$</td>
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<td>0.16 ± 0.02</td>
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<td>−0.1 ± 0.1</td>
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<td>Hg$^{2+}$</td>
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<td>0.32 ± 0.02</td>
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<td>Cu$^{2+}$</td>
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<td>0.16 ± 0.01</td>
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<td>Ni$^{2+}$</td>
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<td>0.45$^{(d)}$</td>
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<td>Co$^{2+}$</td>
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<td>0.45$^{(d)}$</td>
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<td>FeOH$^{2+}$</td>
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<tr>
<td>FeSCN$^{2+}$</td>
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<tr>
<td>Mn$^{2+}$</td>
<td>0.13 ± 0.01</td>
<td>0.39 ± 0.04$^{(d)}$</td>
<td>0.24 ± 0.03$^{(i)}$</td>
<td>0.72 ± 1.0$^{(c)}$</td>
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<td>YHCO$_3^{+}$</td>
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<tr>
<td>UO$_2^{+}$</td>
<td>0.21 ± 0.02$^{(i)}$</td>
<td>0.46 ± 0.03</td>
<td>0.49 ± 0.14$^{(s)}$</td>
<td>0.49 ± 0.09$^{(c)}$</td>
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<td>(UO$_2$)$_3$(OH)$_4^{2+}$</td>
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<td>0.89 ± 0.23$^{(c)}$</td>
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<tr>
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<td>0.39 ± 0.04$^{(i)}$</td>
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<tr>
<td>AmH$_2$PO$_4^{2+}$</td>
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<td>0.39 ± 0.04$^{(i)}$</td>
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<tr>
<td>AmSCN$^{2+}$</td>
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<td>0.39 ± 0.04$^{(i)}$</td>
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<td>Mg$^{2+}$</td>
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<tr>
<td>Ba$^{2+}$</td>
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336
Table IX.1 (continued)

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<th>$j$</th>
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<th>NO$_3^-$</th>
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<td>4</td>
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<td>0.33 ± 0.02</td>
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<td>0.48 ± 0.08(</td>
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<td>La$^{3+}$</td>
<td>0.22 ± 0.02</td>
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<td>0.48 ± 0.08(</td>
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<td>0.59 ± 0.10(</td>
<td>g</td>
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<td>0.52 ± 0.10(</td>
<td>f</td>
</tr>
<tr>
<td></td>
<td>UF$^{3+}$</td>
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<td>0.55 ± 0.10(</td>
<td>f</td>
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<td></td>
<td>UCl$^{3+}$</td>
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<td>0.49 ± 0.03(</td>
<td>i</td>
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<tr>
<td></td>
<td>UP$^{3+}$</td>
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<td>0.50 ± 0.05(</td>
<td>e</td>
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<tr>
<td></td>
<td>UNO$_3^+$</td>
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<td>Am$^{3+}$</td>
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<td>Be$_2$OH$^{3+}$</td>
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</tr>
<tr>
<td></td>
<td>Be$_3$(OH)$_3$$^{3+}$</td>
<td>0.30 ± 0.05(</td>
<td>e</td>
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<tr>
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<td>Al$_3$CO$_3$(OH)$_4$$^{4+}$</td>
<td>0.41(</td>
<td>a</td>
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<tr>
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<td>Fe$_2$(OH)$_4$$^{2+}$</td>
<td></td>
<td>0.82(</td>
<td>d</td>
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<td>Y$_2$CO$_3$$^+$</td>
<td></td>
<td>0.80 ± 0.04(</td>
<td>d</td>
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<td></td>
<td>Pu$^{4+}$</td>
<td></td>
<td>1.03 ± 0.05(</td>
<td>b</td>
</tr>
<tr>
<td></td>
<td>Np$^{4+}$</td>
<td></td>
<td>0.82 ± 0.05(</td>
<td>b</td>
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<td></td>
<td>U$^{4+}$</td>
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<td>0.76 ± 0.06(</td>
<td>f</td>
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<td>Th$^{4+}$</td>
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<td>Al$_3$(OH)$_4$$^{5+}$</td>
<td>0.66(</td>
<td>a</td>
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</table>
Table IX.1 (continued)

Footnotes:

(a) Taken from Hedlund [88HED].
(b) 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 $(M^{3+}, \text{ClO}_4^-)$ interactions, and $\varepsilon_{(\text{Np}^{4+}, \text{ClO}_4^-)} \approx \varepsilon_{(\text{Pu}^{4+}, \text{ClO}_4^-)} \approx \varepsilon_{(\text{UO}^{2+}, \text{ClO}_4^-)} = 0.46 \text{ kg} \cdot \text{mol}^{-1}$.
(c) Evaluated in the NEA-TDB review on uranium thermodynamics [92GRE/FUG], using $\varepsilon_{(\text{UO}^{2+}, X)} = (0.46 \pm 0.03) \text{ kg} \cdot \text{mol}^{-1}$, where $X = \text{Cl}^-$, $\text{ClO}_4^-$ and $\text{NO}_3^-$. 
(d) Taken from Spahiu [83SPA].
(e) 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 $\varepsilon_{(M^{2+}, \text{ClO}_4^-)}$, $\varepsilon_{(\text{Be}^{3+}, \text{Cl}^-)} = 0.17 \text{ kg} \cdot \text{mol}^{-1}$ as for other $\varepsilon_{(M^{3+}, \text{Cl}^-)}$, and $\varepsilon_{(\text{Be}^{3+}, \text{NO}_3^-)} = 0.17 \text{ kg} \cdot \text{mol}^{-1}$ as for other $\varepsilon_{(M^{3+}, \text{NO}_3^-)}$.
(f) Estimated in the NEA-TDB review on uranium thermodynamics [92GRE/FUG].
(g) Evaluated in the NEA-TDB review on uranium thermodynamics [92GRE/FUG] using $\varepsilon_{(\text{U}^{4+}, \text{ClO}_4^-)} = (0.76 \pm 0.06) \text{ kg} \cdot \text{mol}^{-1}$.
(h) Taken from Ferri et al. [85FER/GRE].
(i) It is recalled that these coefficients were not used in the NEA-TDB review on uranium thermodynamics [92GRE/FUG] because they were evaluated by Ciavatta [80CIA] without taking chloride and nitrate complexation into account. Instead, Grethe et al. used $\varepsilon_{(\text{UO}_{2}^{2+}, X)} = (0.46 \pm 0.03) \text{ kg} \cdot \text{mol}^{-1}$, for $X = \text{Cl}^-$, $\text{ClO}_4^-$ and $\text{NO}_3^-$. 
(k) Estimated in the NEA-TDB review on americium thermodynamics [95SIL/BID].
(l) Evaluated in the NEA-TDB review on americium thermodynamics [95SIL/BID].
**Table IX.2: Ion interaction coefficients $\varepsilon_{j,k}$ (kg $\cdot$ mol$^{-1}$) at 25°C and 1 bar for anions $j$ with $k = \text{Li}^+$, $\text{Na}^+$ and $\text{K}^+$, taken from Ciavatta [80CIA] unless indicated otherwise. The uncertainties represent the 95% confidence level, most of them were estimated by Ciavatta [88CIA].**

<table>
<thead>
<tr>
<th>$j \rightarrow k$</th>
<th>Li$^+$</th>
<th>Na$^+$</th>
<th>K$^+$</th>
</tr>
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<tbody>
<tr>
<td>OH$^-$</td>
<td>$-0.02 \pm 0.03$</td>
<td>$0.04 \pm 0.01$</td>
<td>$0.09 \pm 0.01$</td>
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<tr>
<td>F$^-$</td>
<td>$0.02 \pm 0.02^{(a)}$</td>
<td>$0.03 \pm 0.02$</td>
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<td>HF$^-$</td>
<td>$-0.11 \pm 0.06^{(a)}$</td>
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<td>Cl$^-$</td>
<td>$0.10 \pm 0.01$</td>
<td>$0.03 \pm 0.01$</td>
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<tr>
<td>ClO$_3^-$</td>
<td>$0.15 \pm 0.01$</td>
<td>$0.01 \pm 0.01$</td>
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<tr>
<td>ClO$_4^-$</td>
<td>$0.13 \pm 0.02$</td>
<td>$0.05 \pm 0.01$</td>
<td>$0.01 \pm 0.02$</td>
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<td>Br$^-$</td>
<td>$0.16 \pm 0.01$</td>
<td>$0.08 \pm 0.02$</td>
<td>$0.02 \pm 0.01$</td>
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<td>BrO$_3^-$</td>
<td>$0.06 \pm 0.02^{(b)}$</td>
<td>$0.01 \pm 0.02$</td>
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<tr>
<td>I$^-$</td>
<td>$0.00 \pm 0.02^{(b)}$</td>
<td>$0.01 \pm 0.02$</td>
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<td>IO$_3^-$</td>
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<td>$0.01 \pm 0.02$</td>
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<td>HSO$_4^-$</td>
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<td>$0.00 \pm 0.02$</td>
<td>$-0.04 \pm 0.02$</td>
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<td>NO$_3^-$</td>
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<td>H$_2$PO$_4^-$</td>
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<td>$0.00 \pm 0.02^{(c)}$</td>
<td>$-0.14 \pm 0.04$</td>
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<td>HCO$_3^-$</td>
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<td>$0.05 \pm 0.01$</td>
<td>$-0.01 \pm 0.01$</td>
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<td>HCOO$^-$</td>
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<td>CH$_3$COO$^-$</td>
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<td>$0.08 \pm 0.01$</td>
<td>$0.09 \pm 0.01$</td>
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<td>SiO(OH)$_3$</td>
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<td>Si$_2$O$_2$(OH)$_5$</td>
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<td>$-0.08 \pm 0.04^{(b)}$</td>
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<td>B(OH)$_4$</td>
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<td>UO$_2$(OH)$_3$</td>
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<td>UO$_2$F$_3$</td>
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<td>$0.00 \pm 0.05^{(b,d)}$</td>
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<td>(UO$_2$)$_2$CO$_3$(OH)$_3$</td>
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<td>$-0.05 \pm 0.05^{(c)}$</td>
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<td>Am(SO$_4$)$_2$</td>
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<td>$-0.05 \pm 0.05^{(c)}$</td>
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<tr>
<td>Am(CO$_3$)$_2$</td>
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<td>SO$_4^{2-}$</td>
<td>$-0.03 \pm 0.04$</td>
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### Table IX.2 (continued)

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<th>$j \rightarrow k$</th>
<th>Li$^+$</th>
<th>Na$^+$</th>
<th>K$^+$</th>
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<td>$S_2O_3^{2-}$</td>
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<td>$-0.10 \pm 0.06$</td>
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<td>$HPO_4^{2-}$</td>
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<tr>
<td>$CO_3^{2-}$</td>
<td>$-0.08 \pm 0.03^{(c)}$</td>
<td>$0.02 \pm 0.01$</td>
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<td>$SiO_2(OH)_2^{2-}$</td>
<td>$-0.10 \pm 0.07^{(a)}$</td>
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<td>$Si_2O_3(OH)_3^{2-}$</td>
<td>$-0.15 \pm 0.06^{(b)}$</td>
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<td>$CrO_4^{2-}$</td>
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<td>$-0.08 \pm 0.04$</td>
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<td>$-0.12 \pm 0.06^{(b)}$</td>
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<td>$UO_2(N_3)_4^{2-}$</td>
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</tr>
<tr>
<td>$Si_3O_6(OH)_3^{3-}$</td>
<td>$-0.25 \pm 0.03^{(b)}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Si_2O_5(OH)_5^{3-}$</td>
<td>$-0.25 \pm 0.03^{(b)}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Si_4O_7(OH)_5^{3-}$</td>
<td>$-0.25 \pm 0.03^{(b)}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Am(CO_3)_3^{3-}$</td>
<td>$-0.15 \pm 0.05^{(c)}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$P_2O_7^{4-}$</td>
<td>$-0.26 \pm 0.05$</td>
<td></td>
<td>$-0.15 \pm 0.05$</td>
</tr>
<tr>
<td>$Fe(CN)_6^{4-}$</td>
<td>$-0.09 \pm 0.10^{(b,d)}$</td>
<td></td>
<td>$-0.17 \pm 0.03$</td>
</tr>
<tr>
<td>$UO_2(CO_3)_4^{4-}$</td>
<td>$-0.01 \pm 0.11^{(d)}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$UO_2(CO_3)_5^{5-}$</td>
<td>$-0.62 \pm 0.15^{(d)}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$U(CO_3)_6^{6-}$</td>
<td>$-0.30 \pm 0.15^{(d)}$</td>
<td>$0.37 \pm 0.11^{(d)}$</td>
<td></td>
</tr>
<tr>
<td>$(UO_2)_3(CO_3)_6^{6-}$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a) Evaluated in the NEA-TDB review on uranium thermodynamics [92GRE/FUG].
(b) Estimated in the NEA-TDB review on uranium thermodynamics [92GRE/FUG].
(c) From [80CIA]. These values differ from those reported in the NEA-TDB uranium review [92GRE/FUG]. See the discussion in Appendix D of the NEA-TDB review on americium thermodynamics [95SIL/BID].
(d) See the discussion in Appendix D of the NEA-TDB review on americium thermodynamics [95SIL/BID].
(e) Estimated in the NEA-TDB review on americium thermodynamics [95SIL/BID].
The Brønsted-Guggenheim-Scatchard model (SIT)

Figure IX.4: The determination of the SIT coefficient from the mean activity coefficients for HCl at 298.15 K and 1 atm from [59ROB/STO].

IX.3.1. Determination of ion interaction coefficients

Example 1:

Figure IX.4 illustrates both the method used to obtain ion interaction coefficients from mean-activity coefficient data, and the precision of the SIT method in single electrolyte systems. The mean activity coefficient $\gamma_\pm$ (HCl) is equal to:

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

or

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

By plotting $[\log_{10} \gamma_{\pm,\text{HCl}} + D]$ vs. $m_{\text{HCl}}$ 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.

Example 2:

Figure IX.5 illustrates the modelling of equilibrium constant data obtained at different
Estimations of Medium Effects on Thermodynamic Data

Table IX.3: Equilibrium constants for $\text{UO}_2^{2+} + \text{Cl}^- \rightleftharpoons \text{UO}_2\text{Cl}^+$

<table>
<thead>
<tr>
<th>$I_m$ (mol \cdot kg$^{-1}$)</th>
<th>$\log_{10} \beta_1$</th>
<th>$\log_{10} \beta_1 + 4D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>−0.174 ± 0.10</td>
<td>0.264 ± 0.10</td>
</tr>
<tr>
<td>0.20</td>
<td>−0.254 ± 0.10</td>
<td>0.292 ± 0.10</td>
</tr>
<tr>
<td>0.26</td>
<td>−0.357 ± 0.04</td>
<td>0.230 ± 0.04</td>
</tr>
<tr>
<td>0.31</td>
<td>−0.397 ± 0.04</td>
<td>0.220 ± 0.04</td>
</tr>
<tr>
<td>0.41</td>
<td>−0.420 ± 0.04</td>
<td>0.246 ± 0.04</td>
</tr>
<tr>
<td>0.51</td>
<td>−0.331 ± 0.10</td>
<td>0.371 ± 0.10</td>
</tr>
<tr>
<td>0.57</td>
<td>−0.432 ± 0.04</td>
<td>0.288 ± 0.04</td>
</tr>
<tr>
<td>0.67</td>
<td>−0.354 ± 0.04</td>
<td>0.395 ± 0.04</td>
</tr>
<tr>
<td>0.89</td>
<td>−0.438 ± 0.04</td>
<td>0.357 ± 0.04</td>
</tr>
<tr>
<td>1.05</td>
<td>−0.331 ± 0.10</td>
<td>0.491 ± 0.10</td>
</tr>
<tr>
<td>1.05</td>
<td>−0.298 ± 0.26</td>
<td>0.525 ± 0.26</td>
</tr>
<tr>
<td>1.61</td>
<td>−0.272 ± 0.10</td>
<td>0.618 ± 0.10</td>
</tr>
<tr>
<td>2.21</td>
<td>−0.193 ± 0.10</td>
<td>0.744 ± 0.10</td>
</tr>
<tr>
<td>2.21</td>
<td>−0.163 ± 0.10</td>
<td>0.774 ± 0.10</td>
</tr>
<tr>
<td>2.82</td>
<td>−0.021 ± 0.10</td>
<td>0.860 ± 0.10</td>
</tr>
<tr>
<td>3.50</td>
<td>−0.021 ± 0.10</td>
<td>0.974 ± 0.10</td>
</tr>
</tbody>
</table>

ionic strengths for the formation of $\text{UO}_2\text{Cl}^+$, according to $\text{UO}_2^{2+} + \text{Cl}^- \rightleftharpoons \text{UO}_2\text{Cl}^+$. For the reaction

$$\text{UO}_2^{2+} + \text{Cl}^- \rightleftharpoons \text{UO}_2\text{Cl}^+$$

the following formula is deduced for the extrapolation to $I = 0$:

$$\log_{10} \beta_1 + 4D = \log_{10} \beta_1^0 - \Delta \varepsilon I_m$$

where $\Delta \varepsilon = \varepsilon(\text{UO}_2\text{Cl}^+, \text{ClO}_4^-) - \varepsilon(\text{UO}_2^{2+}, \text{ClO}_4^-) - \varepsilon(\text{Na}^+, \text{Cl}^-)$.

Equilibrium constants (the source of the data is [92GRE/FUG]) for this reaction with assigned uncertainties, corrected to 298.15 K where necessary, and recalculated into molality units, are given in Table IX.3.

From the linear regression the following results are obtained: $\log_{10} \beta_1^0 = 0.17 \pm 0.02$, $\Delta \varepsilon = -(0.25 \pm 0.02) \text{kg} \cdot \text{mol}^{-1}$. The experimental data are depicted in Figure IX.5, where the area between the dotted lines represents the uncertainty range that is obtained by using the results in $\log_{10} \beta_1^0$ and $\Delta \varepsilon$ and correcting back to $I \neq 0$. $\Delta \varepsilon \approx \varepsilon(\text{UO}_2\text{Cl}^+, \text{ClO}_4^-) - \varepsilon(\text{UO}_2^{2+}, \text{ClO}_4^-) - \varepsilon(\text{Na}^+, \text{ClO}_4^-)$ only if at most 10% of the ClO$_4^−$ ion medium is replaced by Cl$^−$. (The example refers to a system with weak complex formation. In such systems it is difficult to distinguish between complex formation and specific
The Brønsted-Guggenheim-Scatchard model (SIT)

Figure IX.5: Plot of \[\log_{10}(\beta_1 + 4D)\] vs. \(I_m\) for the reaction \(\text{UO}_2^{2+} + \text{Cl}^- \rightleftharpoons \text{UO}_2\text{Cl}^+\) at 298.15 K and 1 atm. The straight line shows the result of the weighted linear regression, and the dotted lines represent the uncertainty range.

\[
\log_{10}(\beta_1 + 4D)
\]

ion interaction of the type used \(e.g.,\) in the Pitzer model, \textit{vide infra p.352.} Spectroscopic evidence \[92\text{GRE/FUG, p.193-194}\] indicates that chloride complexes are formed in this system.

**Example 3:**

When using the specific interaction theory, the relationship between the redox potential of the 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

\[
\text{Pt(s)} | \text{H}_2(g, f_{\text{H}_2} = 1), \text{H}^+(aq, a_{\text{H}^+} = 1) \parallel \text{UO}_2^{2+}(aq, a_{\text{UO}_2^{2+}}), \text{U}^{4+}(aq, a_{\text{U}^{4+}}), \text{H}^+(aq, a_{\text{H}^+}) | \text{Pt(s)}
\]

is

\[
\text{UO}_2^{2+} + \text{H}_2(g) + 2\text{H}^+ \rightleftharpoons \text{U}^{4+} + 2\text{H}_2\text{O(l)}
\]

For this reaction

\[
\log_{10} K^\circ = \log_{10} \left( \frac{a_{\text{U}^{4+}} \times a_{\text{H}_2\text{O}}}{a_{\text{UO}_2^{2+}} \times a_{\text{H}^+} \times f_{\text{H}_2}} \right)
\]

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= \log_{10} K + \log_{10} \gamma_{U^{4+}} - \log_{10} \gamma_{UO_2^{2+}} - 2 \log_{10} \gamma_{H^+} - \log_{10} \gamma_{f,H_2} \\
+ 2 \log_{10} a_{H_2O}

At reasonably low partial pressure of H_2(g) f_{H_2} \approx p_{H_2}, and on the basis of the SIT model:

\log_{10} \gamma_{U^{4+}} = -16D + \varepsilon(U^{4+}, ClO_4^-) m_{ClO_4^-} \\
\log_{10} \gamma_{UO_2^{2+}} = -4D + \varepsilon(UO_2^{2+}, ClO_4^-) m_{ClO_4^-} \\
\log_{10} \gamma_{H^+} = -D + \varepsilon(H^+, ClO_4^-) m_{ClO_4^-}

Hence,

\log_{10} K^0 = \log_{10} K - 10D + \left( \varepsilon(U^{4+}, ClO_4^-) - \varepsilon(UO_2^{2+}, ClO_4^-) \\
-2\varepsilon(H^+, ClO_4^-) \right) m_{ClO_4^-} + 2 \log_{10} a_{H_2O}

The relationship between the equilibrium constant and the redox potential is

\ln K = \frac{nF}{RT} E

where E is the redox potential in the particular ion medium, n is the number of transferred electrons in the reaction considered. Combining and rearranging the required equation then leads to

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

For n = 2 in the present example and T = 298.15 K, this equation becomes

E[mV] - 295.8 D = E^\circ [mV] - 29.58 \Delta \varepsilon m_{ClO_4^-}

where

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

The same procedure can be followed when using the Pitzer equations.

The following can be used as auxiliary sources of information on the SIT coefficients: a) the experimental data on mean activity coefficients of the electrolyte of interest in its mixture with other electrolytes; b) solubility data in ternary systems with a common ion, where the thermodynamic information (activity product and the SIT coefficient) is available for one component.
Other equations, approximately equivalent with the SIT model

IX.4. Other equations, approximately equivalent with the SIT model

Vasil’ev [62VAS] seems to be the first to systematically use an equation of type (IX.4) to extrapolate equilibrium constant data to zero ionic strength. The Vasil’ev equation for the single-ion activity coefficient has the following form:

\[
\log_{10} \gamma_i = - \frac{AZ_i^2 \sqrt{T_m}}{1 + 4.9B \sqrt{T_m}} + b I_m
\]  

(IX.6)

where the numerical factor 4.9 is used as a constant value of the “effective” diameter for all ions (in Å). At 298.15 K and 1 atm the value of the Debye-Hückel parameter \( B = 0.3283 \cdot 10^8 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2} \cdot \text{cm}^{-1} = 0.3283 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2} \cdot \text{Å}^{-1} \), i.e., the value of product \( 4.9B = 1.6 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2} \) as compared with 1.5 accepted in the SIT model. As far as we know, the value of the parameter \( b \) in the Vasil’ev equation was considered to be a purely empirical constant, the value of which had to be determined separately in each medium by experiments (in contrast to the SIT, where it was assumed that the values of the specific interaction coefficients for pairs of ions could also be evaluated from independent sources of thermodynamic information, if available).

Pitzer and Brewer [61LEW/RAN] have suggested the following equation, similar to the SIT equation (the well known Guggenheim equation):

\[
\log_{10} \gamma_i = - \frac{Z_i^2 A \sqrt{T_m}}{1 + \sqrt{T_m}} + \sum_j B(i, j) m_j
\]  

(IX.7)

where the summation over \( j \) covers all anions in the case where \( i \) is a cation and vice versa. Tables of \( B(i, j) \) are given by Pitzer and Brewer and by Baes and Mesmer [76BAE/MES]. The Debye-Hückel term is different from that used in our version of the SIT model. The Pitzer and Brewer equation has been used by Baes and Mesmer in their monograph on the hydrolysis of cations [76BAE/MES].

The interaction coefficients and the value of \( a_jB \) are correlated with one another, and it is important to use the interaction coefficients only with the model used to determine them. The equations of Vasil’ev, Pitzer and Brewer and the SIT are all essentially equivalent for the extrapolation of laboratory data obtained in different ionic media \( (I < 3-4 \text{ mol} \cdot \text{kg}^{-1}) \) to infinite dilution.

In 1973 Bromley [73BRO], using a trial and error method, proposed the following empirical equation for mean-activity coefficients

\[
\log_{10} \gamma_\pm = - \frac{A |Z_M Z_X| \sqrt{T_m}}{1 + \sqrt{T_m}} + \frac{(0.06 + 0.6B |Z_M Z_X|) I_m}{(1 + \frac{1.5I_m}{|Z_M Z_X|})^2} + BI_m
\]  

(IX.8)

As one can see, the Bromley equation can be considered an empirical extension of the Pitzer-Brewer or the SIT equations. However, the complication resulting from the addition of the second term results only in a very slight improvement of the fitting of \( \log_{10} \gamma_\pm \) for strong electrolytes, cf. [86COE], where it was shown that the Bromley and the SIT
Estimations of Medium Effects on Thermodynamic Data

equations give practically the same descriptions of the concentration dependence of equilibrium constants, and almost identical values of \( \log_{10} K^\circ \) at infinite dilution, for some two-phase equilibria.

Helgeson et al. [81HEL/KIR] have proposed a rather sophisticated semiempirical model involving ion hydration to describe the temperature and pressure dependence of both standard state and excess properties of aqueous ions and electrolytes. The Helgeson model postulates the following equation (with some simplifications) for the mean-activity coefficient of a completely dissociated binary electrolyte, consisting of \( \nu_M \) cations and \( \nu_X \) anions per formula unit, with ion charges \( Z_M \) and \( Z_X \) respectively:

\[
\log_{10} \gamma_\pm = -\frac{A}{1 + a_j B} 10^{1/2} \left[ \frac{Z_M Z_X \sqrt{T_m}}{1 + a_j B} \right] \log_{10}(1 + 0.0180153 m^*) + b_\gamma I_m \tag{IX.9}
\]

where \( b_\gamma \) is

\[
b_\gamma = \frac{(b_{MX}^0 + 2 \nu_M \nu_X b_{MX}^1)}{\nu}
\]

and \( \nu = \nu_M + \nu_X \); \( a_j \), as earlier, is an “effective” ion diameter (particular for each ion or electrolyte); \( B \) is the Debye-Hückel parameter; the term \( -\log_{10}(1 + 0.0180153 m^*) \) is the mole fraction to molality conversion factor; \( m^* \) stands for the sum of the ionic molalities of all species in solution; the parameter \( b_{MX}^0 \) is a constant at constant temperature for each particular ion (electrolyte); \( b_{MX}^1 \) is a short-range interaction parameter due to specific cation-anion (or ion-neutral) interactions. The parameters \( b_\gamma \) are tabulated [81HEL/KIR] for many single electrolytes and ion combinations ([81HEL/KIR], Table 5, 6 there), but not for complex ions. Hence, the Helgeson equation is actually a one-parameter equation. The maximum error between measured and calculated mean-activity coefficients is within 3-4% in a limited ionic strength range (up to 2-6 mol·kg\(^{-1}\)), but may increase up to 20% at ionic strengths 10-12 mol·kg\(^{-1}\) (Tables 5 and 6 in [81HEL/KIR]). This is essentially the same accuracy as for the SIT model. However, the validity of the assumptions on which the Helgeson model are based is not quite clear, e.g., the approximation used for the concentration dependence of the dielectric constant of an aqueous solution. An obvious drawback of this model is the need to use different values of the size parameter \( a_j \), for different ions and electrolytes, which makes it difficult to extend the model to multicomponent solutions. For instance (see [59ROB/STO], p.435) in a mixture of two 1-1 electrolytes B and C the following cross-differential relation must be obeyed:

\[
\left( \frac{\partial \ln \gamma_B}{\partial m_C} \right)_{m_B} = \left( \frac{\partial \ln \gamma_C}{\partial m_B} \right)_{m_C}
\]

and it is impossible to satisfy this equation using different values of the parameter \( a_j \) for each electrolyte. In order to circumvent this problem Helgeson et al. proposed that the average of the \( a_j \) values (see Eq. (124) in [81HEL/KIR]) should be used. However, this is not a strict solution of the problem, although the error introduced is usually less than

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On the magnitude of the specific ion interaction coefficients

10% in the value of the mean-activity coefficient of a certain electrolyte in a mixture with other electrolytes (see [81HEL/KIR], p.1346–1347).

This short survey of the equations proposed for the description of concentration dependence of equilibrium constants in aqueous solutions is rather subjective and incomplete. Many other equations for these purposes have been proposed in literature; see, for instance, [90BEC/NAG]. However, most of them are based on the following equation for mean activity coefficients

$$
\log_{10} \gamma = \frac{A[ZM]^{Zx} I_{m}^{1/2}}{1 + a_j B \sqrt{I_{m}}} + CI_{m} + D I_{m}^{3/2} + E I_{m}^{2} + \ldots
$$

and merely use different number of terms in an ionic strength expansion and different values of the $a_j B$ product. We do not recommend procedures that consider $a_j B$ as a fitting parameter, even though this leads to a “better” description of the ionic strength dependence of the equilibrium constants [94AND/KHO] in one particular ionic medium. These fitting parameters cannot be used for predictions in other ionic media.

IX.5. On the magnitude of the specific ion interaction coefficients

From the previous text it is obvious that in order to model the $p$, $T$, and ionic strength/medium dependence of chemical equilibria in aqueous electrolyte systems, not only do we need a proper model to describe deviations from ideality, but also a number of empirical parameters. An important point for the application of these models is the ability to *estimate* either interaction parameters for which no experimental information is available, or $\Delta \varepsilon$ for reactions. Interaction coefficients for a large number of strong electrolytes, and some complexes, have been listed in Tables IX.1 and IX.2. In the following figures we demonstrate possible internal correlations between these data, and also correlations with size and charge parameters.

Figures IX.6, IX.7, IX.8 and IX.9 shows correlations between the interaction coefficients in chloride and perchlorate media for ions of various charge types. These correlations are useful for the estimation of unknown interaction parameters, provided that information in one system is available.

IX.5.1. Correlations among specific ion interaction parameters for cations

The specific ion interaction coefficients are known for many cations; they may also be estimated by using correlations where experimental data are lacking. Figs. IX.10 to IX.12, show correlations between $\varepsilon(i,j)$ and the ion potential $Z/r$ for various cations, $Z$ and $r$ are the charge and crystallographic ionic radius of the cation, respectively. The scatter indicates that unknown interaction coefficients for cations of charge +3, or less,

$$
\Delta \varepsilon = \sum_i \nu_i \varepsilon(i,Y),
$$

where the summation is taken over all species $i$ in the reaction, and $Y$ stands for the cation of the ionic medium electrolyte if $i$ is an anion, but $Y$ stands for the ionic medium anion if $i$ is a cation. The reaction stoichiometric coefficients, $\nu_i$, are positive for products and negative for reactants, cf. Eq. (II.4).
Figure IX.6: The correlations between interaction coefficients in chloride and perchlorate media for monovalent cations. The units of $\varepsilon$ are kg $\cdot$ mol$^{-1}$.

Figure IX.7: The correlations between interaction coefficients in chloride and nitrate media for monovalent cations. The units of $\varepsilon$ are kg $\cdot$ mol$^{-1}$.
On the magnitude of the specific ion interaction coefficients

Figure IX.8: The correlations between interaction coefficients in chloride and perchlorate media for divalent cations. The units of $\varepsilon$ are $\text{kg} \cdot \text{mol}^{-1}$.

Figure IX.9: The correlations between interaction coefficients in chloride and nitrate media for trivalent cations. The units of $\varepsilon$ are $\text{kg} \cdot \text{mol}^{-1}$.
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Figure IX.10: The correlations between interaction coefficients and the ion potential $Z/r$ ($Z$ and $r$ stand for the charge and crystallographic ionic radius in Å, respectively) for various cations in chloride media. The units of $\varepsilon$ are kg·mol$^{-1}$.

may be estimated with an accuracy of about 0.05 kg·mol$^{-1}$. The interaction coefficients for several tetravalent actinide ions have been determined experimentally and do not have to be estimated. Unhydrolysed M$^{4+}$ ions are in general not present in aqueous systems because of very strong hydrolysis, with the exceptions of Zr$^{4+}$, Hf$^{4+}$ and tetravalent actinides which are present in strongly acid ($>2$ M) solution.

IX.5.2. Correlations among specific ion interaction parameters for complexes

The following general observations might be useful:

- Complexes of high positive charge tend to have interaction parameters close to those for simple cations of the same charge, cf. Table IX.1.

- Complexes with a large negative charge frequently have negative interaction parameters with M$^+$ ions; this may be a result of ion pairing.

Ciavatta [90CIA] has proposed the following method to estimate values of $\varepsilon$ for the complexes ML and ML$_2$ in an ionic medium NX:

$$\varepsilon(\text{ML}, \text{NorX}) \approx \frac{\varepsilon(M, X) + \varepsilon(L, N)}{2}$$

$$\varepsilon(\text{ML}_2, \text{NorX}) \approx \frac{\varepsilon(M, X) + 2\varepsilon(L, N)}{3}$$
On the magnitude of the specific ion interaction coefficients

Figure IX.11: The correlations between interaction coefficients and the ion potential $Z/r$ ($Z$ and $r$ stand for the charge and crystallographic ionic radius in Å, respectively) for various cations in perchlorate media. The units of $\varepsilon$ are kg · mol$^{-1}$.

Figure IX.12: The correlations between interaction coefficients and the ion potential $Z/r$ ($Z$ and $r$ stand for the charge and crystallographic ionic radius, respectively) for various cations in nitrate media. The units of $\varepsilon$ are kg · mol$^{-1}$.
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The average deviations between the estimates based on the equations above and the experimental values was ±0.05 kg · mol⁻¹. However, it is difficult to know how general this estimation method is, because of the few examples.

IX.5.3. Correlations between Δε-values for chemical reactions

Reactions that involve ions of the same charge type have approximately the same values of Δε, and the uncertainty in this estimation is in general equal to, or better than ±(0.05 to 0.1) kg · mol⁻¹.

IX.6. The Pitzer equations

The Pitzer model in its original form describes the thermodynamics of electrolyte mixtures where ionic pairing and complex formation are relatively weak. The physical theory on which the Pitzer model is based takes more interactions between the dissolved species into account than the simpler models. This is essential when describing thermodynamic properties in mixed electrolyte systems at high ionic strength. However, this requires a large number of empirical parameters, which must be obtained from experimental data. Many such parameters for various strong electrolytes have been determined, and they can be used to deduce interaction parameters for complexes by using experimental equilibrium constants at high ionic strength and extrapolated values of these constants at zero ionic strength. There is only a marginal gain to use the Pitzer equations when modelling the thermodynamics of complex formation and similar equilibrium reactions at fairly low ionic strengths, up to 3-4 mol · kg⁻¹. The real advantage is apparent in mixtures of electrolytes at high ionic strength.

The following text is only intended to provide the reader with a brief outline of the Pitzer method. The notation is the same as used by Pitzer, e.g., in [91PIT]. Pitzer’s approach is based on physical models of the interactions in multicomponent ionic systems. Applying relations based on statistical thermodynamics, and using a number of reasonable simplifications/assumptions [73PIT, 91PIT], he proposed an analytical form of a virial type equation for the excess Gibbs energy for the system water + an electroneutral mixture of aqueous ionic species. For the solution of a single electrolyte MX, the mean-activity coefficient may be expressed by Eq. (IX.10)

\[
\ln \gamma_{MX} = |Z_M Z_X| f^\gamma + m \frac{\nu_M \nu_X}{\nu} B_{MX}^\gamma + m^2 \left( \frac{2 (\nu_M \nu_X)^{3/2}}{\nu} \right) C_{MX}^\gamma \tag{IX.10}
\]

and the corresponding equation for the osmotic coefficient by

\[
\Phi - 1 = |Z_M Z_X| f^\Phi + m \frac{\nu_M \nu_X}{\nu} B_{MX}^\Phi + m^2 \left( \frac{2 (\nu_M \nu_X)^{3/2}}{\nu} \right) C_{MX}^\Phi \tag{IX.11}
\]

where \( \nu_M \) and \( \nu_X \) are the number of M and X ions in the formula unit, \( Z_M \) and \( Z_X \) their
The Pitzer equations

charges, \( m \) is the molality of the solution and \( \nu = \nu_M + \nu_X \),

\[
f^\gamma = -A_\Phi \left( \frac{\sqrt{T_m}}{1 + b\sqrt{T_m}} + \frac{2}{b} \ln \left( 1 + b\sqrt{T_m} \right) \right)
\]

(IX.12)

\[
B_M^\gamma = 2 \beta^{(1)}_{MX} + \frac{2 \beta^{(1)}_{MX}}{\alpha^2 T_m} \left( 1 - (1 + \alpha\sqrt{T_m} - \frac{\alpha^2 T_m}{2}) e^{-\alpha\sqrt{T_m}} \right)
\]

(IX.13)

\[
C_M^\gamma = \frac{3}{2} C_{MX}^\phi
\]

(IX.14)

\[
f^\Phi = -A_\Phi \frac{\sqrt{T_m}}{1 + b\sqrt{T_m}}
\]

(IX.15)

\[
B_M^\Phi = \beta^{(1)}_{MX} + \beta^{(1)}_{MX} e^{-\alpha\sqrt{T_m}}
\]

(IX.16)

\( f^\gamma \) and \( f^\Phi \) are the forms of the Debye-Hückel term in the Pitzer model for mean activity coefficient and osmotic coefficients respectively; \( A_\Phi = 0.3915 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2} \) at 298.15 K and 1 atm is the Debye-Hückel parameter for the osmotic coefficient, note that \( A_\Phi = A_\nu/3; \) \( b \) and \( \alpha \) are fixed parameters (\( b = 1.2 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2} ; \alpha = 2.0 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2} \)

for all electrolytes, except the 2-2-charge type). In the case of 2-2 electrolytes Pitzer adds an additional virial term. The Pitzer equations have been extended to cover electrolyte mixtures by including terms allowing for the interaction of ions of the same charge sign and for triplet interactions. This extension results in the following equation for the concentration dependence of the activity coefficient of a cation \( M \) (the corresponding equation for an anion \( L \) is obtained by interchanging \( L \) for \( M \), \( a \) for \( c \), and \( c \) for \( a \) throughout) in a mixed solution containing a number of different ions and neutral species (in the simplified form without the third virial terms for neutral species [91PIT, Eq. 63]):

\[
\ln \gamma_M = Z_M^2 F + \sum_a m_a \left( 2B_{Ma} + ZC_{Ma} \right) + \sum_c m_c \left( 2\phi_{Mc} + \sum_a m_a \psi_{Mca} \right) + \sum_a \sum_{a'} m_a m_{a'} \psi_{Ma'a} + Z_M \sum_c \sum_a m_c m_a C_{ca}
\]

\[
+ 2 \sum_n m_n \lambda_{nM}
\]

(IX.17)

The subscripts \( c \) and \( a \) refer to cations and anions in general, \( n \) denotes neutral species; \( Z_M \) is the charge of a specific cation; \( \phi_{Mc} \) is the second virial coefficient arising from binary interaction between a specific cation and the other cations; \( \lambda_{nM} \) is the second virial coefficient representing the interactions between a specific cation and neutral species; \( \psi_{ijk} \) is the third virial coefficient representing triple interactions between ions \( i, j, \) and \( k \) (where \( i \) and \( j \) are different anions, \( k \) is a cation; when \( i \) and \( j \) are different cations, \( k \) is
an anion). The parameters $\psi$ and $\lambda$ are assumed to be independent of the ionic strength. The quantity $F$ includes the Debye-Hückel and other terms as follows:

$$F = f^\gamma + \sum_c \sum_a m_c m_a B'_a + \sum_c \sum_{i'} m_c m_{i'} \phi'_{c_{i'}} + \sum_a \sum_{i'} m_a m_{i'} \phi'_{a_{i'}}$$

(IX.18)

$\phi'$ and $B'$ are the ionic strength derivatives of $\phi$ and $B$ respectively (see below), and

$$Z = \sum_i m_i |Z_i|$$

(IX.19)

The ionic strength dependence of $B_{M_a}$ is the following:

$$B_{M_a} = \beta^{(0)}_{M_a} + \frac{2 \beta^{(1)}_{M_a}}{\alpha^2 I_m} \left[ 1 - \left( 1 + \alpha \sqrt{I_m} \right) e^{-\alpha \sqrt{I_m}} \right]$$

(IX.20)

$$= \beta^{(0)}_{M_a} + \beta^{(1)}_{M_a} g(I_m)$$

and

$$B'_{M_a} = -\frac{2 \beta^{(1)}_{M_a}}{\alpha^2 I_m^2} \left[ 1 - \left( 1 + \alpha \sqrt{I_m} + \frac{1}{2} \alpha^2 I_m \right) e^{-\alpha \sqrt{I_m}} \right]$$

(IX.21)

$$= \beta^{(1)}_{M_a} \frac{g'(I_m)}{I_m}$$

where the functions $g$ and $g'$ are defined as:

$$g(I_m) = \frac{2}{\alpha^2 I_m} \left[ 1 - \left( 1 + \alpha \sqrt{I_m} \right) e^{-\alpha \sqrt{I_m}} \right]$$

(IX.22)

$$g'(I_m) = -\frac{2}{\alpha^2 I_m} \left[ 1 - \left( 1 + \alpha \sqrt{I_m} + \frac{1}{2} \alpha^2 I_m \right) e^{-\alpha \sqrt{I_m}} \right]$$

(IX.23)

$C_{ca}$ is defined as follows:

$$C_{ca} = \frac{C_{ca}^{\Phi}}{2 |Z_c Z_a|^{1/2}}$$

(IX.24)

The virial coefficient $\phi_{ij}$ has the following form

$$\phi_{ij} = \theta_{ij} + \frac{\Gamma}{2} \theta_{ij}(I_m)$$

(IX.25)
Comparison of the SIT and Pitzer models

where \( E_{ij}(I_m) \) is a function of the ionic strength only, it is zero except for unsymmetrical mixing of ions of the same sign, i.e., when the charges on \( i \) and \( j \) are different, but have the same sign (numerical values of this term are given by theory and several equations have been proposed that accurately represent the results obtained by numerical integration [91PIT]).

Therefore, in order to calculate the activity coefficients for ions the following parameters are needed: \( \beta^{(0)}, \beta^{(1)}, C^\Phi \) for each anion-cation pair; \( \theta_{ij} \) for each unlike cation-cation or anion-anion pair; \( \psi \) for each triple ion interaction where the ions are not all of the same sign, and \( \lambda \) for ion-neutral pairs. We should notice that, for the case of interactions between cations and anions with charges 2 or higher, it is preferable to use an additional parameter \( \beta^{(2)} \) (which is strongly correlated with the association constant for these ions). In some cases triple ion-ion-neutral interactions also have to be taken into account. The full set of the Pitzer parameters is available for many single electrolytes and electrolytes mixtures [91PIT], but only in very few cases for complexes.

The activity coefficient of a neutral species \( \text{N} \) is described by the following equation in the Pitzer approach, which is consistent with the traditional Setchenov equation:

\[
\ln \gamma_N = 2 \left( \sum_c m_c \lambda_{N_c} + \sum_a m_a \lambda_{N_a} + \sum_n m_n \lambda_{N_n} \right)
\]

The individual values of neutral-ion interaction coefficients cannot be determined in any experiment, but only values of electrically neutral combinations. In order to handle the problem of estimation of neutral-ion interaction coefficients Pitzer proposed to set all ion-neutral parameters involving \( \text{H}^+ \) to zero, whereupon the other ion-neutral parameters are determined.

IX.7. Comparison of the SIT and the Pitzer models for the description of concentration dependence of equilibrium constants of complex formation reactions in ionic media

The Brønsted-Guggenheim-Scatchard specific ion interaction model can be considered as a simplified form of the Pitzer ion interaction approach, neglecting triple interactions (which are important only in very concentrated solutions) and the interactions between the ions of the same signs (they are typically small). We have already pointed out that the Pitzer model offers a much more precise description of deviations from ideality in mixtures of strong electrolytes at high ionic strength, than the SIT, provided that the necessary interaction coefficients are available. Many users of the Pitzer formalism interpret experimental data (for instance, mean activity coefficients of electrolytes in electrolyte mixtures) without explicit consideration of complex formation, because this many-parameter model is able to reproduce the measured quantities with high precision without complications of this kind. There is no unambiguous thermodynamic method to distinguish between complex formation/ion-pairing and other types of short-range interactions between species in
solution when the extent of complex formation is small or moderate. Most solution coordination chemists are aware of the ambiguity which this may cause in systems where weak complexes are formed (these are also the systems where large variations in the concentrations of the reactants are necessary in order to detect the effects of “complex” formation), and require additional non-thermodynamic evidence for the formation of complexes, such as spectroscopic (uv/vis, NMR), or kinetic information [61ROS/ROS]). It is up to the modeller to decide if he/she wishes to describe weak interactions between ions in terms of complex formation, or by Pitzer type of ion interactions. However, it is important not to mix the two systems, for instance, to use the Pitzer set of parameters for systems containing both Mg$^{2+}$ and SO$_4^{2-}$ as components, together with an experimental value of log$_{10}$K for the reaction Mg$^{2+}$ + SO$_4^{2-}$ ⇌ MgSO$_4$(aq).

The Pitzer equations have been used to describe the concentration dependence of stoichiometric equilibrium constants for protolytic equilibria involving weak acids and bases where the chemical speciation is known. In these systems most of the parameters needed can be obtained from activity coefficient measurements of pure solutions of electrolytes, or the corresponding mixtures. Information of this type is rarely available for complex formation reactions. However, the data for complexes can be introduced into the Pitzer-type databases, provided that information of concentration equilibrium constants are available. In equilibrium analysis, where the studies are carried out in the presence of an inert electrolyte (ionic medium salt NX) and small (“trace”) concentrations of reactants/products, only the terms involving m$_{NX}$ have to be considered in the equations for the activity coefficients of reactants/products, while those involving molalities of “trace” components can be neglected. For a chemical reaction in the general form

\[ \sum_i \nu_i Q_i + rH_2O(l) = 0 \]  

(IX.27)

we therefore have

\[ \ln K^\circ = \sum_i \nu_i \ln m_i + \sum_i \nu_i \ln \gamma_i + r \ln a_{H_2O} \]

\[ = \ln K + \sum_i \nu_i \ln \gamma_i + r \ln a_{H_2O} \]  

(IX.28)

where the index $i$ denotes a particular reactant/product, $r$ stands for the number of moles of water participating in the reaction. A correction for water activity can easily be made using the available values of the osmotic coefficients for the ionic medium electrolyte. At trace concentrations of the reaction participants, the Pitzer model results in the following analytical equation for the reaction (IX.27) in the ionic medium NX (an 1-1 electrolyte)

\[ \ln K^\circ = \ln K + r \ln a_{H_2O} + \sum_i \nu_i Z_i^2 \left( f + m^2 B_{NX} \right) + 2m \sum_i \nu_i B_{ij} + 2m^2 \sum_i \nu_i C_{ij} \]

\[ + 2m \sum_i \nu_i \phi_{ii} + m^2 \sum_i \psi_{ii} + m^2 \sum_i \nu_i |Z_i| C_{NX} \]  

(IX.29)
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where the index $i$ refers to the reaction participants, $l'$ and $j$ stand for the ionic medium ions, having the same and opposite charge sign respectively, to the species $i$, and $m$ is the molality of the ionic medium electrolyte NX.

The corresponding analytical statement for the concentration dependence of $\log_{10} K$ for the reaction (IX.27) at trace concentrations of reactants/products in a NX electrolyte medium using the SIT equation is:

$$\log_{10} K^\circ = \log_{10} K + r \log_{10} a_{H_2O}$$

$$- D \sum_i n_i Z_i^2 + m \sum_i n_i \varepsilon(i,j)$$

where $D$ is the Debye-Hückel term, defined in Eq. (IX.5); index $i$ refers to a reactant/product, $j$ stands either for an ionic medium ion with charge sign opposite to that of $i$, or for a neutral species, and $m$ is the molality of the ionic medium electrolyte NX.

Example 4:

The first example of an application of both the Pitzer and the SIT methods describes the concentration dependence of the equilibrium constant for the reaction $CO_2(aq) + H_2O(l) \rightleftharpoons H^+ + HCO_3^-$ in a NaCl medium. In accordance with Eq. (IX.28) we have:

$$\ln K^0 = \ln K + \ln \gamma_{H^+} + \ln \gamma_{HCO_3^-} - \ln \gamma_{CO_2(aq)} - \ln a_{H_2O}$$

The Pitzer approach gives the following statements for the activity coefficients of the reaction participants at trace concentrations in the NaCl medium:

$$\ln \gamma_{H^+} = F + m_{Cl}(2B_{H,Cl} + 2m_{Cl} C_{H,Cl}) + m_{Na}(2\phi_{H,Na} + m_{Cl} \psi_{H,Na,Cl}) + m_{Na} m_{Cl} C_{Na,Cl}$$

$$\ln \gamma_{HCO_3^-} = F + m_{Na}(2B_{Na,HCO_3} + 2m_{Na} C_{Na,HCO_3} + m_{Cl}(2\phi_{Cl,HCO_3} + m_{Na} \psi_{Na,Cl,HCO_3}) + m_{Na} m_{Cl} C_{Na,Cl}$$

where

$$F = -A_{\Phi} \left[ \frac{\sqrt{T_m}}{1 + b \sqrt{T_m}} \right] + \frac{2}{b} \ln \left( 1 + b \sqrt{T_m} \right)$$

$$+ m_{Na} m_{Cl} B_{Na,Cl}^\circ$$

The ionic strength dependence of $B_{H,Cl}$ and $B_{Na,HCO_3}$ is given by Eq. (IX.20), the ionic strength dependence of $B_{Na,Cl}^\circ$ by Eq. (IX.21), and the relation between $C_{M,X}$ and the tabulated Pitzer parameter $C_{M,X}^{\Phi}$ is given by Eq. (IX.24).
Estimations of Medium Effects on Thermodynamic Data

As all components are at trace concentrations, except NaCl, the correction for water activity can be made using the values of the osmotic coefficients of pure sodium chloride solutions from the available tabulation [59ROB/STO], or calculated on the basis of the Pitzer approach, keeping in mind the usual relation between water activity and the osmotic coefficient $\Phi$ of an electrolyte:

$$\ln a_{H_2O} = -\frac{\Phi_{\nu m}}{1000} M_w$$

where $M_w$ is the molar mass of water (18.0153 g·mol$^{-1}$) and $\nu = 2$.

The required values of all the relevant Pitzer parameters for the system Na$^+$.Cl$^-$-H$^+$-HCO$_3^-$ are available in literature from the regression analysis of potentiometric and solubility data [84HAR/MOL, 91PIT]:

$$\beta_{\text{H}^+\text{Cl}^-} = 0.1775,$$
$$\beta_{\text{Na}^+\text{Cl}^-} = 0.0765,$$
$$\beta_{\text{Na}^+\text{HCO}_3^-} = 0.0277,$$
$$\theta_{\text{H}^+\text{Na}^+} = 0.036,$$
$$\psi_{\text{H}^+\text{Na}^+\text{Cl}^-} = -0.004,$$
$$\beta_{\text{H}^+\text{Cl}^-}^{(1)} = 0.2945,$$
$$\beta_{\text{Na}^+\text{Cl}^-}^{(1)} = 0.2664,$$
$$\beta_{\text{Na}^+\text{HCO}_3^-}^{(1)} = 0.0411,$$
$$\theta_{\text{H}^+\text{Cl}^-\text{Na}^+} = 0.03,$$
$$\psi_{\text{H}^+\text{Cl}^-\text{Na}^+\text{HCO}_3^-} = -0.015.$$  

The values of neutral-ion interaction coefficients involving CO$_2$(aq) are given in [91PIT]: $\lambda_{\text{CO}_2\text{Na}^+} = 0.100$, $\lambda_{\text{CO}_2\text{Cl}^-} = 0.005$. However, after recommendation of these values a new study on the solubility of CO$_2$ in NaCl solutions [93HE/MOR] was published. Hence, we determined the sum $\lambda_{\text{CO}_2\text{Na}^+} + \lambda_{\text{CO}_2\text{Cl}^-} = 0.096$ from all available consistent data on the solubility of CO$_2$ in sodium chloride solutions [43HAR/DAV, 79YAS/YOS, 93HE/MOR], see Figure IX.13.

The value of $K^\circ$ was taken from the CODATA [89COX/WAG] recommendation, $\ln K^\circ = -14.624 \pm 0.010$ or $\log_{10} K^\circ = -6.351 \pm 0.004$.

The calculated values of $\log_{10} K$ for the reaction H$_2$O(l) + CO$_2$(aq) $\rightleftharpoons$ H$^+$ + HCO$_3^-$ using the Pitzer approach (solid lines) are compared with the experimental ones (dotted symbols) in Figure IX.14. Some experimental data have been reported as $\log_{10} K$ for the reaction H$_2$O(l) + CO$_2$(g) $\rightleftharpoons$ H$^+$ + HCO$_3^-$. By combining these values with the Henry’s law constant for CO$_2$ from the CODATA recommendation and the value for the activity coefficient of CO$_2$(aq) in sodium chloride solutions given above, we obtain a second set of equilibrium constants for the reaction discussed. We should notice that Thurmond and Millero [82THU/MIL] have used a quite different equation for the concentration dependence of the activity coefficient of CO$_2$(aq), namely $\ln \gamma_{\text{CO}_2} = 0.242 m - 0.0106 m^2$ for the interpretation of their potentiometric data. This equation gives a poor fit of $\log_{10} \gamma_{\text{CO}_2}$ data above 3 m NaCl; see Figure IX.13. Therefore, the equilibrium constants from [82THU/MIL] were corrected using the more accurate values of the activity coefficient of CO$_2$(aq) in NaCl solutions.

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Figure IX.13: The concentration dependence of $\log_{10} \gamma$ of $\text{CO}_2(\text{aq})$ in NaCl solutions at 298.15 K and 1 atm. The symbols are the experimental data, the solid line - the regression using the sum $\lambda_{\text{CO}_2,\text{Na}} + \lambda_{\text{CO}_2,\text{Cl}} = 0.096$ (see text), the dashed line - the approximation used in [82THU/MIL].

Many experimental values of $\log_{10} K$ refer to the molar concentration scale and they have to be converted to the molality scale. The concentrations were converted using the following relationship

$$m_i = \frac{1000C_i}{1000\rho - C_iM}$$

where $C_i$ and $m_i$ stand for molarity and molality of the dissolved substance $i$, $\rho$ is the density of the solution and $M$ is the molar mass of the solute; see also Section II.2. The densities of electrolyte solutions are available in the compilation [85SOH/NOV]. The relation between equilibrium constants expressed in molarity ($K_c$) or molality units ($K_m$) is

$$\log_{10} K_m = \log_{10} K_c + \sum \nu \log_{10} \frac{m}{C}$$

where $\sum \nu$ is here the sum of the stoichiometric coefficients for the reaction, $m$ and $C$ stand for molality and molarity of the ionic medium (for the reactions studied at trace concentrations of the reaction participants). We will always use the molality concentration scale and therefore the notation $\ln K$ and $\log_{10} K$ instead of $\ln K_m$ and $\log_{10} K_m$. 

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Figure IX.14: The comparison of the experimental (different symbols) and calculated values of $\log_{10} K$ using the Pitzer approach (solid line) and the SIT model (dashed line) for the reaction $\text{H}_2\text{O}(l) + \text{CO}_2(\text{aq}) \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$ in NaCl solutions at 298.15 K and 1 atm.

From the SIT model we obtain the following statements for the activity coefficients of $\text{H}^+$, $\text{HCO}_3^-$ and $\text{CO}_2(\text{aq})$ at their trace concentrations in NaCl ionic medium:

$$\log_{10} \gamma_{\text{H}^+} = -\frac{A\sqrt{T_m}}{1 + 1.5\sqrt{T_m}} + \varepsilon(\text{H}^+, \text{Cl}^-) m_{\text{Cl}^-}$$

$$\log_{10} \gamma_{\text{HCO}_3^-} = -\frac{A\sqrt{T_m}}{1 + 1.5\sqrt{T_m}} + \varepsilon(\text{Na}^+, \text{HCO}_3^-) m_{\text{Na}^+}$$

$$\log_{10} \gamma_{\text{CO}_2(\text{aq})} = \varepsilon(\text{CO}_2(\text{aq}), \text{Na}^+) m_{\text{Na}^+} + \varepsilon(\text{CO}_2(\text{aq}), \text{Cl}^-) m_{\text{Cl}^-}$$

$$= \varepsilon(\text{CO}_2(\text{aq}), \text{Na}^+ + \text{Cl}^-) m_{\text{NaCl}}$$

The required interaction coefficient for the $\text{H}^+$ and the $\text{Cl}^-$ ion combination was taken from [92GRE/FUG]: $\varepsilon(\text{H}^+, \text{Cl}^-) = 0.12 \pm 0.01 \text{ kg} \cdot \text{mol}^{-1}$, and the value of $\varepsilon(\text{Na}^+, \text{HCO}_3^-) = 0.00 \pm 0.01 \text{ kg} \cdot \text{mol}^{-1}$ was determined by minimisation of the deviations of calculated and experimental $\log_{10} K$ data. In reference [92GRE/FUG] a somewhat different value $-0.02 \pm 0.02$ was used. This was modified in [95SIL/BID] and agrees with the value reported by Ciavatta [80CIA].
\[ \varepsilon(\text{CO}_2(\text{aq}), \text{Na}^+) + \varepsilon(\text{CO}_2(\text{aq}), \text{Cl}^-) = 0.083 \text{ kg} \cdot \text{mol}^{-1} \] was calculated from the corresponding sum \( \lambda_{\text{CO}_2, \text{Na}} + \lambda_{\text{CO}_2, \text{Cl}} \) values using the relationship \( \varepsilon(n, i) = 2\lambda(n, i)/\ln(10) \). In [92GRE/FUG] this value was assumed to be zero. The values of \( \log_{10} K \) calculated from the SIT model are shown in Figure IX.14 by the dashed line.

As one can see, the Pitzer model provides better agreement with the experimental data than the less-parameterised SIT model. Nevertheless, the maximal deviation between the two curves is less than 0.04 \( \log_{10} \) unit, which is close to expected accuracy of the experimental data, \( \pm 0.03 \log_{10} \) units.

An analogous procedure can be used for the description of the concentration dependence of the second dissociation constant of carbonic acid in a NaCl medium, \( \text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-} \). For this reaction we write

\[ \ln K^\circ = \ln K + \ln \gamma_{\text{H}^+} + \ln \gamma_{\text{CO}_3^{2-}} - \ln \gamma_{\text{HCO}_3^-} \]

The analytical equations for the activity coefficients of \( \text{H}^+ \) and \( \text{HCO}_3^- \) at trace concentrations in the NaCl ionic medium based on the Pitzer approach are given above, and for the activity coefficient of \( \text{CO}_3^{2-} \) one can write in accordance with Eq. (IX.17)

\[ \ln \gamma_{\text{CO}_3^{2-}} = 4F + m_{\text{Na}}(2B_{\text{Na}, \text{CO}_3} + 2m_{\text{Na}} C_{\text{Na}, \text{CO}_3}) + m_{\text{Cl}}(2\phi_{\text{Cl}, \text{CO}_3} + m_{\text{Na}} \psi_{\text{Na}, \text{Cl}, \text{CO}_3}) + 2m_{\text{Na}} m_{\text{Cl}} C_{\text{Na}, \text{Cl}} \]

As the charges of \( \text{CO}_3^{2-} \) and \( \text{Cl}^- \) co-ions differ, the interaction parameter \( \phi_{\text{Cl}, \text{CO}_3} \) should be considered to be ionic strength dependent, \( \phi_{\text{Cl}, \text{CO}_3} = \theta_{\text{Cl}, \text{CO}_3} + F \theta_{\text{Cl}, \text{CO}_3}(I) \). The values of the term \( F \theta_{\text{Cl}, \text{CO}_3}(I) \) at different ionic strength can be obtained numerically, as described in [91PIT], Appendix B. The values of the Pitzer parameters used have been taken from the literature [84HAR/MOL, 91PIT):

\[ \beta_{\text{Na}, \text{CO}_3}^{(0)} = 0.0399, \quad \beta_{\text{Na}, \text{CO}_3}^{(1)} = 1.389, \quad C_{\text{Na}, \text{CO}_3}^\Phi = 0.0044, \]
\[ \theta_{\text{Cl}, \text{CO}_3} = -0.02, \quad \psi_{\text{Na}, \text{Cl}, \text{CO}_3} = 0.0085. \]

The value of \( K^\circ \) for the second dissociation constant for \( \text{CO}_2 \) was taken from the CODATA [89COX/WAG] recommendation, \( \ln K^\circ = -23.79 \pm 0.16 \) or \( \log_{10} K^\circ = -10.33 \pm 0.07 \).

The calculated values of \( \log_{10} K \) for the reaction \( \text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-} \), using the Pitzer approach (solid lines) are compared with experimental ones (different symbols) in Figure IX.15. We should note that the experimental values of \( \log_{10} K \) in the NaCl medium have not been considered in the evaluation of the Pitzer parameters for the ion combinations in the system \( \text{Na}^+ - \text{Cl}^- \text{HCO}_3^- - \text{CO}_3^{2-} - \text{H}^+ \). Probably, a small change in the numerical values of mixing terms might improve the quality of reproduction of experimental data on the basis of the Pitzer model at high concentrations of NaCl.

Using the SIT model we obtain the following equation for the activity coefficients of \( \text{CO}_3^{2-} \) at trace concentrations in NaCl ionic medium:

\[ \log_{10} \gamma_{\text{CO}_3^{2-}} = -\frac{4A\sqrt{m}}{1 + 1.5\sqrt{m}} + \varepsilon(\text{Na}^+, \text{CO}_3^{2-}) m_{\text{Na}^+} \]
Figure IX.15: The comparison of the experimental (different symbols) and calculated values of $\log_{10} K$ using the Pitzer approach (solid line) and the SIT model (dashed line) for the reaction $\text{HCO}_3^- \rightleftharpoons H^+ + \text{CO}_3^{2-}$ in NaCl solutions at 298.15 K and 1 atm.

The corresponding equations for the activity coefficients of $H^+$ and $\text{HCO}_3^-$ have been given previously. The value of the interaction coefficient for $\text{Na}^+$ and $\text{CO}_3^{2-}$ ion combination, $\varepsilon(\text{Na}^+, \text{CO}_3^{2-})$, was estimated from the experimental values of $\log_{10} K$ for the reaction and the SIT interaction coefficients $\varepsilon(H^+, \text{Cl}^-)$ and $\varepsilon(\text{Na}^+, \text{HCO}_3^-)$, and found to be $-(0.06 \pm 0.02) \text{ kg} \cdot \text{mol}^{-1}$. The values of $\log_{10} K$ for the reaction, calculated with the SIT, are shown by the dashed line in Figure IX.15.

The Pitzer model provides a better reproduction of the experimental values of $\log_{10} K$ as compared to the SIT model, especially taking into account that the experimental data have not been considered in the evaluation of the Pitzer parameters in [82PEI/PIT, 84HAR/MOL]. However, the accuracy of the SIT model is better than $\pm 0.10 \log_{10}$ unit, which is satisfactory in many cases. In order to better understand the “price” for the higher accuracy in the Pitzer model we turn to Example 5.

Example 5:

This example discusses the dissociation constants of carbonic acid in a NaClO$_4$ ionic medium at 298.15 K and 1 atm.

The equations in this case are identical with those used for the NaCl medium, sub-
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Substituting Cl\(^-\) for ClO\(_4^-\). The difference is that for the first dissociation constant the experimental data refer to the reaction CO\(_2\)(g) + H\(_2\)O(l) \(\rightleftharpoons H^+ + HCO_3^-\). The CODATA [89COX/WAG] recommended value of \(K^\circ\) for this reaction is ln \(K^\circ = -18.001 \pm 0.008\) or log\(_{10}\) \(K^\circ = -7.818 \pm 0.004\).

All the SIT parameters needed are available for the ion combinations in this system, \(\varepsilon(H^+, ClO_4^-) = 0.14 \pm 0.02, \varepsilon(Na^+, HCO_3^-) = 0.00 \pm 0.02,\) and \(\varepsilon(Na^+, CO_3^{2-}) = -0.08 \pm 0.03\) (all in units of kg \cdot mol\(^{-1}\)), e.g., Tables IX.1 and IX.2. Hence, the values of log\(_{10}\) \(K\) for the first and the second dissociation constants for carbonic acid in NaClO\(_4\) medium may be predicted. The predicted and experimental values of log\(_{10}\) \(K\) for the two reactions are shown in Figures IX.16 and IX.17 by dashed lines. As one can see, the SIT model predicts the values of log\(_{10}\) \(K\) in NaClO\(_4\) medium surprisingly well. Indeed, the values of log\(_{10}\) \(K\) for the first dissociation constant of carbonic acid are reproduced practically within the expected experimental uncertainty, \(\pm 0.03\); the deviations between experimental and predicted values of log\(_{10}\) \(K\) for the second dissociation constant are less than \(\pm 0.1\).

The agreement between experimental and calculated values of log\(_{10}\) \(K\) for both reactions in the NaClO\(_4\) medium is better than in the NaCl medium, where the values of the SIT interaction coefficients \(\varepsilon(Na^+, HCO_3^-)\) and \(\varepsilon(Na^+, CO_3^{2-})\) were determined. This better agreement in sodium perchlorate is fortuitous. Nevertheless, our experience shows that, in general, the less-parametrised SIT model gives quite reasonable estimations of equilibrium constants in different media, provided that the necessary interaction coefficients are known.

For the Pitzer model the values of mixing parameters are not available in literature for all the interactions in the system Na\(^+\)-H\(^+\)-ClO\(_4^-\)-HCO\(_3^-\)-CO\(_3^{2-}\). The known values are listed below [91PIT]:

\[
\begin{align*}
\beta^{(1)}_{H,ClO_4} &= 0.2931, & \beta^{(1)}_{H,ClO_4} &= 0.1747, & C^\phi_{H,ClO_4} &= 0.00819, \\
\beta^{(1)}_{Na,ClO_4} &= 0.2755, & \beta^{(1)}_{Na,ClO_4} &= 0.0554, & C^\phi_{Na,ClO_4} &= -0.00118, \\
\beta^{(1)}_{Na,CO_3} &= 1.389, & \beta^{(1)}_{Na,CO_3} &= 0.0399, & C^\phi_{Na,CO_3} &= 0.0044, \\
\theta_{H,Na} &= 0.036, & \psi_{H,Na,ClO_4} &= -0.016, & \theta_{ClO_4,HCO_3} &= unknown, \\
\theta_{ClO_4,CO_3} &= unknown, & \psi_{Na,ClO_4,HCO_3} &= unknown, & \psi_{Na,ClO_4,CO_3} &= unknown.
\end{align*}
\]

In Figures IX.16 and IX.17 the values of log\(_{10}\) \(K\) for the first and second dissociation constants of carbonic acid are calculated from the Pitzer model with the available parameters (solid lines). The difference between the experimental and calculated values (with only the two known mixing parameters reported in the literature) is appreciable, especially for the first dissociation constant. These examples show the accuracy to expect from the Pitzer type of calculations when some mixing parameters are not available. The procedure recommended to improve the performance of the Pitzer model is to estimate the remaining mixing parameters from the differences between the calculated and experimental values of the constants. This resulted in the following values: \(\theta_{ClO_4,HCO_3} = 0.07, \theta_{ClO_4,CO_3} = 0.07, \psi_{Na,ClO_4,HCO_3} = -0.015, \psi_{Na,ClO_4,CO_3} = 0\). These estimations are only
Figure IX.16: Comparison of the experimental (different symbols) values of log_{10} K and the predicted values of log_{10} K using the Pitzer approach for the reaction H_{2}O(l) + CO_{2}(g) \rightleftharpoons H^{+} + HC_{3}O_{5}^{-} in NaClO_{4} solutions at 298.15 K and 1 atm. The solid line has been calculated using literature values for the mixing terms, the dashed line refers to the SIT model. The dotted line represents the calculation based on the Pitzer model with estimated values of the required mixing terms (see text).

preliminary; many more determinations, preferably of better quality, are needed to get reliable values for these parameters. The values of log_{10} K for both reactions calculated using all Pitzer’s parameters are shown in Figures IX.16 and IX.17 by dotted lines. As expected, the additional parameters strongly improve the performance of the Pitzer model.

These examples demonstrate the difference between the two models considered:

- The SIT uses the minimal number of regression parameters. The deviations between experimental and fitted values of log_{10} K are usually within ±0.05-0.10 log_{10} unit. Such deviations are expected, because the uncertainty of the values of mean activity coefficients, log_{10} \gamma_{\pm} for strong 1-1, 2-1, 3-1 electrolytes is usually within 0.02-0.05 log_{10} units, when calculated from this model. This allows a reasonable extrapolation of log_{10} K values in different ionic media, if the required SIT interaction coefficients are known. Hence, using the data from the sodium chloride medium, we could predict the values of equilibrium constants for the same reactions in solutions of sodium perchlorate, practically with the same accuracy as in the NaCl medium. The accuracy of the SIT model does not permit the reproduction of the concentration dependence of the more precise data, to which the dissociation constants of carbonic acid belongs. The number of such examples is limited to the relatively simple chemical systems which can be studied without
Figure IX.17: Comparison of the experimental (different symbols) and the predicted values of $\log_{10} K$ using the Pitzer approach with the available data from the literature values of the mixing terms (solid line) and the SIT model (dashed line) for the reaction $\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$ in NaClO$_4$ solutions at 298.15 K and 1 atm. The dotted line represents the calculation based on the Pitzer model with estimated values of the required mixing terms (see text).

serious experimental difficulties, where the speciation is known, the number of complexes formed is limited, and where it is possible to find the conditions under which the studied complex is the main species in solution, etc. The precision and accuracy of experimental equilibrium constants for metal—ligand systems is in general much smaller than that of simple protolytes, like carbonic acid. This issue will be considered in the following Section.

- The Pitzer model, which was developed for the description of the concentration dependence of very accurate activity coefficient and osmotic coefficient data, is able to reproduce the precise values of $\log_{10} K$ practically within experimental accuracy, provided that the numerical values of all the relevant parameters are available. If the values of a number of parameters are unknown, the quality of the data reproduction and the predictions are much poorer and comparable with the accuracy of the SIT approach. The large number of parameters in the Pitzer model and their strong interrelations and correlations makes it difficult to use this model in systems where complex formation takes place, especially if some parameters have to be determined from concentration equilibrium constant data. By using a large number of fitting parameters in the Pitzer model it is possible to describe very precise emf or isopiestic data for many ternary systems, e.g., MeCl$_2$-HCl-H$_2$O without consid-
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eration of complex formation at all, provided that the extent of complex formation is not large. However, for a solution coordination chemist it is essential to have correct information about the constitution of the complexes formed, because this determines important properties of a metal in solution such as chemical reactivity, toxicity, adsorption etc. The real speciation is important in many technological processes, for instance, the formation of negatively charged chloride complexes of cobalt in concentrated chloride solutions is used for the separation of nickel and cobalt. Progress in the understanding of chemical processes in solutions requires knowledge of their chemistry, i.e., their real speciation! Therefore, one must not use an extensively parametrized Pitzer model as a "substitution" for knowledge of the detailed chemistry, even if this model is excellent for describing the thermodynamic observations. However, it is desirable to extend the Pitzer formalism to all types of complex formation reactions and to obtain experimental values of the required Pitzer parameters for complexes. Such determinations must be based on experimental concentration equilibrium constants in different ionic media, which require an extensive experimental effort, even though a very large amount of stability constants for complex species have already been accumulated during the past 100 years [64SIL/MAR, 71SIL/MAR, 82HOG]. The problems will be described and discussed in the following section.

IX.7.1. The determination of the Pitzer and the SIT parameters from the log_{10} K data

Our primary goal is the description of the concentration dependence of equilibrium constants, since most data on the thermodynamics of complex formation reactions are reported in this way. The existing log_{10} K data have the following characteristics:

- The equilibrium constants have, as a rule, been obtained in a constant ionic medium. As discussed in the Introduction (p.325), the use of high concentrations of supporting electrolyte is a convenient and widely accepted method to establish a unique chemical model of a system under study. The log_{10} K data are not equally distributed on the ionic strength/concentration scale. Usually the experimentally covered interval is between 0.1 and 4 mol·kg^{-1}. The high molality of the ionic medium as compared to the concentrations of reactants/products ensures nearly constant values of the activity coefficients of the reaction participants even for reasonable variations of the total concentrations of reactants/products.

Note. When equilibrium constants are determined using the emf-technique one must know or estimate liquid-junction potentials. However, by using a constant ionic medium the variations of the liquid-junction potential with the composition of the system are small.

- Relatively few experimental determinations, often less than 10 data points, are reported in the literature for a particular reaction in a particular ionic medium.
Comparison of the SIT and Pitzer models

The accuracy of the \( \log_{10} K \) data is often much smaller than the precision of individual measurements, a fact which deserves a separate comment. One has to distinguish between the reproducibility of the determination of the constant for given experimental conditions, with a particular experimental method, and an accepted chemical model and the accuracy of \( \log_{10} K \). As stated in [90BEC/NAG, p.280] “the true error in the stability constants can be estimated with a high degree of certainty only through the comparison of constants obtained with methods differing in basic principles, or of constants obtained in independent laboratories”, and “agreement within \( \pm 0.05 \log_{10} \) unit is classified as very good agreement, even in systems that can be studied experimentally without difficulty”. This means that the \( \log_{10} K \) data are 20-100 times less accurate than the values of mean activity coefficients or osmotic coefficients, which often have an accuracy better than 0.5 per cent. This important fact should be kept in mind when discussing the determination of the Pitzer parameters for a reaction from the \( \log_{10} K \) values.

The analytical statement for the concentration dependence of the equilibrium constant for a general chemical reaction

\[
\sum_{i} \nu_i Q_i + rH_2O(l) = 0
\]

for the Pitzer model is given by Eq. (IX.29), which is valid for constant ionic medium NX, where NX is an 1-1 electrolyte, and for the trace concentrations of the reaction participants. For the purposes of a regression it is convenient to rewrite this equation as follows

\[
\ln K^0 = \ln K + r \ln a_{H_2O} + \Delta(Z^2) \left( f_\gamma + m^2 B_{NX} \right) + m^2 \Delta[Z]C_{NX} + mX_1 + 2m g(I_m) X_2 + 2mX_3
\]

where \( m \) stands for the molality of the supporting NX electrolyte, and

\[
\Delta(Z^2) = \sum_{i} \nu_i Z_i^2
\]

\[
\Delta[Z] = \sum_{i} \nu_i |Z_i|
\]

\[
X_1 = \Delta \beta^{(0)} + \Delta \phi = \sum_{i} \nu_i \beta_{ij}^{(0)} + \sum_{i} \nu_i \phi_{ij}
\]

\[
X_2 = \Delta \beta^{(1)} = \sum_{i} \nu_i \beta_{ij}^{(1)}
\]

\[
X_3 = \Delta C + \frac{1}{2} \Delta \psi = \sum_{i} \nu_i C_{ij} + \frac{1}{2} \sum_{i} \nu_i \psi_{ij}
\]

and \( g(I_m) \) is defined in Eq. (IX.22).
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Eq. (IX.31) is the general equation to be used if we want to determine \( \log_{10} K^\circ \) and the sum of the Pitzer parameters for reactants and products from experimental equilibrium constants at different ionic strengths. The second, third and fourth terms on the right hand side of Eq. (IX.31) can be calculated from the known Pitzer parameters for the ionic medium NX. The equation shows that the coefficients for the other terms in \( m \) and \( m^2 \) contain \( \Delta \beta^{(0)} \) and \( \Delta \phi \), and \( \Delta C \) and \( \Delta \psi \), respectively. Hence, it is not possible to obtain the individual Pitzer parameters \( \Delta \beta^{(0)} \) and \( \Delta C \) from this equation alone. Pitzer [79PIT] points out, that in most cases the mixing parameters are small and may be neglected, hence, \( X_1 = \Delta \beta^{(0)} \) and \( X_3 = \Delta C \) is a reasonable approximation. The main difficulty is still to determine the parameters \( X_1, X_2, X_3 \) (as well as \( \ln K^\circ \)) from a limited number of experimental concentration constants, \( \log_{10} K \), which rarely have a high accuracy, as indicated by the previous discussion. In order to use the Pitzer equations in systems where complex formation takes place, it therefore seems necessary to make some simplifications. A check of the typical values of \( C^\phi \) from [91PIT] showed that the contribution of \( \Delta C \) is significant only at high ionic strength, typically above 5-6 mol \cdot kg\(^{-1}\), and that this term could be neglected at lower ionic strengths. Another simplification was proposed by Millero [83MIL2], who assumed the value \( \beta^{(1)} = 0 \) for complexes. The validity of these two simplifications will be checked below.

The corresponding analytical statement for the concentration dependence of \( \log_{10} K \) for the reaction (IX.27) at trace concentrations of reactants/products in a NX electrolyte medium using the SIT equation is given by Eq. (IX.30), and can be rewritten as follows:

\[
\log_{10} K^\circ = \log_{10} K + r \log_{10} a_{H_2O} - \Delta(Z^2)D + m \Delta \varepsilon \quad (IX.32)
\]

where \( D \) is the Debye-Hückel term, defined in Eq. (IX.5); \( m \) stands for the molality of the ionic medium, the 1-1 electrolyte NX, and

\[
\Delta(Z^2) = \sum_i \nu_i Z_i^2
\]

\[
\Delta \varepsilon = \sum_i \nu_i \varepsilon(i, j)
\]

see Eq. (IX.30) for further explanations. After correction for the water activity and the Debye-Hückel contribution, the SIT equation becomes a simple linear function of the molality of the ionic medium.

We will use the literature data of \( \log_{10} K \) for some selected reactions for the parametrization of both the models discussed. The main questions are:

- The reliability of \( \log_{10} K^\circ \) (\( i.e., \) the thermodynamic constants) obtained by a regression. Therefore, we use the experimental data for the reactions, for which CODATA recommendations [89COX / WAG] are available; see Examples 6 and 7. For the reactions selected, the \( \log_{10} K \) data from solutions of high ionic strength have not been considered when making the CODATA recommendations.

- The typical uncertainty in the fitting parameters, which is decisive for the possibility to determine the Pitzer or the SIT concentration parameters from a limited number of experimental points of limited accuracy.
Comparison of the SIT and Pitzer models

Table IX.4: Equilibrium constants for the dissociation of water in KCl solutions at 298.15 K.

<table>
<thead>
<tr>
<th>mKCl mol−1</th>
<th>−log10 K(m)</th>
<th>−log10 K(m) + log10 aw</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.82</td>
<td>14.27 ± 0.10</td>
<td>14.20 ± 0.10</td>
</tr>
<tr>
<td>4.22</td>
<td>14.24 ± 0.10</td>
<td>14.18 ± 0.10</td>
</tr>
<tr>
<td>3.31</td>
<td>14.08 ± 0.05</td>
<td>14.03 ± 0.05</td>
</tr>
<tr>
<td>3.31</td>
<td>14.09 ± 0.05</td>
<td>14.04 ± 0.05</td>
</tr>
<tr>
<td>3.30</td>
<td>14.08 ± 0.05</td>
<td>14.03 ± 0.05</td>
</tr>
<tr>
<td>2.13</td>
<td>13.90 ± 0.05</td>
<td>13.87 ± 0.05</td>
</tr>
<tr>
<td>2.13</td>
<td>13.91 ± 0.05</td>
<td>13.88 ± 0.05</td>
</tr>
<tr>
<td>2.13</td>
<td>13.90 ± 0.05</td>
<td>13.87 ± 0.05</td>
</tr>
<tr>
<td>1.03</td>
<td>13.77 ± 0.05</td>
<td>13.76 ± 0.05</td>
</tr>
<tr>
<td>1.03</td>
<td>13.93 ± 0.10</td>
<td>13.92 ± 0.10</td>
</tr>
<tr>
<td>1.03</td>
<td>13.90 ± 0.10</td>
<td>13.89 ± 0.10</td>
</tr>
<tr>
<td>0.51</td>
<td>13.75 ± 0.05</td>
<td>13.74 ± 0.05</td>
</tr>
<tr>
<td>0.10</td>
<td>13.78 ± 0.05</td>
<td>13.78 ± 0.05</td>
</tr>
</tbody>
</table>

For the regression we use the weighted general linear regression method as outlined in [65SHC]. The weight ω of an experimental point was defined as ω = 1/δ², where δ is an estimated uncertainty of log10 K value.

Example 6:

This example is a simple chemical reaction, H2O(l) ⇌ H+ + OH− where precise experimental data in KCl media at 298.15 K are available. After recalculating the experimental data of log10 K, quoted from the “Stability constants” compilations [64SIL/MAR, 71SIL/MAR, 82HOG], to molality units and correcting for the water activity log10 aw the values given in Table IX.4 were obtained.

The results of the regression are presented in Table IX.5 and in Figure IX.18. The following methods to estimate the Pitzer parameters are discussed:

I. the determination of the whole set of parameters log10 K°, X1, X2, X3;

II. the determination of log10 K°, X1, X2, i.e., neglecting the contribution of all ternary interactions;

III. the determination of log10 K°, X1, X3, i.e., assuming β(1) = 0 for all reaction participants as suggested in [83MIL2];

IV. the determination of log10 K°, X1, i.e., using the smallest possible number of parameters in the Pitzer model.
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Figure IX.18: The parametrization of the SIT and different variants of the Pitzer models (see text for details) for the reaction $\text{H}_2\text{O}(l) \rightleftharpoons \text{H}^+ + \text{OH}^-$ in KCl medium at 298.15 K and 1 atm.

The symbol (0) in Table IX.5 means that this parameter was set equal to zero in the data fitting. All uncertainties are given as ±3σ, where σ is the mean square error of an unknown [65SHC]. “True” values of the parameters $X_1$ - $X_3$ were calculated from tabulated values of $\beta^{(0)}$, $\beta^{(1)}$, and $C$ for KOH and HCl, as well from φ and ψ for binary and ternary ions interactions, between $\text{H}^+$, $\text{K}^+$ and $\text{OH}^-$, $\text{Cl}^-$; $\text{H}^+$, $\text{K}^+$, $\text{Cl}^-$, and $\text{OH}^-$; $\text{Cl}^-$, $\text{K}^+$ respectively [91PIT]. In accordance with Eq. (IX.31)

$$
X_1 = \Delta \beta^{(0)} + \Delta \phi \\
= \beta^{(0)}_{\text{H,Cl}} + \beta^{(0)}_{\text{K,OH}} + \theta_{\text{H,K}} + \theta_{\text{Cl,OH}} \\
= 0.1775 + 0.1298 + 0.005 - 0.050 \\
= 0.262,
$$

$$
X_2 = \Delta \beta^{(1)} \\
= \beta^{(1)}_{\text{H,Cl}} + \beta^{(1)}_{\text{K,OH}} \\
= 0.295 + 0.320 \\
= 0.615,
$$

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Comparison of the SIT and Pitzer models

Table IX.5: Regression results of data in Table IX.4 following procedures described in the text. The data in italics have been obtained by omitting three experimental determinations that may be in error.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>SIT</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>Accepted values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\log_{10} K^\circ$</td>
<td>14.02 ± 0.06</td>
<td>13.96 ± 0.15</td>
<td>13.97 ± 0.11</td>
<td>14.05 ± 0.10</td>
<td>14.12 ± 0.10</td>
<td>14.001 ± 0.014</td>
</tr>
<tr>
<td>$X_1^\ast$</td>
<td>0.155 ± 0.027</td>
<td>0.16 ± 0.33</td>
<td>0.21 ± 0.06</td>
<td>0.41 ± 0.12</td>
<td>0.292 ± 0.045</td>
<td>0.262</td>
</tr>
<tr>
<td>$X_2$</td>
<td>1.22 ± 1.56</td>
<td>0.73 ± 0.55</td>
<td>1.00 ± 0.68</td>
<td>(0)</td>
<td>(0)</td>
<td>0.615</td>
</tr>
<tr>
<td>$X_3$</td>
<td>0.01 ± 0.27</td>
<td>(0)</td>
<td>$-0.03 ± 0.03$</td>
<td>(0)</td>
<td>$-0.03 ± 0.01$</td>
<td>-0.005</td>
</tr>
</tbody>
</table>

* in the case of the SIT model $X_1 = \Delta \varepsilon$.

$$X_3 = \Delta C + \frac{1}{2}\Delta \psi$$

$$= C_{H,Cl} + C_{K,Cl} + \frac{1}{2}\psi_{H,K,Cl} + \frac{1}{2}\psi_{K,Cl,OH}$$

$$= \frac{1}{2} C_{H,Cl} + \frac{1}{2} C_{K,Cl,OH} + \frac{1}{2} \psi_{H,K,Cl} + \frac{1}{2} \psi_{K,Cl,OH}$$

$$= 0.5 \times 0.0008 + 0.5 \times 0.0041 - 0.5 \times 0.007 - 0.5 \times 0.008$$

$$= -0.0050.$$

The "correct" value of $\log_{10} K^\circ$ was assumed to be that recommended by CODATA [89COX/WAG].

In addition, we tested the possibility of determining the values of the Pitzer parameters for the data set, using the CODATA value of $\log_{10} K^\circ$ as a fixed parameter, and obtained $X_1 = 0.22 \pm 0.25$, $X_2 = 0.85 \pm 0.85$, and $X_3 = 0.001 \pm 0.039$. The parameter $X_3$ is very uncertain and we therefore also tested a refinement involving only $X_1$ and $X_2$ and obtained $0.216 \pm 0.051$ and $0.86 \pm 0.33$, respectively. The second model is in fair
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agreement with the “accepted” values. By using Eq. (IX.34) in p.383 and the average value $X_2/\Delta(Z^2) = 0.337 \pm 0.014$ from Table IX.9, p.384, we obtain $X_2 = 0.74 \pm 0.03$ in good agreement with the “accepted” value 0.62.

We also determined the value of $\log_{10} K^\circ$ from the experimental values of $\log_{10} K$ using the “accepted” values of the Pitzer coefficients. Of 13 experimental values, 10 lie in the interval $-14.00 \pm 0.03$, and only two values (at 1.03 mol·kg$^{-1}$) show a large systematic error, with values of $\log_{10} K^\circ$ equal to $-14.17$ and $-14.14$, respectively. This indicates that the real accuracy of most of these data is within $\pm 0.03 \log_{10}$ units. However, two experimental determinations should be classified as discrepant. When these values are excluded from the data set, one obtains a significant reduction in the uncertainty of the estimated parameters, and much better agreement with the “accepted” values (including the CODATA value for $\log_{10} K^\circ$); these data are shown in italics. A problem facing the evaluators of published thermodynamic data is the lack of all needed experimental details and often primary experimental data (e.g., emf, solubility or absorption data) in the original publication. This makes it very difficult to detect data that are flawed. The consequences are obvious from Example 6!

The reduced versions of the Pitzer equation (variants II-IV) are much less sensitive for erroneous data, presumably due to the smaller number of fitting parameters. However, there is a noticeable increase in the estimated uncertainty. This example indicates that the uncertainty in Pitzer parameters determined from equilibrium constants are likely to be fairly large (of the same magnitude as the $X_i$) even in cases where $\log_{10} K^\circ$ is assumed to be known; the determination is also strongly affected by even a small number of erroneous experimental data.

Example 7:

This example refers to the determination of $\log_{10} K^\circ$ and the Pitzer or the SIT parameters from the experimental values of $\log_{10} K$ for the first protonation constant of the sulphate ion $\text{H}^+ + \text{SO}_4^{2-} \rightleftharpoons \text{HSO}_4^-$ studied in NaClO$_4$ medium. Only the results obtained from a potentiometric method have been used. The experimental data, quoted from “Stability Constants” compilations [64SIL/MAR, 71SIL/MAR, 82HOG] and from more recent work [77SAP/PAT] recalculated into molality units and to 298.15 K where necessary, are given in Table IX.6.

For this reaction one has to take into account the ionic strength dependence of the electrostatic unsymmetrical mixing term $E_{\text{ClO}_4,\text{SO}_4}(I_m)$. This was made as recommended in [91PIT], Appendix B. The results of the regression are given in Table IX.7 and in Figure IX.19. The same models for the estimation of the Pitzer parameters as in Example 6 are discussed:

I. with determinations of the whole set of parameters $\log_{10} K^\circ$, $X_1$, $X_2$, $X_3$; and simplified variants:

II. with determinations $\log_{10} K^\circ$, $X_1$, $X_2$;
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Table IX.6: Equilibrium constants for reaction $H^+ + SO_4^{2-} \rightleftharpoons HSO_4^-$ in NaClO$_4$ solutions.

<table>
<thead>
<tr>
<th>$m$ NaClO$_4$</th>
<th>$\log_{10} K(m)$</th>
<th>$m$ NaClO$_4$</th>
<th>$\log_{10} K(m)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.50</td>
<td>0.82 ± 0.20</td>
<td>1.05</td>
<td>1.00 ± 0.15</td>
</tr>
<tr>
<td>3.06</td>
<td>1.08 ± 0.10</td>
<td>1.05</td>
<td>1.10 ± 0.10</td>
</tr>
<tr>
<td>2.21</td>
<td>1.04 ± 0.10</td>
<td>1.05</td>
<td>1.20 ± 0.10</td>
</tr>
<tr>
<td>2.21</td>
<td>0.95 ± 0.10</td>
<td>1.05</td>
<td>1.14 ± 0.10</td>
</tr>
<tr>
<td>2.21</td>
<td>1.01 ± 0.10</td>
<td>0.78</td>
<td>1.23 ± 0.10</td>
</tr>
<tr>
<td>2.08</td>
<td>1.12 ± 0.10</td>
<td>0.51</td>
<td>1.25 ± 0.10</td>
</tr>
<tr>
<td>1.65</td>
<td>1.10 ± 0.10</td>
<td>0.51</td>
<td>1.30 ± 0.10</td>
</tr>
<tr>
<td>1.62</td>
<td>1.18 ± 0.10</td>
<td>0.25</td>
<td>1.43 ± 0.10</td>
</tr>
<tr>
<td>1.05</td>
<td>1.13 ± 0.10</td>
<td>0.10</td>
<td>1.59 ± 0.10</td>
</tr>
</tbody>
</table>

Figure IX.19: The parametrization of the SIT and different variants of the Pitzer models (see text for details) for the reaction $H^+ + SO_4^{2-} \rightleftharpoons HSO_4^-$ in NaClO$_4$ medium at 298.15 K and 1 atm.
Table IX.7: Regression results for data in Table IX.6 following the procedure indicated in the text.

<table>
<thead>
<tr>
<th>The SIT model</th>
<th>The Pitzer model, the values of parameters in variants I-IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameter</td>
<td>I</td>
</tr>
<tr>
<td>log_{10} K^o</td>
<td>1.987</td>
</tr>
<tr>
<td>Δx = (0.003</td>
<td>−0.45</td>
</tr>
<tr>
<td>kg · mol⁻¹</td>
<td>0.051</td>
</tr>
<tr>
<td>X</td>
<td>0.05</td>
</tr>
<tr>
<td>X</td>
<td>0.05</td>
</tr>
</tbody>
</table>

III. log_{10} K^o, X_1, X_3;

IV. log_{10} K^o, X_1.

All uncertainties are given as 3σ. “Accepted” values of the parameters were calculated only from the values of β^{[0]}, β^{[1]}, C for NaHSO₄, Na₂SO₄, and HClO₄ [91PIT]. The parameters for binary and ternary interactions of ClO₇⁻ with HSO₄ and SO₄^{2⁻} are unknown, but the possible effect of neglecting them is probably within the proposed uncertainties of the “accepted” values. The “accepted” value of log_{10} K^o was chosen to be the CODATA [89COX/WAG] recommendation.

The two examples discussed refer to very simple acid-base equilibria, which can be studied without major experimental difficulties. In addition, a large number of experimental determinations have been reported for each of these reactions, 13 for the first and 18 for the second. In both cases the experimental determinations have also been carried out at relatively low ionic strength, 0.10 mol · kg⁻¹, that facilitates the regression analysis.

The examples considered allow us to conclude that the simple one-parameter SIT model reproduces the experimental data very well. It also results in a reliable determination of log_{10} K^o with small uncertainties in the parameters evaluated (for both reactions the values of log_{10} K^o are in excellent agreement with the CODATA recommendations).
Comparison of the SIT and Pitzer models

The problems encountered when using the Pitzer model are clearly demonstrated in both examples. All refinement models allow a precise data interpolation; however, the estimates of $\log_{10} K^o$ and the values of the coefficients $X_i$ differ fairly much. Determination of the complete set of constants results in very large uncertainties (variant I). Of the other models only II which includes $X_1 (\approx \Delta \beta^{(0)})$ and $X_2 (\Delta \beta^{(1)})$ can be recommended, provided that the ionic strength is not too high (the estimation of $X_3 (\approx \Delta C)$ seems only to be possible if reliable values of $\log_{10} K$ are available at ionic strengths above 6-8 $\text{mol} \cdot \text{kg}^{-1}$). The value of $X_2$ estimated using Eq. (IX.34) in p.383 is equal to $X_2 = -1.35 \pm 0.06$ in fair agreement with the “true” value in Table IX.7. The models III (assuming $X_2 = \Delta \beta^{(1)} = 0$) and IV give unreliable estimations of the parameters and should be avoided.

Model IV (with the determination of $\log_{10} K^o$ and $X_1 \approx \Delta \beta^{(0)}$) deserves a more detailed discussion due to its formal similarity to the SIT model. The single-ion activity coefficient for an ion, $i$, in the SIT model is:

$$\ln \gamma_i = \text{DH-term} + \sum_j \varepsilon_{ij} m_j$$

while the corresponding quantity for a metal ion, $M$, using the simplified one-parameter Pitzer equation is:

$$\ln \gamma_M = \text{DH-term} + 2 \sum_a \beta_{Ma}^{(0)} m_a$$

where “DH-term” denotes the Debye-Hückel term. Formally, both expressions are equivalent. However, the two models use quite different forms of the Debye-Hückel terms. The electrostatic contribution to the activity coefficient of an ion in the Pitzer theory is larger than in the SIT model and has a quite different concentration dependence, see Figure IX.20.

It is important to observe that, in the Pitzer theory, the short-range contributions cannot be represented by a linear function of the concentration. To illustrate this point, we have plotted† $Y = \beta^{(0)} + (\beta^{(1)}/\alpha^2 l_m) [1 - (1 + \alpha \sqrt{l_m} - \alpha^2 l_m/2 \exp(-\alpha \sqrt{l_m})$] versus concentration for 1-1 (curve a in Figure IX.21) and 2-1 electrolytes (curve labeled b), using rather typical values of $\beta^{(0)}$ and $\beta^{(1)}$, (0.10 and 0.25) and (0.40 and 1.7), respectively, for 1-1 and 2-1 electrolytes. From these curves it is obvious that the approximation of a constant value of $Y$ results in an erroneous estimation of both $\log_{10} K^o$ and $\beta^{(0)}$.

† $\alpha = 2.0 \text{kg}^{1/2} \cdot \text{mol}^{-1/2}$ for all three electrolytes, cf. p.353.
Figure IX.20: The relative contributions of the Debye-Hückel term to \( \ln \gamma_\pm \) for the SIT and the Pitzer models at 298.15 K and 1 atm.

Figure IX.21: The concentration dependence of function \( Y = \beta^{(0)} + (\beta^{(1)}/\alpha^2 I_m)[1 - (1 + \alpha\sqrt{I_m} - \alpha^2 I_m/2) \exp(-\alpha\sqrt{I_m})] \) for the typical 1-1 (curve labeled as a) and 2-1 electrolytes (curve labeled as b) at 298.15 K and 1 atm.
Comparison of the SIT and Pitzer models

Figure IX.22: The comparison of the quality of the reproduction of experimental data of mean activity coefficients for different electrolytes (solid lines) at 298.15 K using the SIT model (dashed lines) and the Pitzer model containing only the $\beta^{(0)}$ term (dotted lines).

- The obtained values of $\beta^{(0)}$ always differ from the “true” ones. For instance, for NaCl the obtained value of $\beta^{(0)}$ is equal to 0.110 as compared with 0.0765 from [91PIT]; for MgCl$_2$ the value $\beta^{(0)} = 0.557$ as compared with “true” value 0.352; for NdCl$_3$ $\beta^{(0)} = 1.247$ as compared with 0.586. The noticeable increase in the value of $\beta^{(0)}$ obtained in this way is an inevitable consequence of neglecting the contribution of the $\beta^{(1)}$ term. The higher the valence type of the electrolyte, the larger the error introduced in the $\beta^{(0)}$ value;

- The accuracy of data reproduction is much poorer when using the one-parameter Pitzer model than in the one-parameter SIT model. We may compare the mean and maximum errors (defined as $(1 - \gamma_{\text{calc}}/\gamma_{\text{exp}})$) using both approaches: for NaCl they are 3.3 and 5.3%, in the reduced Pitzer model, and 1.4 and 2.7% in the SIT model; for MgCl$_2$ the corresponding numbers are 9.3 and 15% in the reduced Pitzer model and 0.6 and 1.3% in the SIT; for NdCl$_3$ 17 and 32% in the reduced Pitzer model, and 4.4 and 8% in the SIT model.

This comparison of the mean activity coefficient data (which are supposed to be very precise) by means of the one-parameter Pitzer and SIT models clearly demonstrates the problems of reducing the number of parameters in the Pitzer approach: neglect of the contribution of the $\beta^{(1)}$ term in the Pitzer model results in a significant loss of accuracy.
in the data reproduction (as compared with the SIT model) and a wrong estimate of the 
\( \beta^{(0)} \) term. Hence, the Pitzer equation in general has to be used with both the \( \beta^{(0)} \) and 
\( \beta^{(1)} \) terms. Returning to the concentration dependence of complex formation reactions, 
we emphasise that in order to determine both \( X_1 \) and \( X_2 \), it is necessary to have precise 
data on \( \log_{10} K \) at rather low ionic strengths, less than \( 0.5 \text{ mol} \cdot \text{kg}^{-1} \), where the relative 
contribution of \( \beta^{(1)} \) is largest. The difficulty to determine \( \beta^{(1)} \) is most pronounced for 
reactions where the ions have a charge \( \pm 1 \), for which the uncertainty in \( \log_{10} K \) must 
be far less than \( \pm 0.05 \) in order to determine both parameters. The determination of the 
Pitzer parameters for complexes is an important, but far from simple task. In systems with 
few experimental data, one is forced to use approximations when determining \( \log_{10} K^0 \) 
and the Pitzer parameters. We recommend the correlation methods described below in 
Sections IX.8 and IX.8.1, which are to be preferred to simplistic “procedures” such as: “If 
the data are restricted, just limit the number of parameters used in the Pitzer model”.

**IX.8. The relationship between the SIT \( \varepsilon(i,j) \) and the Pitzer \( \beta_{ij}^{(0)} \) and \( \beta_{ij}^{(1)} \) 
parameters for mean-activity coefficients**

The previous sections indicate some difficulties that may be encountered when using the 
Pitzer model for the description of the concentration dependence of equilibrium constants 
in electrolyte systems of high ionic strength. The problem is the lack of experimental 
Pitzer parameters for complexes, while they are often available for the reactants if 
these are metal ions and simple ionic ligands. This means that the activity coefficients 
of these species can be calculated even in rather complicated systems, like mixtures of 
strong electrolytes. A modeller might then wish to combine known information for the 
strong electrolyte mixture with experimental information on equilibrium constants for 
trace components using the Pitzer formalism. In order to do this it will be necessary to 
make approximations, and some of these will be discussed in the following two sections.

An analysis of the values of \( \beta^{(1)} \) at 298.15 K from the available compilation [91PIT] 
shows that there is a correlation between the values of \( \beta^{(1)} \) and the charge type of the 
electrolyte: for most 1-1 electrolytes the values of the \( \beta^{(1)} \) parameter fall in a range 
0.20 \( \pm \) 0.20; for most 2-1 electrolytes in the range 1.4 \( \pm \) 0.6 and for most 3-1 electrolytes 
in the range 5.2 \( \pm \) 1.2. These averages may then be used as “fixed” values of \( \beta^{(1)} \) in the 
Pitzer equations, thus reducing the number of unknown parameters. A better estimate of 
\( \beta^{(1)} \) is obtained by using the following simple relationship between the Pitzer parameters 
\( \beta^{(0)} \) and \( \beta^{(1)} \) and the \( \varepsilon_\alpha \) parameters, which is valid when the term with \( C_{MX}^0 \) may be 
neglected. The Pitzer equation for the mean-activity coefficient is then equal to:

\[
\ln \gamma_A = -Z_M Z_X |A_\Phi| \frac{\sqrt{I_m}}{1 + b \sqrt{I_m}} + \frac{2}{b} \ln \left( 1 + b \sqrt{I_m} \right) + m \frac{2 \nu M X}{\nu} \left( 2 \beta^{(0)} + 2 \beta^{(1)} X \right)
\]

where

\[
X = \frac{1}{\alpha^2 I_m} \left[ 1 - \left( 1 + \alpha \sqrt{I_m} - \frac{1}{2} \alpha^2 I_m \right) e^{-\alpha \sqrt{I_m}} \right]
\]
Table IX.8: Quantitative relationship between the Pitzer parameters $\beta^{(0)}$ and $\beta^{(1)}$ and the SIT $\varepsilon_\gamma$ parameters for different ion combinations at 298.15 K.

<table>
<thead>
<tr>
<th>Ion combination</th>
<th>$(\beta^{(0)} - \varepsilon_\gamma/2)$</th>
<th>$\beta^{(1)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{M}^+, \text{X}^-$</td>
<td>0.035</td>
<td>0.34 $\approx$ 0.3</td>
</tr>
<tr>
<td>$\text{M}^{2+}, \text{X}^-$ and $\text{M}^+, \text{X}^{2-}$</td>
<td>0.150</td>
<td>1.56 $\approx$ 1.6</td>
</tr>
<tr>
<td>$\text{M}^{3+}, \text{X}^-$ and $\text{M}^+, \text{X}^{-3}$</td>
<td>0.366</td>
<td>4.29 $\approx$ 4.3</td>
</tr>
<tr>
<td>$\text{M}^{4+}, \text{X}^-$ and $\text{M}^+, \text{X}^{4-}$</td>
<td>0.754</td>
<td>8.89 $\approx$ 8.9</td>
</tr>
</tbody>
</table>

From the SIT model we have (taking into account that $A_\gamma = 3A_\phi$)

$$
\ln \gamma_\pm = -\frac{3A_\phi |Z_M Z_X| \sqrt{T_m}}{1 + 1.5 \sqrt{T_m}} + \frac{2 \nu_{MX}}{\nu} \varepsilon_\gamma m
$$

After elementary transformations we obtain

$$
Y = -\frac{A_\phi |Z_M Z_X| \nu}{4 \nu_{MX} m} \left[ \frac{3\sqrt{T_m}}{1 + 1.5 \sqrt{T_m}} - \frac{\sqrt{T_m}}{1 + b \sqrt{T_m}} - \frac{2}{b} \ln \left( 1 + b \sqrt{T_m} \right) \right]
$$

$$
= \left( \beta^{(0)} - \frac{\varepsilon_\gamma}{2} \right) + \beta^{(1)} X
$$

(IX.33)

The values of $X$ and $Y$ can be easily calculated, and $Y$ should be a linear function of $X$ with the intercept $(\beta^{(0)} - \varepsilon_\gamma/2)$ and the slope $\beta^{(1)}$. The quality of linearity is the criterion of the compatibility of the Pitzer and the SIT models. Figures IX.23, IX.24 and IX.25 show plots of $Y$ vs. $X$ for different $M^{2+}$ and $X^{2-}$ combinations. The linearity is good, showing that the SIT model is approximately equivalent to a simplified Pitzer model (without the $C_\phi^{MX}$ term) and results in a constant value of the $\beta^{(1)}$ parameter for each charge type. Table IX.8 summarises the relationships between the two sets of parameters.

Note: Usually the values of $\varepsilon(i, j)$, not $\varepsilon_\gamma(i, j)$ are tabulated, and the relationship between them is: $\varepsilon(i, j) = \varepsilon_\gamma(i, j)/\ln(10)$.

The values of the parameter $\beta^{(1)}$ are in reasonable good agreement with the values tabulated for individual electrolytes (see above). Using these values one obtains approximately the same accuracy of the reproduction of $\gamma_\pm$ values with both models. This approximation allows a good estimate of the $\beta^{(1)}$ parameter for different ion combinations. For a more detailed discussion of the concentration dependence of the second virial coefficient for solutes, see the discussions in [73PIT, 91PIT]. In principle, the same procedure may be used to estimate the temperature dependence of the $\beta^{(1)}$ parameter, because the temperature
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Figure IX.23: The determination of quantitative relationship between the parameter $\varepsilon_{\gamma}$ in the SIT model and the parameters $\beta^{(0)}$ and $\beta^{(1)}$ in the Pitzer model for the case of 1-1 completely dissociated electrolytes at 298.15 K and 1 atm. $X$ and $Y$ are defined in the text. The circles denote data which have been calculated from Eq. (IX.33).

Figure IX.24: The determination of quantitative relationship between the parameter $\varepsilon_{\gamma}$ in the SIT model and the parameters $\beta^{(0)}$ and $\beta^{(1)}$ in the Pitzer model for the case of 2-1 or 1-2 completely dissociated electrolytes at 298.15 K and 1 atm. $X$ and $Y$ are defined in the text.
Relationship of parameters in the SIT and Pitzer models

Figure IX.25: The determination of quantitative relationship between the parameter $\varepsilon_\gamma$ in the SIT model and the parameters $\beta^{(0)}$ and $\beta^{(1)}$ in the Pitzer model for the case of 3-1 or 1-3 completely dissociated electrolytes at 298.15 K and 1 atm. $X$ and $Y$ are defined in the text.

dependence of $A_\delta$ is well known [90ARC/WAN], provided the value of numerical factor 1.5 used in the SIT model is temperature independent. In Figure IX.26 we have plotted the calculated values of $\beta^{(1)}$ for 1-1 and 2-1 electrolytes versus temperature, at saturated water vapor pressure (solid lines) and compared them with “experimental” values for NaCl, NaBr, and MgCl$_2$ from available compilations. The semiquantitative agreement is obvious.

The previous relationships between the SIT and the Pitzer parameters may be used to convert the $\varepsilon(i,j)$ values for the SIT model into $\beta_{ij}^{(0)}$ and $\beta_{ij}^{(1)}$ values of the Pitzer approach, and vice versa. A similar relationship may also be obtained between $\Delta \varepsilon$ and $\Delta \beta^{(0)}$ and $\Delta \beta^{(1)}$ for reactions. It is more convenient to estimate the Pitzer parameters $X_1$ and $X_2$ directly from the experimental values of $\Delta \varepsilon$ than to use estimates of all the individual $\beta_{ij}^{(0)}$ and $\beta_{ij}^{(1)}$ values for the reactants/products.

Example 8:

Let us consider the estimation of the Pitzer parameters for the interaction Fe$^{3+}$-ClO$_4^-$.

In [92GRE/FUG] the value of the SIT interaction coefficient $\varepsilon(\text{Fe}^{3+}, \text{ClO}_4^-) = (0.56 \pm 0.03) \, \text{kg} \cdot \text{mol}^{-1}$ is given, as estimated from the available information by Biedermann [75BIE]. Using the correlation proposed above one may estimate the Pitzer parameters Fe$^{3+}$-ClO$_4^-$ as follows: $\beta^{(0)} = \varepsilon_\gamma/2 + 0.366 = (0.56 \pm 0.03) \times \ln(10)/2 + 0.366 = (1.01 \pm 0.01) \, \text{mol} \cdot \text{kg}^{-1}$.
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Figure IX.26: The comparison of “predicted” (see text for details) and “experimental”
values of the $\beta^{(1)}$ parameter as a function of temperature at saturated water vapor
pressure.

$0.04 \text{ kg} \cdot \text{mol}^{-1}; \beta^{(1)} = 4.3 \text{ kg} \cdot \text{mol}^{-1}.$

Example 9:

Let us consider the estimation of the Pitzer parameters for the interaction Bi$^{3+}$-ClO$_4^-$.
Only a few sets of measurements are available in literature. For the reaction BiOCl(cr) + 2H$^+$ ⇌ Bi$^{3+}$ + Cl$^-$ + H$_2$O(l) the values of $\log_{10} K$ have been obtai-
ned by Ahrland and Grethe [57AHR/GRE] from solubility and potentiometric mea-
surements in mixture 1 M HClO$_4$ + 1 M NaClO$_4$ and by Vasil'ev and Grechikhina
[67VAS/GRE] from solubility measurements in HClO$_4$ solutions of concentrations 0.5-
2.0 M. Using the SIT model to treat these data one obtains the following estimations
of the SIT interaction coefficient $\varepsilon(Bi^{3+}, ClO_4^-) = (0.47 \pm 0.12) \text{ kg} \cdot \text{mol}^{-1}$. For the reaction BiOBr(cr) + 2H$^+$ ⇌ Bi$^{3+}$ + Br$^-$ + H$_2$O(l) the values of $\log_{10} K$ have been reported
by Ahrland and Grethe [57AHR/GRE] and by Fedorov et al. [71FED/KAL] from the
solubility of BiOBr(cr) in HClO$_4$-LiClO$_4$ mixtures of different constant ionic strengths be-
tween 0.5 and 4 M. The SIT results in the value of $\varepsilon(Bi^{3+}, ClO_4^-) = (0.59 \pm 0.07) \text{ kg} \cdot \text{mol}^{-1}$. Vasil'ev and Grechikhina [67VAS/GRE2] have measured the solubility of BiONO$_3$(cr) in
HClO$_4$ solutions of concentrations between 0.30 and 1.35 M and obtained the values
of solubility product of the solid phase after a correction for the formation of nitrate
complexes of Bi(III). From these data the value of $\varepsilon(Bi^{3+}, ClO_4^-)$ was estimated to be
0.59 ± 0.07. These examples illustrate typical uncertainties in the estimation of interaction coefficients from a small number of data from different laboratories. The mean value $\varepsilon(\text{Bi}^{3+}, \text{ClO}_4^-) = (0.54 \pm 0.07) \text{ kg} \cdot \text{mol}^{-1}$, is in reasonable agreement with the corresponding quantities for the lanthanoids, which have the charge 3 and very similar ionic radii. Using the correlation proposed above we obtain for the $\text{Bi}^{3+}-\text{ClO}_4^-$ interaction the following preliminary values of the Pitzer parameters: $\beta^{(0)} = (0.99 \pm 0.08) \text{ kg} \cdot \text{mol}^{-1}$; $\beta^{(1)} = 4.3 \text{ kg} \cdot \text{mol}^{-1}$.

**IX.8.1. The relationship between the $\Delta \varepsilon$ values in the SIT model and the $\Delta \beta^{(0)}$ and $\Delta \beta^{(1)}$ values in the Pitzer models for complex formation reactions at “trace” concentrations of reactants/products**

By neglecting the contribution of all the ternary interactions, and excluding higher order electrostatic unsymmetrical mixing terms in the Pitzer equation we can write the following statement for the ionic medium dependence of $\ln K$:

$$
\ln K^0 = \ln K - \Delta(Z^2) A_\Phi \left[ \frac{\sqrt{T_m}}{1 + b\sqrt{T_m}} + \frac{2}{b} \ln \left( 1 + b\sqrt{T_m} \right) \right] + \Delta(Z^2) m^2 B'_{NM} + 2m X_1 + 2m g(I_m) X_2
$$

See Eq. (IX.31) for explanations. The consequences of excluding the higher order electrostatic unsymmetrical mixing terms will be discussed later. The corresponding analytical statement for the concentration dependence of $\ln K$ using the SIT formalism is:

$$
\ln K^0 = \ln K - \Delta(Z^2) \frac{3A_\Phi \sqrt{T_m}}{1 + 1.5\sqrt{T_m}} + m \Delta \varepsilon
$$

See Eq. (IX.32) for the explanation of abbreviations. Note again that $A_\gamma = 3A_\Phi$ and $\Delta \varepsilon = \Delta \varepsilon_\gamma/\ln(10)$. After elementary transformations we obtain:

$$
Y = \left\{ A_\Phi \left[ \frac{\sqrt{T_m}}{1 + b\sqrt{T_m}} + \frac{2}{b} \ln \left( 1 + b\sqrt{T_m} \right) \right] - \frac{3\sqrt{T_m}}{1 + 1.5\sqrt{T_m}} \right\}/2m
$$

$$
= \frac{1}{\Delta(Z^2)} \left( X_1 - \frac{\Delta \varepsilon_\gamma}{2} \right) + \frac{X_2}{\Delta(Z^2)} g(I_m)
$$

(IX.34)

i.e., $Y$ is a linear function of $g(I_m)$, where the slope is $X_2/\Delta(Z^2)$ and the intercept $(X_1 - \Delta \varepsilon_\gamma/2)/\Delta(Z^2)$. In order to calculate the values of $Y$ one has to know the Debye-Hückel parameter $A_\Phi$ and $B'_{NM}$, i.e., $\beta^{(1)}$ for the 1-1 ionic medium electrolyte, these data are available. The values of $g(I_m)$ are obtained from the ionic strength of the solution. The quality of the linearity will be a criterion of the compatibility of the SIT model and the simplified Pitzer equation. In Figure IX.27 we have plotted the values of $Y$ calculated for reactions in some common 1-1 ionic media. The linearity is good for
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Figure IX.27: The determination of relationship between the SIT parameter $\Delta \varphi$ and the Pitzer parameters $\Delta \beta^{(0)}$ and $\Delta \beta^{(1)}$ for reactions studied in solutions of different 1-1 ionic medium electrolytes at 298.15 K and 1 atm (see text for details). The symbols are calculated values of $Y$ versus $g(I_m)$ using Eq. (IX.34) for the different ionic media.

Table IX.9: Relation between the Pitzer and the SIT parameters for the complex formation reaction studied in different 1-1 supporting electrolytes at 298.15 K.

<table>
<thead>
<tr>
<th>1-1 electrolyte</th>
<th>$(X_1 - \Delta \varphi/2)/\Delta(Z^2)$</th>
<th>$X_2/\Delta(Z^2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaClO$_4$</td>
<td>0.031</td>
<td>0.340</td>
</tr>
<tr>
<td>LiClO$_4$</td>
<td>0.038</td>
<td>0.348</td>
</tr>
<tr>
<td>HClO$_4$</td>
<td>0.032</td>
<td>0.342</td>
</tr>
<tr>
<td>NaNO$_3$</td>
<td>0.026</td>
<td>0.334</td>
</tr>
<tr>
<td>KNO$_3$</td>
<td>0.019</td>
<td>0.327</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.030</td>
<td>0.332</td>
</tr>
<tr>
<td>All data</td>
<td>0.029 ± 0.005</td>
<td>0.337 ± 0.014</td>
</tr>
</tbody>
</table>
all electrolytes considered. The optimal values of the parameters \((X_1 - \Delta \varepsilon_\gamma / 2) / \Delta (Z^2)\) and \(X_2 / \Delta (Z^2)\) can be determined for each electrolyte (see Table IX.9). However, the parameters, especially the slope of the line, which is related to \(X_2 / \Delta Z^2\) or \(\Delta \beta^{(1)}\) for the reaction (see Table IX.9) do not vary much with the nature of electrolyte. Hence we can use all the data to determine one unique set of parameters, (see the last line of Table IX.9 where the uncertainties are given as 3\(\sigma\)). Because of the difficulty of making an accurate determination of \(\Delta \beta^{(1)}\) using regression analysis of \(\log_{10} K\) data, cf. Examples 6 and 7, we suggest that an alternative is to use the proposed correlation to estimate \(\Delta \beta^{(1)}\) (and \(\beta^{(1)}\) for complex species if these values for single ions are available already). For instance, for the Example 6 one estimates the value of \(X_2 = (0.337 \pm 0.14) \times \Delta (Z^2) = (0.337 \pm 0.014) \times 2 = 0.67 \pm 0.03\), which is rather close to the “true” \(X_2 = 0.62\) (the most reliable estimation using regression of the data set without erroneous points gives \(0.90 \pm 0.24\); see Table IX.5 in Example 6). For the Example 7 the estimated value using the proposed correlation is \(X_2 = (0.337 \pm 0.014) \times \Delta (Z^2) = (0.337 \pm 0.014) \times (-4) = -1.35 \pm 0.06\). This result is only in fair agreement with the “true” \(X_2 = -1.00\). However, the value from the regression has very large uncertainties, \(X_2 = -1.39 \pm 1.34\) from Table IX.7 in Example 7.

The analysis must be modified for the case of reactions where \(\Delta (Z^2) = 0\). It is possible to show that in this case the following relationship is valid at any molality:

\[
\left( X_1 - \frac{\Delta \varepsilon_\gamma}{2} \right) + X_2 g(I_m) = 0
\]

Because the first term is constant, and \(g(I_m)\) is a monotone function of the ionic strength, this equality is only possible if \((X_1 - \Delta \varepsilon_\gamma / 2)\) and \(X_2\) both are equal to zero.

The relationship discussed was obtained by neglecting the contribution of the terms for higher order electrostatic unsymmetrical mixing. By including these terms the slope of the function \(Y\) is changed somewhat, particularly for ions of charge 3, or higher. However, for this type of reactions the problem to determine the contributions of the \(\beta^{(0)}\) and \(\beta^{(1)}\) terms is not severe, because of the large absolute values of \(\beta^{(1)}\) for interactions involving ions of high charges. We therefore suggest that the correlation between \(\Delta (Z^2)\) and \(\Delta \beta^{(1)}\) should only be used for reactions involving ions with absolute charges \(\pm 1\) and \(\pm 2\).

Summing up the discussion about the determination of the Pitzer parameters for a reaction from \(\log_{10} K\) data, we conclude that this, as a rule, is an ill-conditioned problem. To obtain reasonable estimates of the parameters in the Pitzer model from few experimental data of limited accuracy, one has to use some simplifications. From our experience, the existing \(\log_{10} K\) data rarely permit the determination of more than one interaction parameter. Therefore, we suggest the following strategy when using the \(\log_{10} K\) data in solutions of an 1:1 ionic medium:

- Step 1, use the SIT equation to obtain \(\log_{10} K^0\) and \(\Delta \varepsilon\).
- Step 2, if the reaction involves ions with charges 1 and 2, then use the \(\Delta (Z^2)\) value for the reaction to estimate the values of \(X_1\) and \(X_2\) for the reaction. This estimate
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of \( X_1 \) is preliminary, a more accurate value is then determined in a new regression using \( \log_{10} K^0 \) from step 1 and \( X_2 \) determined from \( \Delta \varepsilon \) as fixed parameters. For reactions involving ions with charges 3 and higher it is sufficient to use only \( \log_{10} K^0 \) from step 1 as a fixed parameter and then determine \( X_1 \) and \( X_2 \) in the regression.

If the values of the Pitzer parameters for single ion reactants/products are known, one can proceed to determine the corresponding coefficients for the complexes in the following way:

- Use the SIT equation to obtain \( \log_{10} K^0 \) for the reaction.
- Use the Pitzer interaction coefficients for single ions, the known values of binary and ternary mixing terms for interactions involving single ion reactants/products and the ions of the ionic medium, and \( \log_{10} K^0 \) value as fixed parameters in the regression analysis to obtain \( \beta^{(0)} \) and \( \beta^{(1)} \) for the complexes. If the charge of the complexes does not exceed 2, estimate \( X_2 \) from the \( \Delta(Z^2) \) value for the reaction, followed by the calculation of \( \beta^{(1)} \) for the complex species. Then use the regression analysis to obtain \( \beta^{(0)} \) for the complex using \( \log_{10} K^0 \) and \( X_2 \) as fixed parameters.

All terms, including \( m^2 \Delta[Z]C_{NX} \) (see Eq. (IX.31)) and higher order electrostatic unsymmetrical mixing terms, should be taken into account in the regression procedure.

Example 10:

The reaction \( \text{Cd}^{2+} + \text{NO}_3^- \rightleftharpoons \text{CdNO}_2^+ \) has been studied in NaClO\(_4\) ionic media. The experimental results, quoted from “Stability Constants” [64SIL/MAR, 71SIL/MAR, 82HOG], recalculated into molality units, are given in Table IX.10. The total number of experimental points is only 7, their real accuracy can be estimated to be ±0.1 \( \log_{10} \) units based on comparison of the values from 5 different laboratories, using different experimental methods (potentiometry, spectrophotometry, polarography). The experimentally covered range of ionic medium concentrations is 1.0-3.5 mol·kg\(^{-1}\).

Using the SIT model one obtains the following results: \( \log_{10} K^0 = 2.43 \pm 0.33, \Delta \varepsilon = -0.13 \pm 0.13 \text{ kg} \cdot \text{mol}^{-1} \). All errors are here given as 3\( \sigma \).

The Pitzer parameters for the ion combinations \( \text{Cd}^{2+}-\text{ClO}_4^- \) and \( \text{Na}^+-\text{NO}_3^- \) were taken from the literature: \( \beta^{(0)}_{\text{Cd,ClO}_4} = 0.3899, \beta^{(1)}_{\text{Cd,ClO}_4} = 1.996, C^\Phi_{\text{Cd,ClO}_4} = 0.0208 \) [88KIM/FRE], \( \beta^{(0)}_{\text{Na,NO}_2} = 0.0641, \beta^{(1)}_{\text{Na,NO}_2} = 0.1015, C^\Phi = -0.0049 \) [91PIT]. No values of binary and ternary mixing terms for these ion combinations are available, so they were assumed to be zero. The task is to determine the values of the Pitzer parameters for the \( \text{CdNO}_2^+\)-\( \text{ClO}_4^- \) interaction, \( \beta^{(0)}_{\text{CdNO}_2,\text{ClO}_4} \) and \( \beta^{(1)}_{\text{CdNO}_2,\text{ClO}_4} \), and \( \log_{10} K^0 \) using a regression analysis.

First we used the regression in an attempt to determine all the required parameters from the existing \( \log_{10} K \) data set. The results are: \( \log_{10} K^0 = 2.3 \pm 3.0, \beta^{(0)}_{\text{CdNO}_2,\text{ClO}_4} = 0.21 \pm 0.82, \beta^{(1)}_{\text{CdNO}_2,\text{ClO}_4} = -0.2 \pm 13.6 \). All uncertainties are given here as 3\( \sigma \). These very large uncertainties are typical when making a data evaluation using a Pitzer model from

386
Table IX.10: Equilibrium constants for reaction Cd$^{2+}$ + NO$_2^-$ $\rightleftharpoons$ CdNO$_2^+$ in NaClO$_4$ solutions at 298.15 K.

<table>
<thead>
<tr>
<th>m NaClO$_4$ mol/kg$^{-1}$</th>
<th>log$_{10}$ $K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.05</td>
<td>1.68 ± 0.10</td>
</tr>
<tr>
<td>1.05</td>
<td>1.80 ± 0.10</td>
</tr>
<tr>
<td>2.21</td>
<td>1.74 ± 0.10</td>
</tr>
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<td>2.80</td>
<td>1.91 ± 0.10</td>
</tr>
<tr>
<td>2.80</td>
<td>1.74 ± 0.10</td>
</tr>
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<td>3.50</td>
<td>1.99 ± 0.10</td>
</tr>
<tr>
<td>3.50</td>
<td>1.73 ± 0.10</td>
</tr>
</tbody>
</table>

a limited number of experimental points of low accuracy. It is obvious that the data do not allow an accurate determination of the parameters. Therefore, we used the regression with a fixed value of log$_{10}$ $K^o$ as it was obtained in the SIT-type of data treatment, i.e., log$_{10}$ $K^o$ = 2.43 ± 0.33. The resulting Pitzer parameters are: $\beta^{(0)}_{\text{CdNO}_2\text{ClO}_4} = 0.19 \pm 0.23$, $\beta^{(1)}_{\text{CdNO}_2\text{ClO}_4} = 0.2 \pm 1.5$ (3σ). Finally, we used the procedure recommended above. As the reaction under consideration involves only ions with the charges 1 and 2, we can estimate the value of $X_2 = \Delta \beta^{(1)}$ from $\Delta(Z^2) = -4$ and obtain $X_2 = (0.337 \pm 0.014) \times \Delta(Z^2) \approx -1.35$. As the values of $\beta^{(1)}$ for the single ions are available, we can estimate the value of the Pitzer parameter $\beta^{(1)}_{\text{CdNO}_2\text{ClO}_4} = -1.35 + 1.996 + 0.102 \approx 0.75$. This value seems to be rather high for 1-1 ions but it does not contradict the estimate 0.2 ± 1.5, obtained above. Using log$_{10}$ $K^o$ and $\beta^{(1)}_{\text{CdNO}_2\text{ClO}_4} = 0.75$ as fixed parameters, we obtained from the regression $\beta^{(0)}_{\text{CdNO}_2\text{ClO}_4} = 0.11 \pm 0.05$ (3σ). This quantity can also be estimated from the correlation between $\Delta \varepsilon$ and $X_1$ for the reaction, $(X_1 - \Delta \varepsilon /2) / \Delta(Z^2) = (0.029 \pm 0.005)$. We find: $X_1 = (-4) \times [(0.029 \pm 0.005) + \ln(10) \times (-0.13 \pm 0.13)/2] \approx -0.27 \pm 0.15$. For this reaction $X_1 = \beta^{(0)}_{\text{CdNO}_2\text{ClO}_4} - \beta^{(0)}_{\text{CdClO}_4} - \beta^{(0)}_{\text{NaNO}_2}$, hence, the estimated value from the correlation is $\beta^{(0)}_{\text{CdNO}_2\text{ClO}_4} \approx -0.27 \pm 0.15 + 0.39 + 0.06 = 0.18 \pm 0.15$, which is rather close to $\beta^{(0)}_{\text{CdNO}_2\text{ClO}_4} = 0.11 \pm 0.05$. We recommend the use of the regression procedure to get more accurate values of the $\beta^{(0)}$ parameters.

The experimental log$_{10}$ $K$ data and those obtained using the SIT (solid line) and the simplified Pitzer (dashed line) models are shown in Figure IX.28.

Example 11:

The reaction Fe$^{3+}$ + Cl$^-$ $\rightleftharpoons$ FeCl$^{2+}$ has been studied in HClO$_4$/NaClO$_4$ media over a
Estimations of ionic strength corrections of thermodynamic data

Figure IX.28: The comparison of the experimental (circles) and the calculated values of the $\log_{10} K$ obtained using the SIT (solid line) and the simplified Pitzer (dashed line) models for the reaction $\text{Cd}^{2+} + \text{NO}_2^- \rightleftharpoons \text{CdNO}_2^+$ in NaClO$_4$ solutions at 298.15 K and 1 atm (see text for details).

wide concentration range. The experimental results in pure HClO$_4$, quoted from “Stability Constants” [64SIL/MAR, 71SIL/MAR, 82HOG], recalculated to molality units and to 298.15 K where necessary, are given in Table IX.11. The results obtained at ionic strength above 6 M (8.13 mol·kg$^{-1}$) HClO$_4$ have not been included in the Table.

The example considered is exceptional: in all there are 25 experimental $\log_{10} K$ values from 9 independent laboratories, obtained using spectrophotometric, potentiometric or distribution methods. All the data are in good agreement with each other, and the estimated uncertainties of the experimental $\log_{10} K$ points seem to be within $\pm 0.05$-$0.08 \log_{10}$ units. Using the SIT-type of data treatment the following values of the parameters have been obtained by the least-square method: $\log_{10} K^0 = 1.55 \pm 0.10$, $\Delta \varepsilon = -0.241 \pm 0.023 \text{ kg} \cdot \text{mol}^{-1}$ (all errors are given as $3\sigma$). The results of the regression in comparison with the experimental data are shown in Figure IX.29 (solid line).

Accurate values of the Pitzer parameters for the Fe$^{3+}$-ClO$_4^-$ interaction are unknown (only preliminary estimations can be made, see Example 8). Hence, we can only determine the Pitzer parameters for the reaction. First we tried to determine all the relevant parameters ($\log_{10} K^0, X_1, X_2, X_3$) from the regression; the obtained results are: $\log_{10} K^0 = 1.66 \pm 0.38, X_1 = -0.62 \pm 0.27, X_2 = -3.64 \pm 2.36, X_3 = +0.01 \pm 0.10$; the errors are given as $3\sigma$. Although there are a large number of experimental points (25) of good accuracy ($< 0.08 \log_{10}$ unit), the result of the regression is very uncertain. Another point to
be noticed is that despite the large range of HClO₄ concentrations covered in experiments (0.2-8 mol · kg⁻¹), the $X_3$ parameter is statistically insignificant. In a second attempt we tried to determine all parameters, except $X_3$ and obtained $\log_{10} K^\circ = 1.60 \pm 0.27$, $X_1 = -0.56 \pm 0.05$, $X_2 = -4.14 \pm 1.14$. Finally we applied the procedure discussed in the previous examples for the determination of the Pitzer parameters for the reaction using the value of $\log_{10} K^\circ$, obtained from the SIT-type of data treatment as a fixed parameter. The parameters $X_1$ and $X_2$ were then determined by regression. The final set of the Pitzer parameters is: $X_1 = -0.55 \pm 0.04$, $X_2 = -4.34 \pm 0.40$. The result of the simplified Pitzer-type of regression is shown in comparison with experimental data in Figure IX.29 (dashed line). This example shows that the contribution of ternary terms ($X_3$) are relatively small in this case, and can be neglected even at very high ionic medium concentrations.

It is interesting to test the ability of the SIT and the Pitzer model (with the simplifications outlined above) to predict the $\log_{10} K$ for the reaction Fe³⁺ + Cl⁻ ⇌ FeCl²⁺ in different perchlorate media. The concentration quotient ($\log_{10} K$) is a function of the ionic medium composition, as indicated by the experimental data in (Na,H)ClO₄ mixtures as given in [63HEI/CLE]. We have used both the SIT and the Pitzer models, to predict the changes of the equilibrium constant as a function of the composition of the ionic medium. Using the SIT model we obtain the following statement for $\log_{10} K$ of the reaction in a medium of constant total ionic strength and constant total perchlorate-ion concentration,
Estimations of ionic strength corrections of thermodynamic data

Figure IX.29: The comparison of experimental (circles) and calculated values of $\log_{10} K$ for the reaction $\text{Fe}^{3+} + \text{Cl}^{-} \rightleftharpoons \text{FeCl}^{2+}$ in HClO$_4$ medium at 298.15 K and 1 atm (see text for details) using the SIT (solid line) or the simplified Pitzer (dashed line).

but with varying H$^+$ and Na$^+$ concentrations:

$$\log_{10} K_{(\text{HClO}_4)} - \log_{10} K_{([\text{Na},\text{H}]\text{ClO}_4)} = \left[ \varepsilon(\text{H}^+, \text{Cl}^-) - \varepsilon(\text{Na}^+, \text{Cl}^-) \right] m_{\text{Na}^+}$$

This simple relation is consistent with Harned’s rule [58HAR/OWE], which postulates a linear dependence of the logarithm of the activity coefficient of a solute on the molality of the second electrolyte in mixtures of constant total ionic strength. The calculated values of the difference in $\log_{10} K$ when replacing H$^+$ for Na$^+$ at constant ionic strength 6.5 mol·kg$^{-1}$ are shown in Figure IX.30 (the solid line) in comparison with the experimental values (the triangles, with uncertainty estimates) from [63HE1/CLE]. The following SIT interaction coefficients were used: $\varepsilon(\text{H}^+, \text{Cl}^-) = 0.12 \pm 0.01$ kg·mol$^{-1}$, $\varepsilon(\text{Na}^+, \text{Cl}^-) = 0.04 \pm 0.01$ kg·mol$^{-1}$. The quantitative agreement between experimental and predicted data is apparent in Figure IX.30.

On the basis of the Pitzer model the following equation is obtained (neglecting the ternary interaction parameters for the reaction participants):
Figure IX.30: The comparison of the experimental and predicted values of the difference in log$_{10} K$ values for the reaction Fe$^{3+} + Cl^- \rightleftharpoons FeCl^{2+}$ in pure HClO$_4$ and mixed HClO$_4$-NaClO$_4$ media at 298.15 K and 1 atm. Triangles are the experimental results from [63HEI/CLE]; the solid line - the prediction based on the SIT model; the dashed line - the prediction based on the Pitzer model.

\[
\ln K_{[HClO_4]} - \ln K_{[(H,Na)ClO_4]} = \Delta(Z^2)m_{Na}m \left( B_{Na,ClO_4}' - B_{H,ClO_4}' \right) \\
+ \Delta |Z|m_{Na}m \left( C_{Na,ClO_4} - C_{H,ClO_4} \right) \\
- 2m_{Na}m \left[ \beta_{Na,Cl}^{(0)} - \beta_{H,Cl}^{(0)} \right] \left( \beta_{Na,Cl}^{(1)} - \beta_{H,Cl}^{(1)} \right) g(I_m) \\
+ 2m_{Na} \left( \phi_{Fe,H} - \phi_{Fe,Na} - \phi_{Fe,Cl,H} - \phi_{Fe,Cl,Na} \right)
\]

where \( m \) refers to the total molality of the ionic medium (or perchlorate ion concentration), \( m_{Na} \) stands for the molality of Na$^+$ in mixture. The numerical values of binary mixing terms for the interactions Fe$^{3+}$-H$^+$, Fe$^{3+}$-Na$^+$, FeCl$^{2+}$-Na$^+$, FeCl$^{2+}$-H$^+$ are unknown. The numerical values of the other relevant Pitzer parameters were taken from [91PIT]. The calculated differences in log$_{10} K$ from this equation are also shown in Figure IX.30 by a dashed line. The agreement is qualitative, due to lack of all parameters needed in the model. This situation is not unusual, if not all the needed parameters of the Pitzer model are available, then the accuracy of predictions of log$_{10} K$ data using this approach may be no better than those obtained from the simpler SIT model. By fitting the unknown interaction parameters to the data one will obtain a much better agreement with the Pitzer model. This requires many additional experiments of high precision.
Estimations of ionic strength corrections of thermodynamic data

Example 12:

The example refers to the reaction \( \text{Cd}^{2+} + \text{Cl}^- \rightleftharpoons \text{CdCl}^+ \), studied in different perchlorate media. The experimental results, quoted from “Stability constants” compilations [64SIL/MAR, 71SIL/MAR, 82HOG] and more recent studies [75FED/CHE, 75KUT/LES, 83GRA/SJO, 84PRO/EIN, 85PRO/BEL], and recalculated into molality units and to 298.15 K where necessary, are given in Table IX.12. Only data in NaClO₄, LiClO₄ and Mg(ClO₄)₂ media, where most of the experimental determinations have been made, are included.

The data have been obtained in different laboratories using different experimental methods and different perchlorate media. How can we check the compatibility of the different sets of data?

Using the SIT-type of data treatment, we obtain the following statement for the reaction in perchlorate media

\[
\log_{10} K^\circ = \log_{10} K + 4D + \varepsilon(\text{CdCl}^+, \text{ClO}_4^-)m_{\text{ClO}_4^-} - \varepsilon(\text{Cd}^{2+}, \text{ClO}_4^-)m_{\text{ClO}_4^-} - \varepsilon(\text{N}^{n+}, \text{Cl}^-)m_{\text{N}^{n+}}
\]

Only the terms \( \log_{10} K^\circ \) and \( \varepsilon(\text{CdCl}^+, \text{ClO}_4^-) \) are unknown (we have not used the value of \( \varepsilon(\text{CdCl}^+, \text{ClO}_4^-) \) proposed by Ciavatta [80CIA] because this is based on a smaller data set). It is convenient to define a function \( Y \) as follows

\[
Y = \log_{10} K - \varepsilon(\text{CdCl}^+, \text{ClO}_4^-)m_{\text{ClO}_4^-} - \varepsilon(\text{N}^{n+}, \text{Cl}^-)m_{\text{N}^{n+}}
\]

\[
Y = \log_{10} K^\circ - \varepsilon(\text{CdCl}^+, \text{ClO}_4^-)m_{\text{ClO}_4^-}
\]

According to this equation, the function \( Y \) must be represented by a straight line with a slope equal to \( -\varepsilon(\text{CdCl}^+, \text{ClO}_4^-) \) and an intercept equal to \( \log_{10} K^\circ \). In Figure IX.31 we have plotted the values of \( Y \) calculated from \( \log_{10} K \) in different perchlorate media using auxiliary SIT coefficients \( \varepsilon(\text{Cd}^{2+}, \text{ClO}_4^-) = (0.34 \pm 0.04) \text{ kg} \cdot \text{mol}^{-1}, \varepsilon(\text{Na}^{+}, \text{Cl}^-) = (0.04 \pm 0.01) \text{ kg} \cdot \text{mol}^{-1}, \varepsilon(\text{Li}^{+}, \text{Cl}^-) = (0.10 \pm 0.01) \text{ kg} \cdot \text{mol}^{-1}, \varepsilon(\text{Mg}^{2+}, \text{Cl}^-) = (0.19 \pm 0.02) \text{ kg} \cdot \text{mol}^{-1} \). All values of \( Y \) have been treated together. The results of the least-square regression are: \( \log_{10} K^\circ = 2.07 \pm 0.11, \varepsilon(\text{CdCl}^+, \text{ClO}_4^-) = (0.318 \pm 0.033) \text{ kg} \cdot \text{mol}^{-1} \), the errors are given as 3σ. This value differs from the one reported by Ciavatta [80CIA], namely \( \varepsilon(\text{CdCl}^+, \text{ClO}_4^-) = 0.25 \pm 0.02 \), which was based on data for NaClO₄ solutions only. In the majority of cases the deviations between the “experimental” and calculated values of \( Y \) do not exceed 0.2 \( \log_{10} \) units, which is consistent with the estimated uncertainty in the experimental \( \log_{10} K \) values. This means that the data obtained in different perchlorate media are consistent. This result indicates that the specific effects of the ionic media, which are not taken into account in the SIT approximation (triple ion-ion interactions, mixing terms, etc.) are expected to be of the same order of magnitude as the estimated accuracy of \( \log_{10} K \) data. Hence, they are not statistically significant, and their determination requires much more accurate \( \log_{10} K \) data.

The data treatment based on the Pitzer approach is discussed, taking into account only the binary interaction terms for the complex \( \text{CdCl}^+ \). The equation for the concentration...
Table IX.12: Equilibrium constants for reaction $\text{Cd}^{2+} + \text{Cl}^- \rightleftharpoons \text{CdCl}^+$ in NaClO$_4$, LiClO$_4$ and Mg(ClO$_4$)$_2$ media.

<table>
<thead>
<tr>
<th>Medium</th>
<th>$m$ (mol · kg$^{-1}$)</th>
<th>$\log_{10} K(m)$</th>
<th>Medium</th>
<th>$m$ (mol · kg$^{-1}$)</th>
<th>$\log_{10} K(m)$</th>
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<tr>
<td>NaClO$_4$</td>
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<td>NaClO$_4$</td>
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Figure IX.31: The values of function $Y$ (see text for details) calculated from the $\log_{10} K$ data for the reaction $\text{Cd}^{2+} + \text{Cl}^- \rightleftharpoons \text{CdCl}^+$ in $\text{NaClO}_4$ (circles), $\text{LiClO}_4$ (squares) and $\text{Mg(ClO}_4)_2$ (triangles) media at 298.15 K and 1 atm based on the SIT model.

The concentration dependence of $\log_{10} K$ for the reaction is

$$\ln K^o = \ln K + \ln \gamma_{\text{CdCl}^+} - \ln \gamma_{\text{Cd}^{2+}} - \ln \gamma_{\text{Cl}^-}$$

The equations for the concentration dependence of the activity coefficient of $\text{Cd}^{2+}$, $\text{Cl}^-$, $\text{CdCl}^+$ in perchlorate media $M^{n+}(\text{ClO}_4)_n$ are given below:

$$\ln \gamma_{\text{Cd}^{2+}} = f^{\gamma} + mn \left[2\beta_{\text{Cd},\text{ClO}_4}^{(0)} + 2\beta_{\text{Cd},\text{ClO}_4}^{(1)} g(I_m)\right] + 2m^2n^2C_{\text{Cd},\text{ClO}_4} + 2m^2nC_{M,\text{ClO}_4}$$

$$\ln \gamma_{\text{Cl}^-} = f^{\gamma} + m \left[2\beta_{M,\text{Cl}}^{(0)} + 2\beta_{M,\text{Cl}}^{(1)} g(I_m)\right] + 2m^2nC_{M,\text{Cl}}$$

$$\ln \gamma_{\text{CdCl}^+} = f^{\gamma} + mn \left[2\beta_{\text{CdCl},\text{ClO}_4}^{(0)} + 2\beta_{\text{CdCl},\text{ClO}_4}^{(1)} g(I_m)\right] + 2m^2nC_{M,\text{ClO}_4}$$

where $n$ reflects the charge type of the ionic medium ($n = 1$ for $\text{NaClO}_4$ and $\text{LiClO}_4$, $n = 2$ for $\text{Mg(ClO}_4)_2$), $m$ is the molality of the ionic medium, all other symbols have been defined before. The binary mixing parameter $\phi_{\text{Cd},M}$ is ionic strength dependent if $M = \text{Na}$.
Figure IX.32: The values of function $Y$ (see text for details) calculated from the $\log_{10} K$ data for the reaction $\text{Cd}^{2+} + \text{Cl}^- \rightleftharpoons \text{CdCl}^+$ in NaClO$_4$ (circles), LiClO$_4$ (squares) and Mg(ClO$_4$)$_2$ (triangles) media at 298.15 K and 1 atm based on the Pitzer model.

or Li, and $\phi_{\text{CdClM}}$ if $M = \text{Mg}$. For further simplification the parameter $\beta^{(1)}_{\text{CdCl,CIO}_4} = 0.9$ was estimated from the $\Delta(Z^2)$ value for the reaction and known values of the $\beta^{(1)}$ for other reaction participants in NaClO$_4$ and LiClO$_4$ media (note that the proposed correlation between $\Delta(Z^2)$ and $X_2 = \Delta\beta^{(1)}$ is valid only for the supporting electrolyte of 1-1 type). Now we can define the function $Y$

$$Y = \log_{10} K - \left[ \ln \gamma_{\text{Cd}^{2+}} + \ln \gamma_{\text{Cl}^-} - f^\gamma - 2m n \beta_{\text{CdCl,CIO}_4} g(I_m) - m^2 n C_{M,CIO}_4 \right] / \ln(10)$$

$$= \log_{10} K^0 - 2m n \left[ \beta^{(0)}_{\text{CdCl,CIO}_4} + \frac{1}{n} \phi_{\text{CdClM}} \right] / \ln(10)$$

The function $Y$ calculated from $\log_{10} K$ data in different perchlorate media is shown in Figure IX.32, the values of the $\beta^{(0)}$ and $\beta^{(1)}$ for Cd$^{2+}$-ClO$_4^-$ interaction are taken from [88KIM/FRE], and other Pitzer parameters are quoted from [91PIT]. Neither the relevant binary mixing parameters $\phi_{\text{CdLi}}$, $\phi_{\text{CdNa}}$, $\phi_{\text{CdMg}}$, $\phi_{\text{CdClO}_4}$, nor the ternary mixing parameter are available. As the Pitzer parameters reported are valid up to ionic strength 6 mol·kg$^{-1}$, only the results obtained at lower ionic strength were considered. As expected, the data scatter considerably, and the $Y$ values referring to the Mg(ClO$_4$)$_2$ ionic
medium, shown by triangles, deviate from the points in LiClO$_4$ (squares) and NaClO$_4$ (circles) media. There are several possible explanations for these deviations, e.g., the contribution from the $\phi_{CdM}$ and $\phi_{CdClM}$ terms. This issue cannot be resolved due to lack of experimental values of $\phi_{CdM}$. Nevertheless, we used the linear regression of all the data to obtain $\log_{10} K^\circ = 2.16 \pm 0.17$ as intercept and $-0.25 \pm 0.06$ as the slope of the resulting linear plot (see Figure IX.32). The value of $\log_{10} K^\circ$ is, within the estimated uncertainty, in agreement with the value from the SIT-type of data treatment.

Before using experimental concentration equilibrium constants for the determination of $\log_{10} K^\circ$ and the various interaction parameters one must be aware of the following:

- The experimental concentration constants have been determined on the assumption that the activity coefficients of reactants/products are constant at a constant ionic strength. This may not be the case if a sufficiently large part of the ionic medium has been replaced by the reactants/products. As a result one may have introduced a systematic error in the equilibrium constants, but rarely with the chemical model. These errors will then be propagated in the determination of $\log_{10} K^\circ$ and the interaction parameters. The magnitude of the systematic error will be ionic strength dependent.

- The presence of other types of systematic errors, related to the method of investigation, are difficult to spot unless different experimental methods are used.

These factors result in an accuracy of most published equilibrium constants that is much lower than the claimed uncertainty of the results, which in general describe the precision of the experiment. With this in mind, one will often find that even the SIT model provides reasonably good estimates of the concentration/ionic medium dependence of most equilibrium constants, especially for complex systems such as the ones encountered in nature. We can conclude that the simple SIT approach, which uses only one parameter for each ion-counter ion, ion-neutral, and neutral-neutral interaction, results in a reliable value of the equilibrium constant at infinite dilution, and an adequate reproduction of $\log_{10} K$ data for complex formation equilibria as a function of both the ionic strength and the ionic composition of the medium. The “intrinsic error” in the SIT model, due to the approximations used is less than 5-10 per cent for the mean activity coefficients of completely dissociated electrolytes, even at ionic strengths as high as 6-10 mol $\cdot$ kg$^{-1}$. Hence, the expected “intrinsic” error (which will depend on the number of reactants/products in the equilibrium expression) in the reproduction of the $\log_{10} K$ data is less than $0.10 \log_{10}$ units for reactions involving two reactants and one product. The agreement of the experimental $\log_{10} K$ data obtained in independent laboratories using different methods is seldom better than 0.1 ($\log_{10}$-unit), for complex formation reactions. As discussed by Beck and Nagypal [90BEC/NAG], the errors claimed by authors usually reflect the reproducibility of $\log_{10} K$ values from the experimental data set for the particular experimental method used, and the particular chemical model of the system under study.
IX.9. The use of the SIT at elevated temperatures

In order to describe the concentration behavior of \( \log_{10} K \) at elevated temperatures and pressures it is necessary to have information on the temperature and pressure dependence of the interaction parameters (either the Pitzer, or the SIT parameters). The equations involving temperature and pressure derivatives of the chemical potential of the solute on the basis of the Pitzer model are published [91PIT]. Below we give the corresponding equations for the SIT model.

IX.9.1. Osmotic coefficient

The following formulae are all based on the application of standard thermodynamic relations to the SIT expression for the activity coefficient (Eq. (IX.4)) of the dissolved species in an aqueous system. The reader is referred to [58HAR/OWE, 61LEW/RAN] for additional details.

The mean activity coefficient of single electrolytes is equal to

\[
\ln \gamma_\pm = -\frac{A_\gamma |Z_+ Z_-| \sqrt{t_m}}{t} + \frac{2 \nu_+ \nu_-}{\nu} \varepsilon_\gamma m
\]

where

\[
I_m = \frac{m}{2} \left( \nu_+ Z_+^2 + \nu_- Z_-^2 \right)
\]

\[
t = 1 + 1.5 \sqrt{I_m}
\]

all other symbols have been explained before.

Using the definition of the osmotic coefficient \( \Phi \) for a single electrolyte [58HAR/OWE] we obtain:

\[
\Phi = 1 - \frac{A_\gamma |Z_+ Z_-|}{1.5 I_m} \left( t - 2 \ln t - \frac{1}{t} \right) + \frac{\nu_+ \nu_-}{\nu} \varepsilon_\gamma m
\]

Equilibria involving \( \text{H}_2\text{O(l)} \) as a reactant or product require a correction for the activity of water, \( a_{\text{H}_2\text{O}} \). In an electrolyte mixture this can be calculated from \( \Phi \), by using Eqs. (IX.33), (IX.35), or from the experimentally determined osmotic coefficient of the mixture:

\[
\ln a_{\text{H}_2\text{O}} = -\frac{\Phi \sum_k m_k}{55.5084}
\]

The summation extends over all solutes \( k \) with molality \( m_k \) present in the solution. The SIT model, with the analytical statement for the activity coefficients for the dissolved species (ions and neutral species), can be used to obtain an analytical statement for the osmotic coefficients of the solution. The deduction which uses the Gibbs-Duhem equation is straightforward and results in the following expression (the subscripts \( c \) and \( a \) refer
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to cations and anions in general, \( n_i \) and \( n_j \) denote the different kinds of neutral species, subscript \( k \) refer to any species):

\[
\Phi - 1 = \frac{2A_n}{1.5^3} \left( t - 2\ln t - \frac{1}{t} \right) + \frac{1}{\sum_k m_k} \left[ \sum_c \sum_a \varepsilon_\gamma(c, a) m_a m_c 
+ \sum_c \sum_n \varepsilon_\gamma(c, n) m_c m_n + \sum_a \sum_n \varepsilon_\gamma(a, n) m_a m_n 
+ \frac{1}{2} \sum_{n_i} \sum_{n_j} \varepsilon_\gamma(n_i, n_j) m_{n_i} m_{n_j} \right]
\] (IX.39)

If no uncharged species are present the last three terms are zero and the expression for the osmotic coefficient is then very close to the expression given by Pitzer and Brewer [61LEW/RAN, their Eq. (23-39)].

IX.9.2. The analytical statements for partial and apparent molar properties of single electrolytes on the basis of the SIT model

The equation presented below have been derived using the approximation that the quantity \( a_j B = 1.5 \) is independent of temperature and pressure.

1. The relative partial molar enthalpy is defined as [58HAR/OWE]:

\[
L_2 = H_2 - H_2^0 = -\nu RT^2 \left( \frac{\partial \ln \gamma_\pm}{\partial T} \right)_P
\] (IX.40)

where \( H_2 \) and \( H_2^0 \) are the partial molar enthalpies in a given solution and at infinite dilution, respectively. Only the relative value, \( L_2 \), can be determined from experimental measurements. We have:

\[
L_2 = \frac{3}{4} \nu \frac{A_L |Z_\pm| \sqrt{T_m}}{t} - 2 \nu_+ \nu_- RT^2 \varepsilon_L m
\] (IX.41)

where

\[
\varepsilon_L = \left( \frac{\partial \varepsilon_\gamma}{\partial T} \right)_P
\] (IX.42)

\( A_L \) is a Debye-Hückel slope defined in Section IX.9.3. Using the general relation between partial and apparent properties

\[
\Xi_2 = \frac{\partial}{\partial n_2} (\phi \Xi n_2)_{\nu, T}
\] (IX.43)
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where \( \Xi \) and \( \phi \Xi \) are partial and apparent properties respectively, and \( n_2 \) the solute concentration, we obtain the analytical statement for the concentration dependence of the relative apparent molar enthalpy \( \phi L \):

\[
\phi L = \frac{3}{4} \nu \frac{A_v |Z_+ Z_-|}{1.5^3 T_m} (t^2 - 4t + 2\ln t + 3) - \nu_+ \nu_- RT^2 \varepsilon_L m \tag{IX.44}
\]

2. The partial molar volume is defined as [58HAR/OWN]:

\[
V_2 - V_2^\circ = \nu RT \left( \frac{\partial \ln \gamma_\pm}{\partial \rho} \right)_T \tag{IX.45}
\]

where \( V_2 \) and \( V_2^\circ \) are partial molar volumes in a given solution and at infinite dilution, respectively. We have

\[
V_2 - V_2^\circ = \frac{3}{4} \nu \frac{A_v |Z_+ Z_-| \sqrt{T_m}}{t} + 2 \nu_+ \nu_- RT \varepsilon_V m \tag{IX.46}
\]

where

\[
\varepsilon_V = \left( \frac{\partial \ln \gamma_\pm}{\partial \rho} \right)_T \tag{IX.47}
\]

and we obtain the analytical statement for the concentration dependence of the apparent molar volume \( \phi V \)

\[
\phi V - V_2^\circ = \frac{3}{4} \nu \frac{A_v |Z_+ Z_-| \sqrt{T_m}}{1.5^3 T_m} (t^2 - 4t + 2\ln t + 3) + \nu_+ \nu_- RT \varepsilon_V m \tag{IX.48}
\]

\( A_v \) is a Debye-Hückel slope defined in Section IX.9.3.

3. By definition [58HAR/OWN]

\[
C_{p_2} - C_{p_2}^\circ = \left( \frac{\partial L_2}{\partial T} \right)_p \tag{IX.49}
\]

where \( C_{p_2} \) and \( C_{p_2}^\circ \) are partial molar heat capacities in a given solution and at infinite dilution, respectively. Hence

\[
C_{p_2} - C_{p_2}^\circ = \frac{3}{4} \nu \frac{A_j |Z_+ Z_-| \sqrt{T_m}}{t} - 2 \nu_+ \nu_- RT^2 \varepsilon_J m \tag{IX.50}
\]
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where

\[ \varepsilon_J = \frac{2\varepsilon_L}{T} + \frac{\partial\varepsilon_L}{\partial T} + \frac{2}{T} \left( \frac{\partial\varepsilon_\gamma}{\partial T} \right)_p + \left( \frac{\partial^2\varepsilon_\gamma}{\partial T^2} \right)_p \]  \hspace{1cm} (IX.51)

The analytical statement for the concentration dependence of the molar apparent heat capacity \( \phi_J \) (\( A_J \) is a Debye-Hückel slope, cf. Section IX.9.3) is:

\[ \phi_J - C_{p_2} = \frac{3}{4} \nu A_J \frac{|Z_+ Z_-|}{1.5^3 I_m} (t^2 - 4t + 2 \ln t + 3) \]

\[ - \nu_+ \nu_- RT^2 \varepsilon_J m \]  \hspace{1cm} (IX.52)

4. For the partial molar isothermal compressibility \( k_2 \) we use the definition

\[ k_2 = \left( \frac{\partial V_2}{\partial p} \right)_T \]  \hspace{1cm} (IX.53)

Hence

\[ k_2 - k_2^\circ = \frac{3}{4} \nu A_k \frac{|Z_+ Z_-|\sqrt{I_m}}{I_m} + 2 \nu_+ \nu_- RT \varepsilon_k m \]  \hspace{1cm} (IX.54)

where \( k_2^\circ \) is the partial molar isothermal compressibility at infinite dilution, and

\[ \varepsilon_k = \left( \frac{\partial\varepsilon_\nu}{\partial p} \right)_T = \left( \frac{\partial^2\varepsilon_\nu}{\partial p^2} \right)_T \]  \hspace{1cm} (IX.55)

\( A_k \) is the Debye-Hückel limiting slope defined in Section IX.9.3. The concentration dependence of the apparent molar isothermal compressibility \( \phi k \) is given by

\[ \phi k - k_2^\circ = \frac{3}{4} \nu A_k \frac{|Z_+ Z_-|}{1.5^3 I_m} (t^2 - 4t + 2 \ln t + 3) \]

\[ + \nu_+ \nu_- RT \varepsilon_k m \]  \hspace{1cm} (IX.56)

With the model assumptions made, we obtain very simple analytical expressions for the concentration dependence of partial and apparent molar properties of aqueous electrolytes as compared to more parametrized versions of extended Debye-Hückel equations (e.g., Helgeson et al. [81 HEL/KIR]).

IX.9.3. The Debye-Hückel limiting law slopes

We use the following definitions of the Debye-Hückel limiting law slopes [79BRA/PIT, 84ANA/ATK]:

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For activity and osmotic coefficients:

\[ A_\gamma = \frac{(2\pi N)^{1/2}}{(1000)^{1/2}} \frac{e^3}{k^{3/2}} \frac{\rho^{1/2}}{(\epsilon T)^{3/2}} \]  
\[ A_\Phi = \frac{A_\gamma}{3} \]  

where \( N \) is the Avogadro number, \( \epsilon \) stands for absolute electronic charge, \( \epsilon \) is here the dielectric constant of water, \( \rho \) is the pure water density, \( k \) is Boltzman constant, \( T \) is absolute temperature, \( K \).

For partial and apparent molar relative enthalpies:

\[ A_L = 4RT^2 \left( \frac{\partial A_\Phi}{\partial T} \right)_p = -2A_\gamma RT \left( 1 + \frac{T}{\epsilon} \left( \frac{\partial \epsilon}{\partial T} \right)_p + \frac{T\alpha}{3} \right) \]  

where \( R \) is gas constant, \( \alpha \) is expansivity of pure water (\( \alpha = (\partial \ln V/\partial T)_p \)).

For partial and apparent molar volumes:

\[ A_V = -4RT \left( \frac{\partial A_\Phi}{\partial p} \right)_T = 2A_\gamma RT \left( \frac{1}{\epsilon} \left( \frac{\partial \epsilon}{\partial p} \right)_T - \frac{\beta}{3} \right) \]  

where \( \beta \) is compressibility of pure water (\( \beta = -(\partial \ln V/\partial p)_T \)).

For partial and apparent molar heat capacities:

\[ A_J = \left( \frac{\partial A_H}{\partial T} \right)_p = -2A_\gamma RT^2 \left( \frac{1}{\epsilon} \left( \frac{\partial^2 \epsilon}{\partial T^2} \right)_p - \frac{1}{\epsilon^2} \left( \frac{\partial \epsilon}{\partial T} \right)_p \right) - \frac{1}{T^2} + \frac{1}{3} \left( \frac{\partial \alpha}{\partial T} \right)_p \]  

\[ + \frac{2A_L}{T} + \frac{3A_\gamma^2}{4A_\gamma RT^2} \]  

For partial and apparent isothermal molar compressibilities:

\[ A_k = \left( \frac{\partial A_V}{\partial p} \right)_T = 2A_\gamma RT \left( \frac{1}{\epsilon} \left( \frac{\partial \epsilon}{\partial p} \right)_T - \frac{1}{\epsilon^2} \left( \frac{\partial \epsilon}{\partial p} \right)_T \right) \]  

\[ - \frac{A_V}{2} \left( \frac{3}{\epsilon} \left( \frac{\partial \epsilon}{\partial p} \right)_T - \beta \right) \]  

When calculating the Debye-Hückel limiting law slopes we use the Haar-Gallagher-Kell equation of state for pure water [84KES/SEN] and the Archer-Wang [90ARC/WAN] equation for the dielectric constant of pure water.

Example 13:

The equations given above have been used to correlate the experimental data on activity coefficients, relative apparent molar enthalpies, apparent molar heat capacities and apparent molar volumes for NaCl at different temperatures at saturated water vapor pressure.
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Figure IX.33: Comparison of experimental (solid line) and smoothed values of activity coefficients of aqueous NaCl solutions at saturated water vapor pressure on the basis of the SIT model. The numbers adjacent to the curves are Celsius temperatures.

See Figures IX.33, IX.34, IX.35 and IX.36 where the recent precise experimental data are shown by full-drawn lines and the values obtained from the SIT model are shown by the filled circles.

The accuracy of the fitting of the experimental data using the SIT model is far less than that obtained by using the three-parameter Pitzer model, which describes the thermodynamic properties of electrolyte solutions practically within the experimental errors in most cases. The one-parameter SIT approach should not be used for the treatment of experimental thermochemical data and data at different pressure, when information on the Pitzer parameters for the system is available. Nevertheless, the following points should be noticed:

- The SIT model provides a reasonably good description of data on the activity coefficients, relative apparent molar enthalpies, apparent molar heat capacities and apparent molar volumes of the NaCl aqueous solutions both at 298.15 K and elevated temperatures;

- The SIT model works better at temperatures above 298.15 K, both for other 1-1 and 2-1 electrolytes, indicating that the “intrinsic” error of the model decreases with increasing temperature. Hence, we recommend the use of this approach for the description of the concentration dependence of the equilibrium constants at elevated temperatures, cf. Example 14.
Figure IX.34: Comparison of experimental (solid line) and smoothed values of relative apparent molar enthalpies, $\phi L$, of aqueous NaCl solutions at saturated water vapor pressure on the basis of the SIT model. The numbers adjacent to the curves are Celsius temperatures.

Figure IX.35: Comparison of experimental (solid line) and smoothed values of apparent molar volumes of aqueous NaCl solutions at saturated water vapor pressure on the basis of the SIT model. The numbers adjacent to the curves are Celsius temperatures.
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Figure IX.36: Comparison of experimental (solid line) and smoothed values of the apparent molar heat capacities of aqueous NaCl solutions at saturated water vapor pressure on the basis of the SIT model. The numbers adjacent to the curves are Celsius temperatures.

Example 14:

The main field of application of the SIT approach is the description of the ionic strength/ionic medium dependence of complex formation reactions. It was repeatedly shown [80CIA, 92GRE/FUG] that the SIT model results in fair reproduction of experimental results and a correct estimation of $\log_{10} K^*$ for data at 298.15 K. In this example we will check the applicability of this model to data obtained at elevated temperatures. The equilibrium constants for the following reactions have been studied experimentally by potentiometric method at different temperatures in NaCl ionic media [82PAT/SLO, 84PAT/BUS, 90DIC/WES]:

$$\begin{align*}
\text{CO}_2^{\text{aq}} + \text{H}_2\text{O}(l) & \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \\
\text{HCO}_3^- & \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-} \\
\text{HSO}_4^- & \rightleftharpoons \text{H}^+ + \text{SO}_4^{2-}
\end{align*}$$

A comparison between experimental data and those fitted using the SIT model are shown in Figures IX.37, IX.38, IX.39 and in Table IX.13. When using the SIT model we have assumed that

- $A$ is a temperature- and pressure-dependent function, cf. Eq. IX.57.
- The numerical factor 1.5 is independent of temperature.
The use of the SIT at elevated temperatures

Table IX.13: Test of the SIT approach for some reactions at elevated temperatures in NaCl media \( (\log_{10} K_{exp}^\circ) \) is the value from the original publications. The results at 300°C are shown in parenthesis, because these data may be affected by a partial association of the ionic medium.

<table>
<thead>
<tr>
<th>( t(°C) )</th>
<th>([-\log_{10} K_{exp}^\circ ± 3\sigma] )</th>
<th>([-\log_{10} K_{calc}^\circ ± 3\sigma] )</th>
<th>[\log_{10} K_{exp}^\circ - \log_{10} K_{calc}^\circ]</th>
<th>( \Delta\varepsilon ± 3\sigma ) (kg \cdot mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactions: CO(_2)(aq) + H(_2)O(l) ⇌ H(^+) + HCO(_3^-) [82PAT/SLO]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>6.569 ± 0.007</td>
<td>6.549 ± 0.021</td>
<td>−0.020 ± 0.022</td>
<td>0.002 ± 0.033</td>
</tr>
<tr>
<td>25</td>
<td>6.349 ± 0.005</td>
<td>6.327 ± 0.024</td>
<td>−0.022 ± 0.025</td>
<td>0.011 ± 0.036</td>
</tr>
<tr>
<td>50</td>
<td>6.279 ± 0.005</td>
<td>6.251 ± 0.030</td>
<td>−0.028 ± 0.031</td>
<td>0.039 ± 0.036</td>
</tr>
<tr>
<td>100</td>
<td>6.307 ± 0.012</td>
<td>6.351 ± 0.042</td>
<td>−0.046 ± 0.044</td>
<td>0.036 ± 0.024</td>
</tr>
<tr>
<td>150</td>
<td>6.721 ± 0.018</td>
<td>6.658 ± 0.054</td>
<td>−0.063 ± 0.057</td>
<td>−0.001 ± 0.024</td>
</tr>
<tr>
<td>200</td>
<td>7.189 ± 0.023</td>
<td>7.112 ± 0.063</td>
<td>−0.077 ± 0.067</td>
<td>−0.062 ± 0.027</td>
</tr>
<tr>
<td>250</td>
<td>7.783 ± 0.027</td>
<td>7.685 ± 0.078</td>
<td>−0.098 ± 0.083</td>
<td>−0.146 ± 0.039</td>
</tr>
<tr>
<td>300</td>
<td>8.498 ± 0.060</td>
<td>(8.348 ± 0.120)</td>
<td>(−0.150 ± 0.134)</td>
<td>(−0.252 ± 0.051)</td>
</tr>
<tr>
<td>Reactions: HCO(_3^-) ⇌ H(^+) + CO(_3^{2-}) [84PAT/BUS]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>10.627 ± 0.005</td>
<td>10.585 ± 0.042</td>
<td>−0.042 ± 0.042</td>
<td>0.073 ± 0.057</td>
</tr>
<tr>
<td>25</td>
<td>10.337 ± 0.003</td>
<td>10.288 ± 0.054</td>
<td>−0.049 ± 0.054</td>
<td>0.061 ± 0.039</td>
</tr>
<tr>
<td>50</td>
<td>10.180 ± 0.004</td>
<td>10.127 ± 0.057</td>
<td>−0.053 ± 0.057</td>
<td>0.041 ± 0.045</td>
</tr>
<tr>
<td>100</td>
<td>10.120 ± 0.017</td>
<td>10.032 ± 0.084</td>
<td>−0.088 ± 0.086</td>
<td>0.008 ± 0.057</td>
</tr>
<tr>
<td>150</td>
<td>10.255 ± 0.039</td>
<td>10.120 ± 0.114</td>
<td>−0.135 ± 0.120</td>
<td>−0.015 ± 0.048</td>
</tr>
<tr>
<td>200</td>
<td>10.491 ± 0.056</td>
<td>10.317 ± 0.144</td>
<td>−0.174 ± 0.155</td>
<td>−0.047 ± 0.051</td>
</tr>
<tr>
<td>250</td>
<td>10.777 ± 0.073</td>
<td>10.560 ± 0.171</td>
<td>−0.217 ± 0.186</td>
<td>−0.095 ± 0.072</td>
</tr>
<tr>
<td>Reactions: HSO(_4^-) ⇌ H(^+) + SO(_4^{2-}) [90DIC/WES]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1.659 ± 0.030</td>
<td>1.565 ± 0.078</td>
<td>−0.094 ± 0.084</td>
<td>0.046 ± 0.030</td>
</tr>
<tr>
<td>25</td>
<td>1.964 ± 0.018</td>
<td>1.876 ± 0.075</td>
<td>−0.088 ± 0.077</td>
<td>0.032 ± 0.030</td>
</tr>
<tr>
<td>50</td>
<td>2.316 ± 0.012</td>
<td>2.227 ± 0.069</td>
<td>−0.089 ± 0.070</td>
<td>0.020 ± 0.030</td>
</tr>
<tr>
<td>100</td>
<td>3.061 ± 0.008</td>
<td>2.960 ± 0.066</td>
<td>−0.101 ± 0.067</td>
<td>−0.003 ± 0.027</td>
</tr>
<tr>
<td>150</td>
<td>3.809 ± 0.007</td>
<td>3.691 ± 0.072</td>
<td>−0.118 ± 0.073</td>
<td>−0.032 ± 0.030</td>
</tr>
<tr>
<td>200</td>
<td>4.561 ± 0.008</td>
<td>4.419 ± 0.099</td>
<td>−0.142 ± 0.100</td>
<td>−0.070 ± 0.039</td>
</tr>
<tr>
<td>250</td>
<td>5.355 ± 0.012</td>
<td>5.187 ± 0.141</td>
<td>−0.168 ± 0.142</td>
<td>−0.124 ± 0.063</td>
</tr>
</tbody>
</table>
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Figure IX.37: The differences \( \log_{10} K_{\text{exp}} - \log_{10} K_{\text{calc}} \) between experimental and calculated values of \( \log_{10} K \) using the SIT model as a function of the molality of the ionic medium (NaCl) and temperatures (at saturated water vapor pressure) for the reaction \( \text{CO}_2(\text{aq}) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \) [82PAT/SLO].

- \( \Delta \varepsilon \) is a temperature- and pressure-dependent parameter.

One can conclude that it is possible to describe the concentration dependence of the equilibrium constants at temperatures up to 250°C (saturation water vapor pressure) in fairly good agreement with experimental data (in almost all cases the difference between experimental and calculated data do not exceed 0.05-0.08 \( \log_{10} \) units up to the ionic strength 5 mol kg\(^{-1}\)). The values of \( \log_{10} K^\circ \) (i.e., at infinite dilution) agree almost within the obtained uncertainties with the estimates based on more complicated models containing 2-3 fitting parameters. However, the values of \( \log_{10} K^\circ \) obtained using the SIT are systematically slightly higher than the values reported in the original publications. This is due to the fact that \( \log_{10} K^\circ \) value depends somewhat on the extrapolation method used. However, these variations are small.

IX.10. The concentration dependence of heats of reactions

The enthalpy of reaction, \( \Delta_r H_m \), is another characteristic of importance for complex formation reactions. All problems, which were discussed for the description of the concentration dependence of \( \log_{10} K \) are relevant also for \( \Delta_r H_m \) data. Determinations of standard heats of reactions in aqueous solutions (i.e., at infinite dilution) in general in-
The concentration dependence of heats of reactions

Figure IX.38: The differences \((\log_{10} K_{\text{exp}} - \log_{10} K_{\text{calc}})\) between experimental and calculated values of \(\log_{10} K\) using the SIT model as a function of the molality of the ionic medium (NaCl) and temperatures (at saturated water vapor pressure) for the reaction \(\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}\) [84PAT/BUS].

Figure IX.39: The differences \((\log_{10} K_{\text{exp}} - \log_{10} K_{\text{calc}})\) between experimental and calculated values of \(\log_{10} K\) using the SIT model as a function of the molality of the ionic medium (NaCl) and temperatures (at saturated water vapor pressure) for the reaction \(\text{HSO}_4^- \rightleftharpoons \text{H}^+ + \text{SO}_4^{2-}\) [90DIC/WES].
Estimations of ionic strength corrections of thermodynamic data

volve the determinations of heats of reactions at finite concentrations and the relevant heats of mixing and dilution of the components. Typical examples are the papers of Berg and Vanderzee [75BER/VAN, 75BER/VAN2], where the value of the standard enthalpy of formation of aqueous zinc ion was calculated from the enthalpies of solution of ZnO(cr) in HClO₄ solutions, the enthalpy of dilution of Zn(ClO₄)₂(aq) and the enthalpy of mixing of Zn(ClO₄)₂(aq) and HClO₄(aq) solutions. There are many examples in the literature where only the enthalpies of reaction at finite concentrations, often in solution with a large excess of ionic medium electrolyte, have been measured experimentally. These data have then been extrapolated to infinite dilution by using some empirical or semi-empirical methods, for instance, assuming that the thermochemical quantities follow a simple square root dependence of the ionic strength of the solution, etc. The use of such methods may result in a loss of accuracy of the value at infinite dilution, as compared to the accuracy of the experimental data, and were abandoned a long time ago for the determination of \( \log_{10} K^\circ \). A clear and unambiguous discussion of the problem to describe the concentration dependence of \( \Delta_r H_m \) and to determine \( \Delta_r H_m^\circ \) for complex formation reactions is still absent (or we are not aware of it).

As discussed in Section IX.7 for a chemical reaction in the general form

\[
\sum_i \nu_i Q_i + rH_2O(l) = 0
\]  

the equation for the concentration dependence of \( \ln K \) is given as follows:

\[
\ln K^\circ = \ln K + \sum_i \nu_i \ln \gamma_i + r \ln a_{H_2O}
\]  

Using the known thermodynamic relations and definitions

\[
\Delta_r H_m = RT^2 \left( \frac{\partial \ln K^\circ}{\partial T} \right)_p
\]  

\[
L_1 = -RT^2 \left( \frac{\partial \ln a_{H_2O}}{\partial T} \right)_{p,m}
\]  

\[
L_{2,i} = -RT^2 \left( \frac{\partial \ln \gamma_i}{\partial T} \right)_{p,m,i}
\]

where \( L_1 \) and \( L_{2,i} \) stand for the relative partial molar enthalpies of water and solute \( i \) respectively, one obtains the following basic equation for the concentration dependence of the enthalpy of reaction:

\[
\Delta_r H_m^\circ = \Delta_r H_m - \sum_i \nu_i L_{2,i} - rL_1
\]

Values of the relative partial molar enthalpy of water, \( L_1 \), in solutions of some common electrolytes are given in Table IX.14.
The concentration dependence of heats of reactions

Table IX.14: Values of the relative partial molar enthalpy of water, $L_1$, in solutions of some common electrolytes [91PIT]. The values in parenthesis are short range extrapolations.

<table>
<thead>
<tr>
<th>$m$ [mol kg$^{-1}$]</th>
<th>$L_1$ / (kJ mol$^{-1}$)</th>
<th>HCl</th>
<th>HBr</th>
<th>HClO$_4$</th>
<th>LiCl</th>
<th>LiClO$_4$</th>
<th>NaCl</th>
</tr>
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<tr>
<td>0.50</td>
<td>-0.005</td>
<td>-0.004</td>
<td>0.003</td>
<td>-0.004</td>
<td>-0.002</td>
<td>0.002</td>
<td></td>
</tr>
<tr>
<td>1.00</td>
<td>-0.017</td>
<td>-0.013</td>
<td>0.009</td>
<td>-0.012</td>
<td>-0.007</td>
<td>0.011</td>
<td></td>
</tr>
<tr>
<td>1.50</td>
<td>-0.037</td>
<td>-0.028</td>
<td>0.015</td>
<td>-0.025</td>
<td>-0.014</td>
<td>0.024</td>
<td></td>
</tr>
<tr>
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<td>-0.050</td>
<td>0.021</td>
<td>-0.043</td>
<td>-0.027</td>
<td>0.039</td>
<td></td>
</tr>
<tr>
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<td>0.022</td>
<td>-0.067</td>
<td>-0.045</td>
<td>0.056</td>
<td></td>
</tr>
<tr>
<td>3.00</td>
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<td>-0.117</td>
<td>0.017</td>
<td>-0.099</td>
<td>-0.071</td>
<td>0.071</td>
<td></td>
</tr>
<tr>
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<td>0.004</td>
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<td>-0.152</td>
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<td>-0.313</td>
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<table>
<thead>
<tr>
<th>$m$ [mol kg$^{-1}$]</th>
<th>NaBr</th>
<th>NaNO$_3$</th>
<th>NaClO$_4$</th>
<th>NaOH</th>
<th>KCl</th>
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<td>0.008</td>
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<td>0.099</td>
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<td>0.128</td>
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<td>0.073</td>
<td>(0.10)</td>
<td>0.140</td>
<td>0.014</td>
<td>0.058</td>
<td>(0.22)</td>
</tr>
<tr>
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<td>0.095</td>
<td>0.181</td>
<td>0.002</td>
<td>0.080</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>0.117</td>
<td>0.219</td>
<td>-0.023</td>
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</tr>
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<tr>
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<td>0.143</td>
<td>0.259</td>
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</tbody>
</table>
Estimations of ionic strength corrections of thermodynamic data

The particular analytical form of the equation will depend on the model used to describe the activity coefficients. Most complex formation reactions have been studied at trace concentrations of the reactants/products in a large excess of supporting electrolytes. In the following sections we will describe two equations based on the Pitzer and the SIT models that could be used for the description of the concentration dependence of the $\Delta_r H_m$ for such reactions.

**IX.10.1. The calculation of the standard enthalpy of reaction from experimental $\Delta_r H_m$ data using the Pitzer equation**

Using the Pitzer equations the following statement is obtained for the relative partial molar enthalpy of a cation $M$ present at trace concentration in a solution of a “supporting” electrolyte $NX$ (see Eqs. (IX.12), (IX.17-IX.21), (IX.59), (IX.65)):

$$L_{2M} = \frac{Z_M^2 A_L}{4} \left[ \frac{\sqrt{I_m}}{1 + b \sqrt{I_m}} + \frac{2}{b} \ln \left( 1 + b \sqrt{I_m} \right) \right] - RT^2 Z_M^2 m_N m_X \frac{\beta^{(1)L}_{NX} g'(I_m)}{I_m} - 2RT^2 m_X \left[ \beta^{(0)L}_{MX} + \beta^{(1)L}_{MX} g(I_m) \right]$$

$$- RT^2 m_N \left[ 2 \left( \frac{\partial \phi_{MN}}{\partial T} \right)_p + m_X \left( \frac{\partial \psi_{MNX}}{\partial T} \right)_p \right]$$

$$- RT^2 m_X \left( m_N Z_N + m_X Z_X \right) C^L_{MX} - RT^2 Z_M m_N m_X C^L_{NX}$$

where $A_L$ is the Debye-Hückel parameter for the enthalpy (at 25°C and 1 atm $A_L = 1.986 \text{ kJ} \cdot \text{kg}^{1/2} \cdot \text{mol}^{-3/2}$ [91PIT]); $Z_M$, $Z_N$, $Z_X$ stand for the charges of M, N, and X respectively; $g$ and $g'$ are defined in Eqs. (IX.22) and (IX.23) in p.354; and the parameters $\beta^{(0)L}$, $\beta^{(1)L}$, $C^L$ are defined as

$$\beta^{(0)L} = \left( \frac{\partial \beta^{(0)}}{\partial T} \right)_p ; \quad \beta^{(1)L} = \left( \frac{\partial \beta^{(1)}}{\partial T} \right)_p ; \quad C^L = \left( \frac{\partial C}{\partial T} \right)_p$$

where $\beta^{(0)}$, $\beta^{(1)}$ and $C$ are the parameters for the osmotic and activity coefficients in the Pitzer model. The corresponding expression for the relative partial molar enthalpy of an anion $Y$ is obtained by changing the subscript $M$ for $Y$ and the subscript $X$ for $N$.

For the relative partial molar enthalpy of water in solution of NX electrolyte, the following equation is obtained:
The concentration dependence of heats of reactions

\[ L_1 = \frac{M_w}{1000} \left[ -\frac{A_L}{2} \left( \frac{I_m^{3/2}}{1 + b\sqrt{I_m}} \right) + 2RT^2 \nu_M \nu_X m^2 \left( \beta_{NX}^{(0)L} + \beta_{NX}^{(1)L} e^{-\alpha\sqrt{I_m}} \right) 
+ 2\nu_N Z_N m C_{NX}^L \right] \]

(IX.68)

where \( M_w \) is the molar mass of water; \( \nu_N \) and \( \nu_X \) are the number of N and X in the electrolyte \( NX \).

The Pitzer approach gives the following equation for the concentration dependence of the enthalpy of the reaction studied at trace concentrations of the reactants/products in solution with a large excess of a 1-1 electrolyte ionic medium:

\[ \Delta_r H_m - r L_1 = \Delta_r H_m^o + \frac{\Delta(Z^2) A_L}{4} \left[ \frac{\sqrt{I_m}}{1 + b\sqrt{I_m}} + \frac{2}{b} \ln \left( 1 + b\sqrt{I_m} \right) \right] 
- RT^2 \Delta(Z^2) m^2 \beta_{NX}^{(1)L} g(I_m) \frac{g'(I_m)}{I_m} - RT^2 m^2 \Delta[Z] C_{NX}^L 
- 2RT^2 m \Delta\beta^{(0)L} - 2RT^2 m \Delta \left( \frac{\partial\phi}{\partial T} \right)_p - 2RT^2 m \Delta\beta^{(1)L} g(I_m) 
- 2RT^2 m^2 \Delta C^L - RT^2 m^2 \Delta \left( \frac{\partial\psi}{\partial T} \right)_p 
\]

(IX.69)

where

\[ \Delta(Z^2) = \sum_i \nu_i Z_i^2 \quad \Delta[Z] = \sum_i \nu_i |Z_i| \]

\[ \Delta\beta^{(0)L} = \sum_i \nu_i \beta_{ij}^{(0)L} \quad \Delta\beta^{(1)L} = \sum_i \nu_i \beta_{ij}^{(1)L} \quad \Delta C^L = \sum_i \nu_i C_{ij}^L \]

\[ \Delta \left( \frac{\partial\phi}{\partial T} \right)_p = \sum_i \nu_i \left( \frac{\partial\phi_i}{\partial T} \right)_p \quad \Delta \left( \frac{\partial\psi}{\partial T} \right)_p = \sum_i \nu_i \left( \frac{\partial\psi_i}{\partial T} \right)_p \]

Here subscript \( i \) refers to reaction participants, \( i' \) and \( j \) stand for the ionic medium ions, having the same and opposite charge sign respectively, to the species \( i \), and \( m \) denotes the molality of the ionic medium 1-1 electrolyte, NX. The Pitzer parameters \( \beta^{(0)L}, \beta^{(1)L}, C_L \) are tabulated for many electrolytes [91 PIT]. However, the information on the temperature derivatives of the mixing terms \( (\partial\phi/\partial T)_p \) and \( (\partial\psi/\partial T)_p \) is scarce due to the small number of studies of the enthalpy of mixing of electrolyte solutions that have been analysed with this method. We did not include the analytical expression of the contribution of \( r L_1 \) term in order not to complicate the resulting equation. From a practical point of view it is
more convenient to correct the experimental values of $\Delta_rH_m$ with the contribution from the term $r/1$, when necessary, using the values of the relative partial molar enthalpies of water in electrolyte solutions from the thermochemical tables or calculating them using the Pitzer model.

**IX.10.2. The calculation of the standard enthalpy of a reaction from experimental $\Delta_rH_m$ data using the SIT model**

The corresponding equations for the concentration dependence of the relative partial molar enthalpy of cation M present at trace concentration in an ionic medium electrolyte NX and for relative partial molar enthalpy of water ($L_1$) are given below (considering the numerical factor $1.5 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$ to be a constant, independent of temperature)

\[
L_{2M} = -RT^2 \left( \frac{\partial \ln \gamma_M}{\partial T} \right)_{p,m_j} = \frac{3}{4} \frac{A_L Z_i^2 \sqrt{T_m}}{1 + 1.5 \sqrt{T_m}} - RT^2 \varepsilon_L (M,X) m_X
\]

\[
L_1 = \frac{M_m}{1000} \left[ - \frac{3}{2} \frac{A_L}{1.5^3} \left( t - 2 \ln t - \frac{1}{t} \right) + RT^2 \nu_N Z_N m^2 \varepsilon_L (N,X) \right]
\]

where $t = 1 + 1.5 \sqrt{T_m}$ was defined before.

The concentration dependence of the heat of reaction studied at trace concentrations of reactants/products in a solution with a large excess of an 1-1 ionic medium is then equal to:

\[
\Delta_rH_m - r L_1 = \Delta_rH_m^\circ + \frac{3}{4} \frac{A_L \Delta(Z^2) \sqrt{T_m}}{1 + 1.5 \sqrt{T_m}} - RT^2 m \Delta \varepsilon_L
\]

where

\[
\Delta \varepsilon_L = \sum_i \nu_i \varepsilon_L (i,j)
\]

here subscript $i$ refers to a reaction participant and $j$ to the counter-ion of the ionic medium.

**Example 15:**

This example refers to the determination of the $\Delta_rH_m^\circ$ value for the reaction $\text{Mg}(c) + 2\text{H}^+ \rightleftharpoons \text{Mg}^{2+} + \text{H}_2(g)$, which is equal to the standard enthalpy of formation of the magnesium ion. In 1943 Shomate and Huffman [43SHO/HUF] measured the enthalpy of reaction of very pure magnesium metal in $1.02 \text{ mol} \cdot \text{kg}^{-1} \text{ HCl}$ at 298.15 K and obtained the value of $\Delta_rH_m = -465.48 \pm 0.17 \text{ kJ} \cdot \text{mol}^{-1}$ (as recalculated by Morss and Williams
The concentration dependence of heats of reactions

[83MOR/WIL] using a more accurate value of the molar mass of Mg). This measurement has been accepted as a standard for metal-dissolution calorimetry and has been confirmed many times (see [83MOR/WIL]).

For this reaction we obtain

$$\Delta_r H_m^o = \Delta_r H_m - L_{2,Mg^{2+}} + 2L_{2,H^+}$$

The corresponding statements for the relative partial molar enthalpies of this reaction participants in a solution with a large excess of HCl based on the Pitzer model are given as follows

$$L_{2,Mg} = A_L \left[ \frac{\sqrt{T_m}}{1 + b \sqrt{T_m}} + \frac{2}{b} \ln \left( 1 + b \sqrt{T_m} \right) \right] - 4RT^2m^2 \beta_{H,Cl}^{(1)L} g'(I_m) \frac{g'(I_m)}{I_m}$$

$$- 2RT^2m \left[ \beta_{Mg,Cl}^{(0)L} + \beta_{Mg,Cl}^{(1)L} \right]$$

$$- RT^2 \left[ 2 \left( \frac{\partial \phi_{Mg,H}}{\partial T} \right)_{p} + m \left( \frac{\partial \psi_{Mg,H,Cl}}{\partial T} \right)_{p} \right]$$

$$- 2RT^2m^2 C_{Mg,Cl}^L - 2RT^2m^2 C_{H,Cl}^L$$

$$L_{2,H} = \frac{A_L}{4} \left[ \frac{\sqrt{T_m}}{1 + b \sqrt{T_m}} + \frac{2}{b} \ln \left( 1 + b \sqrt{T_m} \right) \right] - 2RT^2m \beta_{H,Cl}^{(0)L}$$

$$- 2RT^2m \frac{\beta_{H,Cl}^{(1)L}}{\alpha^2 I_m} \left[ 1 - \left( 1 + \alpha \sqrt{T_m} - \frac{\alpha^2 I_m}{2} \right) e^{-\alpha \sqrt{T_m}} \right] - 3RT^2m^2 C_{H,Cl}^L$$

where $m$ stands for the molality of HCl. The required values of the Pitzer parameters for the HCl and MgCl$_2$ electrolytes are available from the compilation [91PIT]:

$$\beta_{H,Cl}^{(0)L} = -3.081 \times 10^{-4} \text{ kg} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}, \beta_{H,Cl}^{(1)L} = 1.419 \times 10^{-4} \text{ kg} \cdot \text{mol}^{-1} \cdot \text{K}^{-1},$$

$$C_{H,Cl}^L = -3.107 \times 10^{-8} \text{ kg}^2 \cdot \text{mol}^{-2} \cdot \text{K}^{-1},$$

$$\beta_{Mg,Cl}^{(0)L} = -1.94 \times 10^{-4} \text{ kg} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}, \beta_{Mg,Cl}^{(1)L} = 2.78 \times 10^{-3} \text{ kg} \cdot \text{mol}^{-1} \cdot \text{K}^{-1},$$

$$C_{Mg,Cl}^L = -5.8 \times 10^{-5} \text{ kg}^2 \cdot \text{mol}^{-2} \cdot \text{K}^{-1}.$$

The temperature derivatives of the mixing terms $(\partial \phi_{Mg,H}/\partial T)_p$ and $(\partial \psi_{Mg,H,Cl}/\partial T)_p$ are not given in the literature due to lack of the experimental determinations of the enthalpy of mixing HCl and MgCl$_2$ solutions. Only rough estimations can be made from the potentiometric determinations of the mean activity coefficients of HCl in its mixtures with alkali earth halides at different temperatures [86ROY/GIB, 90ROY/RIC, etc.]: $(\partial \phi_{Mg,H}/\partial T)_p = (-8 \pm 4) \times 10^{-4} \text{ kg} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ and $(\partial \psi_{Mg,H,Cl}/\partial T)_p = (5 \pm 5) \times 10^{-4} \text{ kg}^2 \cdot \text{mol}^{-2} \cdot \text{K}^{-1}$.
Estimations of ionic strength corrections of thermodynamic data

using the reported sets of \( \phi \) and \( \psi \) values without consideration of the higher order electrostatic terms. We did not take into account the contribution of the unsymmetrical mixing terms. As pointed out by Pitzer [83PIT] the effect of the higher order electrostatic term is non-linear with the ionic strength only at low concentrations and can be omitted for simplicity.

The calculated values are \( L_{2,H} = 1.37 \text{ kJ} \cdot \text{mol}^{-1} \) and \( L_{2,Mg} = 3.62 \pm 0.25 \text{ kJ} \cdot \text{mol}^{-1} \), where the error is due to uncertainty in the contributions of the mixing terms. Therefore, \( \Delta_r H^0_m = \Delta_l H^0(Mg^{2+}, 298.15 \text{ K}) = \Delta_r H_m - L_{2,Mg} + 2L_{2,H} = (-465.48 \pm 0.17) - (3.62 \pm 0.25) + 2 \times 1.37 = -466.36 \pm 0.30 \text{ kJ} \cdot \text{mol}^{-1} \).

Using the SIT model, we obtain the following equations for the relative partial molar enthalpies of the reaction participants:

\[
L_{2,Mg^{2+}} = 3 \frac{A_L \sqrt{T_m}}{1 + 1.5 \sqrt{T_m}} - RT^2 \varepsilon_L(Mg^{2+}, Cl^-) m
\]

\[
L_{2,H^+} = 3 \frac{A_L \sqrt{T_m}}{4(1 + 1.5 \sqrt{T_m})} - RT^2 \varepsilon_L(H^+, Cl^-) m
\]

where \( m \) stands for the molality of HCl. The values of the SIT interaction coefficients can be evaluated from the available [91PIT] data on the heats of dilution of MgCl\(_2\) and HCl: \( \varepsilon_L(Mg^{2+}, Cl^-) = (-1.2 \pm 0.2) \times 10^{-3} \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \), \( \varepsilon_L(H^+, Cl^-) = (-1.0 \pm 0.1) \times 10^{-3} \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \). The calculated results are: \( L_{2,H} = 1.35 \pm 0.16 \text{ kJ} \cdot \text{mol}^{-1} \) and \( L_{2,Mg} = 3.30 \pm 0.30 \text{ kJ} \cdot \text{mol}^{-1} \) (the uncertainties have been doubled to take the neglect of specific mixing effects in the SIT model into account). Hence, \( \Delta_r H^0_m = \Delta_l H^0(Mg^{2+}, 298.15 \text{ K}) = (-465.48 \pm 0.17) - (3.30 \pm 0.30) + 2 \times (1.35 \pm 0.16) = -466.08 \pm 0.41 \text{ kJ} \cdot \text{mol}^{-1} \).

Both of the values, \(-466.36 \pm 0.30 \text{ kJ} \cdot \text{mol}^{-1}\) from the Pitzer model and \(-466.08 \pm 0.41 \text{ kJ} \cdot \text{mol}^{-1}\) from the SIT model can be compared with the CODATA [89COX/WAG] recommended value \(-467.0 \pm 0.6 \text{ kJ} \cdot \text{mol}^{-1}\), which is based on different experimental sets varying from \(-465.3 \pm 1.0 \text{ to } -468.86 \pm 0.80 \text{ kJ} \cdot \text{mol}^{-1}\). These values of the enthalpy of formation of the magnesium ion were obtained from a number of different thermochemical cycles. In most cases the values of \( \Delta_r H^0_m \) deduced by the authors of the original works were quoted in [89COX/WAG] without critical discussion of the extrapolation procedures employed, although this might be an additional reason for the discrepancies between the reported values of the enthalpy changes at infinite dilution. For instance, the extrapolation equation widely used by Vasil’ev with coworkers [67VAS, 78VAS/YAS2] is actually based on the assumption \( H_{2,m} = H^0_2 + \phi L \) (see Eq. (5) in [78VAS/YAS2]), where \( H_{2,m} \) is the enthalpy of a species in a solution of finite concentration, \( H^0_2 \) stands for the enthalpy of the species at infinite dilution, \( \phi L \) is the relative apparent molar enthalpy. This relation is in contradiction to the strict thermodynamic relation \( H_{2,m} = H^0_2 + L_2 \), which follows from the definition of the relative partial molar enthalpy of the species of the solution (see Eq. (IX.40)). The relative apparent molar enthalpy is not a characteristic of the solute, in fact it is the characteristic of the system, which follows from the following relation [58SHAR/OWE]

\[
L = n_1 L_1 + n_2 L_2 = n_2 \phi L
\]
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where $L$ is the relative enthalpy of the solution, $n_1$ and $n_2$ stand for the concentrations of water and solute, respectively. Hence, the extrapolation equation used by Vasil’ev and coworkers seems to be based on erroneous assumptions, and the numerous results of $\Delta_r H^o_m$ obtained using this equation should be revised; a discussion is given in [96PLY/GRE].

Example 16:

The previous example referred to a situation where very accurate data for $\Delta_r H_m$ in an ionic medium was available, but where the $\Delta_r H^o_m$ value from the CODATA recommendation had a rather large uncertainty. In this example we will discuss the dissociation of water in NaCl media, where the $\Delta_r H^o_m = 55.82 \pm 0.06$ kJ mol$^{-1}$ [89COX/WAG] is known with very high precision, but where individual experimental results might be subject to undiscovered experimental errors.

A number of sets of $\Delta_r H_m$ data for the reaction $\text{H}_2\text{O}(l) \rightleftharpoons \text{H}^+ + \text{OH}^-$ in NaCl ionic media have been reported in the literature at 298.15 K; Harned and Mannweiler [35HAR/MAN] have obtained the $\Delta_r H_m$ values at different NaCl concentrations from the temperature dependence of the very accurate $\log_{10} K$ data in the temperature range 0-60°C; Lobanov and Vasil’ev [69LOB/VAS] have made calorimetric determinations of the corresponding quantities; Busey and Mesmer [78BUS/MES] have tabulated the $\Delta_r H_m$ values consistent with $\log_{10} K$ data at different temperatures; Maeda [86MAE] has reported the calorimetric results. These values of the enthalpy changes, corrected for the values of the relative partial molar enthalpies of water in NaCl solutions, are given in Table IX.15.

For this reaction one obtains

$$\Delta_r H^o_m = \Delta_r H_m + L_1 - L_{2.H} - L_{2.OH}$$

The Pitzer model results on the following equations for the relative partial molar enthalpies of the reaction participants:

$$L_{2.H} = \frac{A_L}{4} \left[ \frac{\sqrt{I_m}}{1 + b \sqrt{I_m}} + \frac{2}{b} \ln \left( 1 + b \sqrt{I_m} \right) \right] - RT^2 m^2 \beta_{\text{Na,Cl}}^{(1)l} \frac{g'(I_m)}{I_m}$$

$$- 2RT^2 m \left[ \beta_{\text{H,Cl}}^{(0)l} \right]$$

$$- RT^2 m \left[ 2 \left( \frac{\partial \phi_{\text{H,Na}}}{\partial T} \right)_p + m \left( \frac{\partial \psi_{\text{H,Na,Cl}}}{\partial T} \right)_p \right]$$

$$- 2RT^2 m^2 C_{\text{Na,Cl}}^L - RT^2 m^2 C_{\text{Na,Cl}}^L$$

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\[
L_{2,\text{OH}} = \frac{A_L}{4} \left[ \frac{\sqrt{T_m}}{1 + b\sqrt{T_m}} + \frac{2}{b} \ln \left( 1 + b\sqrt{T_m} \right) \right] - RT^2m^2\beta_{\text{Na,Cl}}^{(1)\text{L}} \frac{g'(I_m)}{I_m} - 2RT^2m \left[ \beta_{\text{Na,OH}}^{(0)\text{L}} + \beta_{\text{Na,OH}}^{(1)\text{L}} g(I_m) \right] - RT^2m \left[ 2 \left( \frac{\partial \phi_{\text{OH,Cl}}}{\partial T} \right)_p + m \left( \frac{\partial \psi_{\text{OH,Na,Cl}}}{\partial T} \right)_p \right]
\]

\[-2RT^2m^2C_L^{\text{Na,OH}} - RT^2m^2C_L^{\text{Na,Cl}} \]

The Pitzer parameters are available [91PIT] for the single electrolytes NaOH, HCl and NaOH (the dimensions are kg \cdot mol^{-1} \cdot K^{-1} for the \beta^{(0)\text{L}} and \beta^{(1)\text{L}}; kg^2 \cdot mol^{-2} \cdot K^{-1} for the \(C^L\)):

\[
\begin{align*}
\beta_{\text{H,Cl}}^{(0)\text{L}} &= -3.081 \times 10^{-4}, & \beta_{\text{H,Cl}}^{(1)\text{L}} &= 1.419 \times 10^{-4}, & C_{\text{H,Cl}}^L &= -3.107 \times 10^{-5}, \\
\beta_{\text{Na,OH}}^{(0)\text{L}} &= 7.00 \times 10^{-4}, & \beta_{\text{Na,OH}}^{(1)\text{L}} &= 1.34 \times 10^{-4}, & C_{\text{Na,OH}}^L &= -9.47 \times 10^{-5}, \\
\beta_{\text{Na,Cl}}^{(0)\text{L}} &= 7.159 \times 10^{-4}, & \beta_{\text{Na,Cl}}^{(1)\text{L}} &= 7.005 \times 10^{-4}, & C_{\text{Na,Cl}}^L &= -5.27 \times 10^{-5}.
\end{align*}
\]

The parameters for the NaOH solutions are valid up to concentration 4.2 mol \cdot kg^{-1}, those for the HCl solutions up to 4.5 mol \cdot kg^{-1}. The temperature derivatives of the mixing terms \(\left( \partial \phi_{\text{H,Na}}/\partial T \right)_p\), \(\left( \partial \psi_{\text{H,Na,Cl}}/\partial T \right)_p\), \(\left( \partial \phi_{\text{Cl,OH}}/\partial T \right)_p\), \(\left( \partial \psi_{\text{Cl,OH,Na}}/\partial T \right)_p\) are not known. We assume that the sum of the terms \(\left( \partial \phi_{\text{H,Na}}/\partial T \right)_p + \left( \partial \phi_{\text{Cl,OH}}/\partial T \right)_p\) is less than \(\pm 2 \times 10^{-4}\), and that the sum of the terms \(\left( \partial \psi_{\text{H,Na}}/\partial T \right)_p + \left( \partial \psi_{\text{Cl,OH,Na}}/\partial T \right)_p\) is less than \(\pm 3 \times 10^{-5}\) based on the available information on the temperature dependence of the mixing terms in some binary systems [90HOL,MES]. Using the equations given above we have calculated the values of the sum of the \(L_{2,\text{H}} + L_{2,\text{OH}}\) at different NaCl concentrations, considering the possible contribution of the mixing terms as an estimate of the uncertainty of the derived sum. The value of \(\Delta_s \tilde{H}_m^\circ\) obtained from the experimental enthalpy changes are given in Table IX.15, the errors quoted are the square root of the sum of the squares of the uncertainty of experimental determinations and the estimated uncertainty of the sum of \(L_{2,\text{H}} + L_{2,\text{OH}}\).

From the SIT model we obtain for the relative partial molar enthalpies of \(\text{H}^+\) and \(\text{OH}^-\) in NaCl solutions:

\[
L_{2,\text{H}^+} = \frac{3}{4} A_L \sqrt{T_m} - RT^2 \varepsilon_L(\text{H}^+, \text{Cl}^-) m
\]

\[
L_{2,\text{OH}^-} = \frac{3}{4} A_L \sqrt{T_m} - RT^2 \varepsilon_L(\text{Na}^+, \text{OH}^-) m
\]

The values of the SIT interaction coefficients are obtained from the enthalpy of dilution data for HCl and NaOH solutions: \(\varepsilon_L(\text{H}^+, \text{Cl}^-) = (-1.0 \pm 0.1) \times 10^{-1} \ \text{kg} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}\),
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\[ \varepsilon_L(\text{Na}^+, \text{OH}^-) = (0.5 \pm 0.2) \times 10^{-3} \text{ kg} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}. \]

These values were used to calculate the sum of the relative partial molar enthalpies of H\(^+\) and OH\(^-\) in NaCl solutions and to obtain the values of \(\Delta_r H_m^\circ\) from the experimental enthalpy changes (see Table IX.15). When estimating the possible error in the \(\Delta_r H_m^\circ\), the uncertainty in the correction was doubled, to account for the specific mixing effects which are ignored in this model.

The values of the sum \(L_{2H} + L_{2OH}\) calculated from the Pitzer and the SIT models, are in satisfactory agreement with one another only at concentrations of NaCl less than 3-3.5 mol·kg\(^{-1}\), where the difference between them is less than 1 kJ·mol\(^{-1}\), with an expected uncertainty within 1.0-1.2 kJ·mol\(^{-1}\). In this concentration range the experimental values of \(\Delta_r H_m\), reported in the different studies, are in acceptable agreement with one another. The values of the enthalpy change at infinite dilution, \(\Delta_r H_m^\circ\), calculated based on either the Pitzer or the SIT approaches are also in excellent agreement (within the expected uncertainties of the calculations) with the CODATA recommendation. The analysis of the results at higher NaCl concentrations is ambiguous: the Pitzer and the SIT models result in quite different values of the sum of the relative partial molar enthalpies of the H\(^+\) and OH\(^-\) ions, and the differences exceed the expected uncertainty of the calculated values. One also obtains different values of \(\Delta_r H_m^\circ\) from the same experimental data at high NaCl concentrations, using the two models. The reasons can be the approximate character of the postulates used in the SIT approach and a larger than expected contribution of the mixing terms in the Pitzer model. This ambiguity cannot be resolved due to lack of the experimental determinations of the enthalpy of mixing for the NaCl-NaOH aqueous mixtures. The example indicates that the Pitzer model gives a precise description of the ionic strength/medium dependence of the enthalpy of reaction even at high concentrations, provided that all the relevant Pitzer parameters for the reaction participants are known. Unfortunately, the data on the temperature derivative of the mixing parameters for the Pitzer models are scarce, and the omission of these terms in a “reduced” Pitzer model at high concentrations may result in errors, which are comparable with those of the SIT model at these concentrations. We recommend to use the Pitzer and SIT models only for the \(\Delta_r H_m\) data in the limited ionic strength range up to 3-4 mol·kg\(^{-1}\).

**IX.10.3. The extrapolation equations for the determination of the standard enthalpy of reaction from the experimental \(\Delta_r H_m\) data based on the Pitzer and the SIT models**

The previous discussion was made for a reaction, where the Pitzer or the SIT parameters are known for the reaction participants in the ionic medium. However, these parameters are in general only known for the single ion combinations, and not for complexes. When discussing the experimental results for the enthalpy change of complex formation reactions using the Pitzer model it is convenient to write Eq. (IX.69) as follows (as before, this equation is valid only for the case of reactions studied at trace concentrations of the
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Table IX.15: The results of the calculation of the $\Delta_r H_m^\circ$ value for the reaction $\text{H}_2\text{O}(l) \rightleftharpoons \text{H}^+ + \text{OH}^-$ in NaCl medium at 298.15 K from the heat effects at finite concentrations based on the Pitzer and the SIT model. The uncertainties of the experimental results are quoted from the original studies, the uncertainties of the calculated values of $\Delta_r H_m^\circ$ result from both of the claimed error in the experimental data and the error of the correction terms. The CODATA recommended value for the reaction of water dissociation is $\Delta_r H_m^\circ = 55.82 \pm 0.06 \text{ kJ} \cdot \text{mol}^{-1}$ [89COX/WAG].

<table>
<thead>
<tr>
<th>Reference</th>
<th>$m$ (mol·kg$^{-1}$)</th>
<th>$\Delta_r H_m + L_1$ (kJ·mol$^{-1}$)</th>
<th>The calculated value of $\Delta_r H_m^\circ$, kJ·mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>The Pitzer model</td>
</tr>
<tr>
<td>[35HAR/MAN]</td>
<td>0.51</td>
<td>$57.17 \pm 0.3^a$</td>
<td>55.99±0.34</td>
</tr>
<tr>
<td></td>
<td>1.01</td>
<td>$57.55 \pm 0.3$</td>
<td>56.06±0.44</td>
</tr>
<tr>
<td></td>
<td>2.01</td>
<td>$58.08 \pm 0.3$</td>
<td>55.89±0.74</td>
</tr>
<tr>
<td></td>
<td>3.01</td>
<td>$58.49 \pm 0.3$</td>
<td>55.25±1.13</td>
</tr>
<tr>
<td>[69LOB/VAS]</td>
<td>0.51</td>
<td>$57.24 \pm 0.13$</td>
<td>56.06±0.21</td>
</tr>
<tr>
<td></td>
<td>1.02</td>
<td>$57.50 \pm 0.16$</td>
<td>56.00±0.36</td>
</tr>
<tr>
<td></td>
<td>2.09</td>
<td>$57.99 \pm 0.10$</td>
<td>55.73±0.69</td>
</tr>
<tr>
<td></td>
<td>3.20</td>
<td>$58.49 \pm 0.11$</td>
<td>55.00±1.18</td>
</tr>
<tr>
<td>[78BUS/MES]</td>
<td>0.50</td>
<td>$57.12 \pm 0.19$</td>
<td>55.94±0.24</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>$57.41 \pm 0.23$</td>
<td>55.92±0.39</td>
</tr>
<tr>
<td></td>
<td>3.00</td>
<td>$57.93 \pm 0.71$</td>
<td>54.70±1.30</td>
</tr>
<tr>
<td></td>
<td>5.00</td>
<td>$58.15 \pm 1.17$</td>
<td>(51.46±2.34)$^b$</td>
</tr>
<tr>
<td>[86MAE]</td>
<td>4.37</td>
<td>$60.29 \pm 0.30$</td>
<td>54.89±1.74</td>
</tr>
<tr>
<td></td>
<td>5.61</td>
<td>$62.45 \pm 0.30$</td>
<td>(54.32±2.38)$^b$</td>
</tr>
</tbody>
</table>

$^a$ Our estimation of the uncertainty of the data from [35HAR/MAN];

$^b$ The concentration exceeds the range of applicability of the Pitzer parameters for the HCl and NaOH electrolytes.
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reaction participants in solutions with a large excess of supporting 1-1 electrolyte):

\[
\Delta_r H_m^c = \Delta_r H_m - rL_1 - \frac{\Delta(Z^2)A_L}{4} \left[ \frac{\sqrt{T_m}}{1 + b\sqrt{T_m}} + \frac{2}{b} \ln \left( 1 + b\sqrt{T_m} \right) \right]
+ RT^2 \Delta(Z^2)m^2 \beta_{NL}^{(1) L} g'(I_m) + RT^2 m^2 \Delta[Z]C_{NX}^L + 2RT^2 m X_1
+ 2RT^2 m X_2 g(I_m) + 2RT^2 m^2 X_3
\]  

(IX.73)

where

\[
X_1 = \Delta \beta^{(0) L} + \Delta \left( \frac{\partial \phi}{\partial T} \right)_p = \sum_i \nu_i \beta_{ij}^{(0) L} + \sum_i \nu_i \left( \frac{\partial \phi_i}{\partial T} \right)_p
\]

\[
X_2 = \Delta \beta^{(1) L} = \sum_i \nu_i \beta_{ij}^{(1) L}
\]

\[
X_3 = \Delta C^L + \frac{1}{2} \Delta \left( \frac{\partial \psi}{\partial T} \right)_p = \sum_i \nu_i C_{ij}^L + \frac{1}{2} \sum_i \nu_i \left( \frac{\partial \psi_i}{\partial T} \right)_p
\]

the notation has been defined before (see Eq. (IX.69)). As practically all experimental determinations of the enthalpy changes for the complex formation reactions have been studied at relatively high concentration of the ionic medium electrolytes, there is no reason to take into account the contribution of higher order electrostatic terms for the reaction participants, because this contribution is approximately linear with the concentration [83PIT] and therefore is accounted for mainly in the term \(X_1\).

The corresponding extrapolation equation for the SIT model is given by Eq. (IX.72).

Example 17:

In order to test the equations for the description of the concentration dependence of \(\Delta_r H_m\) and the determination of \(\Delta_r H_m^c\) at infinite dilution, we have used data for the reaction \(H_2O(1) \rightarrow H^+ + OH^-\) in NaClO\(_4\) ionic medium. For this reaction the value of \(\Delta_r H_m^c\) is recommended by CODATA [89COX/WAG]. The experimental calorimetric data in NaClO\(_4\) medium at 25°C have been obtained in three laboratories by Arneke and Kakolowicz [67ARN/KAK] at 3.50 mol \cdot kg\(^{-1}\), Lobanov and Vasil’ev [69LOB/VAS] at 0.51-3.50 mol \cdot kg\(^{-1}\), and Maeda [86MAE] at 3.50 and 4.95 mol \cdot kg\(^{-1}\). The results at the same ionic medium concentration, 3.50 mol \cdot kg\(^{-1}\), agree within \(\pm 0.25\) kJ \cdot mol\(^{-1}\).

The experimental results on \(\Delta_r H_m\) corrected for the value of \(L_1\) are given in Table IX.16.

We used the weighted linear least-square method to obtain the regression parameters for both the Pitzer and the Brønsted-Guggenheim-Scatchard models. The regression analysis was made by using the uncertainty estimates in \(\Delta_r H_m\), equal to \(\pm 0.3\) kJ \cdot mol\(^{-1}\). The point at highest molality, 4.95 mol \cdot kg\(^{-1}\), was not used in the regression, because as discussed

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Table IX.16: The results of the experimental determinations of the $\Delta_r H_m$ for the reaction $H_2O(l) \rightleftharpoons H^+ + OH^-$ in NaClO$_4$ medium. The uncertainties are given as claimed by the authors.

<table>
<thead>
<tr>
<th>Reference</th>
<th>$m$ (NaClO$_4$) (mol · kg$^{-1}$)</th>
<th>$\Delta_r H_m + L_1$ (kJ · mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[67ARN/KAK]</td>
<td>3.50</td>
<td>54.82 ± 0.13</td>
</tr>
<tr>
<td>[69LOB/VAS]</td>
<td>0.51</td>
<td>56.49 ± 0.27</td>
</tr>
<tr>
<td></td>
<td>1.05</td>
<td>56.14 ± 0.07</td>
</tr>
<tr>
<td></td>
<td>2.20</td>
<td>55.64 ± 0.09</td>
</tr>
<tr>
<td></td>
<td>3.50</td>
<td>55.07 ± 0.09</td>
</tr>
<tr>
<td>[86MAE]</td>
<td>3.50</td>
<td>55.02 ± 0.30</td>
</tr>
<tr>
<td></td>
<td>4.95</td>
<td>56.09 ± 0.30</td>
</tr>
</tbody>
</table>

in the previous example, the concentration range used should not exceed 4 mol · kg$^{-1}$ (this point also deviates from the general trend of the $\Delta_r H_m$ values). The results of the regression are given in Table IX.17 and shown in Figure IX.40.

For the case of the Pitzer equation we tested 3 models:

- with the determination of all the relevant parameters,
- neglecting the contribution of the $X_3$ term, *i.e.*, all the ternary interactions,
- neglecting the contribution of the $X_2$ and $X_3$ terms, *i.e.*, neglecting the all ternary interactions and the ionic strength dependence of the second virial coefficients.

The value of the Pitzer terms can only be predicted for $X_2$: $X_2 = \beta_{Na,OH}^{(1)L} + \beta_{H,ClO_4}^{(1)L} = 1.34 \times 10^{-4} + 19.31 \times 10^{-4} \approx 2.1 \times 10^{-3}$ kg · mol$^{-1}$ · K$^{-1}$. As the temperature derivatives of the mixing terms are not available, we can only estimate the values of the parameters $X_1$ and $X_3$: $X_1 \approx \beta_{Na,OH}^{(0)L} + \beta_{H,ClO_4}^{(0)L} = 7.00 \times 10^{-4} + 4.905 \times 10^{-4} \approx 1.19 \times 10^{-3}$ kg · mol$^{-1}$ · K$^{-1}$, $X_3 \approx C_{Na,OH}^{L} + C_{H,ClO_4}^{L} = -9.47 \times 10^{-5} - 5.89 \times 10^{-5} \approx -1.5 \times 10^{-4}$ kg$^2$ · mol$^{-2}$ · K$^{-1}$. As in Examples 5 and 6 where we attempted to determine the Pitzer terms for a log$_{10} \tilde{K}$ regression, we also obtain in this case very large uncertainties in the estimated values of the fitting parameters. By neglecting the contribution of the ternary terms we obtain more precise estimates of the unknowns. Even so, the error in the $X_2$ term exceeds the magnitude of this term. However, the contribution of this term affects the value of
Table IX.17: The results of the least square determination of unknowns in fitting equations for the reaction \(\text{H}_2\text{O(l)} \rightleftharpoons \text{H}^+ + \text{OH}^-\) in NaClO4 medium. All the errors are given as 3\(\sigma\). The concentration units: for \(X_1, X_2, \Delta\varepsilon_L\) - kg \cdot mol\(^{-1}\) \cdot K\(^{-1}\), for \(X_3\) - kg\(^2\) \cdot mol\(^{-2}\) \cdot K\(^{-1}\).

<table>
<thead>
<tr>
<th>Fitting equation</th>
<th>(\Delta_r H_m^o) (\text{kJ} \cdot \text{mol}^{-1})</th>
<th>Concentration parameters</th>
<th>The mean square error per unit (\sigma_o)(^{(a)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pitzer(^{(b)})</td>
<td>55.50 ± 0.32</td>
<td>(X_1 = (1.11 \pm 0.08) \times 10^{-3})</td>
<td>0.406</td>
</tr>
<tr>
<td>Pitzer(^{(c)})</td>
<td>55.88 ± 1.40</td>
<td>(X_1 = (1.02 \pm 0.31) \times 10^{-3}) (X_2 = (1.3 \pm 4.4) \times 10^{-3})</td>
<td>0.419</td>
</tr>
<tr>
<td>Pitzer</td>
<td>57.30 ± 5.38</td>
<td>(X_1 = (-0.5 \pm 5.5) \times 10^{-3}) (X_2 = (9.1 \pm 29.0) \times 10^{-3}) (X_3 = (2.3 \pm 9.3) \times 10^{-4})</td>
<td>0.450</td>
</tr>
<tr>
<td>SIT</td>
<td>55.70 ± 0.35</td>
<td>(\Delta\varepsilon_L = (0.85 \pm 0.16) \times 10^{-3})</td>
<td>0.425</td>
</tr>
<tr>
<td>CODATA</td>
<td>55.82 ± 0.06</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a) the mean square error per unit weight \(\sigma_o\) is defined as \(\sigma_o^2 = \sum w(\Delta_r H_m - \Delta_r H_m,\text{calc})^2/(n - m)\), where \(w\) is the weighting factor determined as the reciprocal square of the estimated uncertainty in \(\Delta_r H_m\) value; \(\Delta_r H_m,\text{calc}\) is the value of the heat of reaction calculated using the obtained regression parameters; \(n\) is the number of experimental data; \(m\) is the number of variables;

(b) neglecting the contribution of \(X_2\) and \(X_3\) terms;

(c) neglecting the contribution of \(X_3\) term.

The enthalpy change at infinite dilution. The application of the Pitzer equation both for the description of the concentration dependence of heats of reaction, and of \(\log_{10} K\) data is an ill-conditioned task. The main problem is the reliable estimation of the \(\Delta\beta^{(1)L}\) parameter, which determines the concentration dependence of the second virial coefficient in the Pitzer approach and, therefore, has a substantial influence on the estimated value of \(\Delta_r H_m^o\) for the reaction. However, the determination of \(\Delta\beta^{(1)L}\) parameter requires precise experimental data at low ionic strengths, where the relative contribution of this parameter to the value of \(\Delta B^L\) is most pronounced.

The SIT model results in a reliable value of the \(\Delta_r H_m^o\) term, and the value \(\Delta\varepsilon_L = (0.85 \pm 0.16) \times 10^{-3}\) kg \cdot mol\(^{-1}\) \cdot K\(^{-1}\) obtained by the regression is consistent with the estimate based on the parameters \(\varepsilon_L(\text{H}^+, \text{ClO}_7^-)\) and \(\varepsilon_L(\text{Na}^+, \text{OH}^-)\), obtained from the enthalpies of dilution of the corresponding electrolytes: \(\Delta\varepsilon_L = \varepsilon_L(\text{H}^+, \text{ClO}_7^-) + \varepsilon_L(\text{Na}^+, \text{OH}) = (0.9 \pm 0.2) \times 10^{-3} + (0.5 \pm 0.2) \times 10^{-3} = (1.4 \pm 0.3) \times 10^{-3}\) kg \cdot mol\(^{-1}\) \cdot K\(^{-1}\).

It should be kept in mind that the omission of the parameter \(\Delta\beta^{(1)L}\) may be essential
Estimations of ionic strength corrections of thermodynamic data

Figure IX.40: The parametrization of the SIT and different variants of the Pitzer models (see text for details) from the experimental values of $\Delta_r H_m$ for the reaction $\text{H}_2\text{O}(l) \rightleftharpoons \text{H}^+ + \text{OH}^-$ in NaClO$_4$ medium at 298.15 K and 1 atm.

The accuracy of the $\Delta_r H_m$ determination. The Pitzer equation with only the $\Delta \beta^{(0)} L$ is not analogous to the SIT equation (see previous discussion of the simplified one-parameter Pitzer and the SIT model IV in Examples 6 and 7). The choice between the Pitzer and the SIT models must be based on the number of data available, the ionic strength range used and the precision of the experimental results. In our experience, the existing data on heats of complex formation reactions do not allow the use of extrapolation equations more complex than the linear expression used here. In principle, one could try to estimate the values of the Pitzer parameter $\beta^{(1)} L$ using a procedure like the one employed to estimate the $\beta^{(1)}$ parameters. This can be done by comparison of the analytical equations for the relative partial molar enthalpies based on the SIT and the simplified (without $C^L$ term) Pitzer approaches. However, an analysis of the typical values of the $C^L$ parameters for the different electrolytes from the available compilation [91PIT] showed that in general the contribution of the $C^L$ term cannot be neglected even at moderate (1-2 mol · kg$^{-1}$) ionic strengths.

Example 18:

Another example of the use of the Pitzer and the SIT model to obtain the value of $\Delta_r H_m^0$ for a complex formation equilibrium is the determination of $\Delta_r H_m^0$ for the reaction
The concentration dependence of heats of reactions

Table IX.18: The experimental values of the enthalpy change for the reaction Hg\(^{2+}\) + Cl\(^-\) ⇌ HgCl\(^+\) in NaClO\(_4\) ionic medium at 298.15 K, with our estimations of the uncertainties.

<table>
<thead>
<tr>
<th>Reference</th>
<th>(m) (NaClO(_4)) (mol · kg(^{-1}))</th>
<th>(\Delta_r H_m) (kJ · mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>[64CHR/IZA]</td>
<td>0.51</td>
<td>-23.0 ± 1.0</td>
</tr>
<tr>
<td>[65ARN]</td>
<td>3.50</td>
<td>-24.2 ± 1.0</td>
</tr>
<tr>
<td>[75CIA/GRI]</td>
<td>1.05</td>
<td>-23.2 ± 0.5</td>
</tr>
<tr>
<td>[80VAS/KOZ]</td>
<td>0.51</td>
<td>-23.64 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>1.05</td>
<td>-24.35 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>2.20</td>
<td>-24.60 ± 0.5</td>
</tr>
</tbody>
</table>

Hg\(^{2+}\) + Cl\(^-\) ⇌ HgCl\(^+\) at 298.15 K. There are a number of experimental calorimetric determinations of the enthalpies of this reaction in NaClO\(_4\) medium [64CHR/IZA, 65ARN, 75CIA/GRI, 80VAS/KOZ], see Table IX.18.

We should notice that the example considered is exceptional in the sense that we have experimental results from 4 independent laboratories, which are in good agreement with one another.

We used the simplified Pitzer-type of the regression neglecting the contribution of the \(X_3\) term. For this reaction \(\Delta(Z^2) = -4\), \(\Delta|Z| = -2\). The function to be fitted is given by

\[
Y = \Delta_r H_m + A_L \left[ \frac{\sqrt{I_m}}{1 + b \sqrt{I_m}} + \frac{2}{b} \ln \left( 1 + b \sqrt{I_m} \right) \right] - 4RT^2m^2\beta_{Na,ClO_4}^{(1)L} \frac{g'(I_m)}{I_m} - 2RT^2m^2c_{Na,ClO_4}^L
\]

\[
= \Delta_r H_m^o - 2RT^2mX_1 + 2RT^2mX_2 \cdot g(I_m)
\]

In Figure IX.41 we plotted the function \(Y\) versus the concentration of the supporting electrolyte. The parameters \(\Delta_r H_m^o\) and \(X_2\) depend on the relative contribution of the term \(g(I_m)\), which is maximal at low concentrations. However, the existing data cannot define this function with any reliability, which results in very large uncertainties in the fitting parameters values: \(\Delta_r H_m^o = -21.0 ± 6.5\) kJ · mol\(^{-1}\), \(X_1 = (-9.0 ± 20.6) \times 10^{-3}\) kg · mol\(^{-1}\) · K\(^{-1}\), \(X_2 = (1.2 ± 20.0) \times 10^{-3}\) kg · mol\(^{-1}\) · K\(^{-1}\). All errors are given as 3\(\sigma\).
Figure IX.41: The concentration dependence of the fitting function $Y$ (see text for details) for the reaction $\text{Hg}^{2+} + \text{Cl}^- \rightleftharpoons \text{HgCl}^+$ in $\text{NaClO}_4$ solutions at 298.15 K and 1 atm based on the Pitzer model.

$$Y = \Delta_r H_m + \frac{3A_L\sqrt{t_m}}{1 + 1.5\sqrt{t_m}} = \Delta_r H_m^0 - RT^2m\Delta\varepsilon_L$$

where $\Delta_r H_m^0$ and the $\Delta\varepsilon_L$ can be determined using the weighted linear regression procedure. Figure IX.42 shows that the agreement between the experimental data and the model function, and the deviations from the linear dependence are within the estimated uncertainty of experimental values ($\pm0.5$-1.0 kJ·mol$^{-1}$). The results are: $\Delta_r H_m^0 = -21.36 \pm 1.26$ kJ·mol$^{-1}$, $\Delta\varepsilon_L = (0.14 \pm 1.12) \times 10^{-3}$ kg·mol$^{-1}$·K$^{-1}$. This value of $\Delta_r H_m^0$ can be compared with the reported literature estimates: $-20.1 \pm 2.1$ [61MAL/PAR] and $-22.3 \pm 0.35$ kJ·mol$^{-1}$ [80VAS/KOZ].

**IX.11. Conclusions**

Our findings may be summarised as follows:

- The more extensively parametrized Pitzer model allows the most precise modelling of mean-activity coefficient data and equilibrium constants, *provided that all interaction parameters are known*. If some parameters are missing (e.g. for ternary interactions between the “strong electrolyte” reactants, or interaction parameters for complexes) they have to be determined experimentally or to be *estimated*, otherwise there may be a substantial loss of accuracy.
Conclusions

Figure IX.42: The concentration dependence of the fitting function \( Y \) (see text for details) for the reaction \( \text{Hg}^{2+} + \text{Cl}^- \rightleftharpoons \text{HgCl}^+ \) in NaClO\(_4\) solutions at 298.15 K and 1 atm based on the SIT model.

- Estimations of missing Pitzer parameters must be made from thermodynamic data obtained in media of different composition. The estimate of parameters for complex formation reactions and other equilibria is a particular case. They are based on concentration equilibrium constants determined in different ionic media/ionic strength, and we have demonstrated that it is difficult, or impossible, to make precise estimates from such data using the complete Pitzer formalism. Approximations are necessary, and this will reduce the precision of the model.

- In the different examples we have demonstrated how different model assumptions will influence both the precision in the parameter estimates and the description of the concentration/ionic strength dependence of the experimental data.

- The SIT model is inherently less precise than the Pitzer model, because it contains fewer parameters. Hence, the precision in the description of mean-activity coefficient data in systems of strong electrolytes is much lower than for the Pitzer model. As indicated above, it is in general necessary to make approximations in the complete Pitzer model, when describing complex formation reactions. For these cases, we have shown that the less parametrized SIT model is in good agreement with the Pitzer model in the concentration range 0.1-4 mol·kg\(^{-1}\).

- The Pitzer and SIT models are equivalent for the intercomparison of equilibrium constants determined in ionic media. The structure of the Pitzer formalism makes it more suitable for recalculation of tabulated equilibrium constants to concentration
Estimations of ionic strength corrections of thermodynamic data

constants valid for media containing different strong electrolytes and/or of very high ionic strength, *e.g.* in salt brines.

Both models are internally consistent and the same formalism may also be used to describe the concentration dependence of other thermodynamic quantities, such as enthalpies of reaction, partial molar heat capacities, partial molar volumes, *etc.*

From the structure of the models follows that their range of validity varies with the chemical system studied. The information we have provided should enable the user of these models to make estimates of the precision to be expected from them, and to make a sensitivity analysis of how various assumptions affect the modelling of the system.

The Pitzer model is included in many computer codes and a user of thermodynamic data for complex formation reactions may therefore wish to use this formalism rather than the SIT model. One may then re-evaluate existing equilibrium constant data to deduce the required Pitzer parameters (very few such analyses have been reported in the literature). We have proposed the transformation of existing SIT interaction parameters into a set of Pitzer parameters using correlations established in Sections IX.7.1 and IX.8, as an alternative. However, this requires approximations in the Pitzer model, as indicated above.

When modelling *e.g.* the speciation of trace elements in the systems encountered in nature, one invariably has to make approximations of various kinds. The most important information for the model is the identification of the key chemical reactions, and this can nearly always be achieved, even if the relevant equilibrium constants are known no better than within 0.2-0.3 logarithmic units. The uncertainty expected from both the Pitzer and the SIT models is smaller than this.

Finally, the relative merits of different models may give rise to controversy among the users. Let us remind the reader that no model can give a "complete" description of a system, or a process. A model is designed to achieve a "practical" purpose, a "partial" description of a more complex phenomenon. It is up to the user to decide if a particular model is useful, or not, for his/her purpose! In this chapter we have tried to make a description/discussion of the advantages/draw-backs of two such models.