PAUL SCHERRER INSTITUT	Registrierung TM-44-14-04
Titel: The PSI/Nagra Chemical Thermodynamic Database 12/07 (Update of the Nagra/PSI TDB 01/01): Data Selection for Zirconium	Ersetzt
Autoren: Tres Thoenen and Enzo Curti	Erstellt 05.05.2014

Summary:

The data for zirconium compiled in the Nagra/PSI TDB 01/01 (HUMMEL et al., 2002) were taken from an in-house literature review.

In the meantime, newer literature on zirconium has been reviewed in OECD NEA's book "Chemical Thermodynamics of Zirconium" by BROWN et al. (2005), which served as a basis for this complete rewrite of Chapter 5.24 on zirconium in HUMMEL et al. (2002). The updated database will be called PSI/Nagra Chemical Thermodynamic Database 12/07.

This is the 10th of a continuing series of reports concerning the PSI/Nagra Chemical Thermodynamic Database 12/07.

Verteiler

Abt.	Empfänger / Empfängerinnen	Expl.	Abt.	Empfänger / Empfängerinnen	Expl.
44	B. Baeyens	1	Nagra	V. Cloet	1
	U. Berner	1		L. Johnson	1
	S. Churakov	1		J. Mibus	1
	E. Curti	1		J. Schneider	1
	R. Dähn	1		B. Schwyn	1
	T. Gimmi	1		P. Zuidema	1
	M. Glaus	1			
	W. Hummel	1	NewBern	F.J. Pearson	1
	G. Kosakowski	1			
	D. Kulik	1			
	M. Marques	1			
	W. Pfingsten	1			
	T. Thoenen	1			
	J. Tits	1			
	L. Van Loon	1			
	E. Wieland	1			

	Expl.
Bibliothek	2
Reserve	4
Total	29
Seiten	33
Beilagen	-

Informationsliste

D | 1 | 2 | 3 | 4 | 5 | 8 | 9 | A

Visum ~~Abt. /Laborleitung~~:

1 Introduction

The data compiled for Zr in HUMMEL et al. (2002) were based on the in-house review carried out by CURTI (2001). In the meantime, newer literature on zirconium has been evaluated in OECD NEA's review "Chemical Thermodynamics of Zirconium" by BROWN et al. (2005). The present report very closely follows the review by BROWN et al. (2005) and all of the data on zirconium contained in the PSI/Nagra Chemical Thermodynamic Database 12/07 (in the following referred to as "our database") originate from BROWN et al. (2005) with the exception of the data for ternary calcium zirconium hydroxide complexes, which were taken from ALTMAIER et al. (2008), and some estimates of SIT ion interaction coefficients. The selected data are compiled in Tables 1.2 – 1.4.

Not all data recommended by BROWN et al. (2005) are included in our database since the NEA reviews (unlike our database) are not restricted to data relevant for radioactive waste management or even environmental modeling in general. We tried to exclude from our database all phases and aqueous species which most probably will never be relevant in low temperature (T < about 150°C) environmental systems. The omitted solids, liquids and gases are listed in Table 1.1, while all aqueous species were accepted.

The NEA review volumes provide tables with selected SIT coefficients for the interaction of cations with Cl^-, ClO_4^-, and NO_3^-, and of anions with Li^+, Na^+, and K^+. Since numerous ion interaction coefficients are not known, we used an estimation method to fill the gaps. Based on a statistical analysis of published SIT ion interaction coefficients, HUMMEL (2009) provided an expression that allows the estimation of such coefficients for cations with Cl^- and ClO_4^-, and for anions with Na^+ from the charge of the considered cation or anion.

The notation of formulae and symbols used in this text follows the NEA recommendations.

2 Elemental Zirconium

Zirconium metal, liquid and gas are not relevant under environmental conditions. Therefore, the thermodynamic data selected by BROWN et al. (2005) for Zr(β), Zr(ω), Zr(l), and Zr(g) are not included in our database. However, the absolute entropy and heat capacity of Zr(α), in our database referred to as Zr(cr), are included as they are used for the calculation of certain thermodynamic reaction properties. The values selected by BROWN et al. (2005)

$$S_m^\circ(\text{Zr, cr, 298.15 K}) = (39.08 \pm 0.10)\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$C_{p,m}^\circ(\text{Zr, cr, 298.15 K}) = (26.08 \pm 0.05)\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

were derived from calorimetric heat capacity measurements.

3 Zirconium aqua ions

Zirconium exists in aqueous solution only in the +4 oxidation state. In earlier times (until the middle of the last century) it was believed that the solution chemistry of zirconium was dominated by the zirconyl ion ZrO^{2+}. Crystal structure determinations, however, of so-called zirconyl chloride and bromide octahydrates by CLEARFIELD & VAUGHAN (1956) disproved the existence of a zirconyl ionic structure. No zirconium halogen bonds were found and the central moiety of the solid zirconium halogen "complexes" turned out to be $[Zr_4(OH)_8 \cdot 16\ H_2O]^{8+}$. Hence, the formula for "zirconyl chloride octahydrate" "$ZrOCl_2 \cdot 8\ H_2O$(cr)" should rather be understood as $Zr(OH)_2(H_2O)_7Cl_2$(cr). X-ray diffraction results by MUHA & VAUGHAN (1960) for 0.5 - 2 m aqueous solutions of "$MOX_2 \cdot 8\ H_2O$" (with M = Zr and Hf, and X = Cl and Br) could be explained by the existence of aqueous complexes of the type $M_4(OH)_8(H_2O)_{16}X_8$, with a structure very similar to that found in the solids. According to BROWN et al. (2005), there has never been found any unequivocal evidence for the zirconyl ion, neither in solids, nor in aqueous solution.

The free aqua ion Zr^{4+} is only stable under very acidic conditions due to its strong tendency for hydrolysis and polymerization. BROWN et al. (2005) stressed that the thermodynamic data they selected for Zr^{4+} strongly relies on the overall fit of the hydrolysis data (discussed in Section 4.1 below). The standard molar Gibbs free energy of formation for Zr^{4+} selected by BROWN et al. (2005)

$$\Delta_f G_m^\circ(Zr^{4+}, 298.15\ K) = -(528.5 \pm 9.2)\ kJ \cdot mol^{-1}$$

was calculated from the selected equilibrium constant $\log_{10}K_{s,0}^\circ = -7.0 \pm 1.6$ (see Section 4.3 below), equivalent to $\Delta_r G_m^\circ = (40.0 \pm 9.1)\ kJ \cdot mol^{-1}$, for the reaction

$$ZrO_2(cr) + 4\ H^+ \Leftrightarrow Zr^{4+} + 2\ H_2O(l)$$

and from the selected $\Delta_f G_m^\circ(ZrO_2, cr, 298.15\ K) = -(1042.6 \pm 0.7)\ kJ \cdot mol^{-1}$ (see Section 4.3 below) and $\Delta_f G_m^\circ(H_2O, l, 298.15\ K) = -(237.140 \pm 0.041)\ kJ \cdot mol^{-1}$. The standard molar enthalpy of formation selected by BROWN et al. (2005)

$$\Delta_f H_m^\circ(Zr^{4+}, 298.15\ K) = -(608.5 \pm 5.0)\ kJ \cdot mol^{-1}$$

is based on calorimetrically determined enthalpies of dissolution for $ZrCl_4$(cr) and $ZrBr_4$(cr) in $HClO_4$, HNO_3, and HCl, corrected by BROWN et al. (2005) for the formation of polynuclear complexes at high concentrations of Zr. $\Delta_f S_m^\circ(Zr^{4+}, 298.15\ K)$ was calculated by BROWN et al. (2005) from $\Delta_f G_m^\circ(Zr^{4+}, 298.15\ K)$ and $\Delta_f H_m^\circ(Zr^{4+}, 298.15\ K)$ by means of G = H - TS. Using the

selected values $S_m°$(Zr, cr, 298.15 K) = (39.08 ± 0.10) J · K^{-1} · mol^{-1} and $S_m°$(H_2, g, 298.15 K) = (130.680 ± 0.003) J · K^{-1} · mol^{-1}, BROWN et al. (2005) obtained

$$S_m°(Zr^{4+}, 298.15\ K) = -(491.0 \pm 35.2)\ J \cdot K^{-1} \cdot mol^{-1}$$

The values of $\Delta_f G_m°$, $\Delta_f H_m°$, and $S_m°$ selected by BROWN et al. (2005) for Zr^{4+} are included in our database.

The SIT interaction coefficient of Zr^{4+} with ClO_4^- was obtained by BROWN et al. (2005) from an SIT analysis of experimental data for the reaction $Zr^{4+} + F^- \Leftrightarrow ZrF^{3+}$ (see Section 5.1.1 below), resulting in

$$\varepsilon(Zr^{4+}, ClO_4^-) = (0.89 \pm 0.10)\ kg \cdot mol^{-1}$$

The interaction coefficients of Zr^{4+} with Cl^- and NO_3^- could not be derived from experimental data and BROWN et al. (2005) had to take recourse to estimation methods. From an empirical linear relation between the values of interaction coefficients of simple cations in perchlorate media and the ratios of their charge with the square root of their radius, BROWN et al. (2005) estimated

$$\varepsilon(Zr^{4+}, Cl^-) = (0.33 \pm 0.09)\ kg \cdot mol^{-1}$$

For the interaction with NO_3^-, BROWN et al. (2005) used Th^{4+} as a substitute for Zr^{4+}, assuming that homovalent pairs of ions have similar ion interaction coefficients. Hence,

$$\varepsilon(Zr^{4+}, NO_3^-) \approx \varepsilon(Th^{4+}, NO_3^-) = (0.33 \pm 0.35)\ kg \cdot mol^{-1}$$

The ion interaction coefficients selected by BROWN et al. (2005) for Zr^{4+} are also included in our database.

4 Zirconium hydrogen and oxygen compounds and complexes

4.1 Aqueous zirconium hydroxide complexes

There is a large number of experimental data on the stoichiometry and stability of aqueous zirconium hydroxide complexes. BROWN et al. (2005) noted, however, that the hydrolysis constants reported in the literature are highly contradictory. For a given ionic strength, e.g., the reported stability constants for $Zr(OH)_2^{2+}$ and for $Zr(OH)_3^-$ vary over four orders of magnitude, those for $Zr(OH)_4$(aq) over five orders of magnitude, and those for $Zr_4(OH)_8^{8+}$ over ten orders of magnitude (in this case the ionic strength varies between 1 and 2 m). In addition, many investigators based their interpretations of experimental data on untested or on inconsistent hypotheses, especially with respect to the nature and predominance of monomeric species under experimental conditions where polymers might be favored. By direct SIT-regression of published results, BROWN et al. (2005) were

only able to derive standard stability constants for $ZrOH^{3+}$ and $Zr_3(OH)_4^{8+}$. The stability constants for all other zirconium hydroxide complexes needed a global reinterpretation of the experimental data using common and consistent hypotheses for all data.

The main points of the reinterpretation by BROWN et al. (2005) are as follows: There is clear evidence that polynuclear hydroxide complexes are formed even in extremely acid solutions, i.e., they become dominant at a pH as low as about 0.5 for zirconium concentrations around 10^{-4} m. Polymerization increases with increasing pH and Zr concentration. Structural studies of highly concentrated Zr solutions and of the solids precipitated from these solutions reveal that tetrameric hydroxide complexes are the dominant stable polynuclear solution species over a wide range of pH. Higher degrees of polymerization are sometimes observed and the degree of polymerization increases with time, suggesting that such highly polymerized species are metastable intermediates at the onset of precipitation. Thus, the maximum degree of polymerization in the hydrolysis model is four. At high pH, there appears to be a region where a negatively charged monomer becomes dominant.

Based on these observations, BROWN et al. (2005) concluded that many zirconium hydrolysis models in the literature are erroneous, but that their basic experimental data can still be taken advantage of in a global reevaluation. For this purpose, BROWN et al. (2005) used the following procedure: In a first step, the stability constants and ion interaction coefficients for $ZrOH^{3+}$ and for $Zr_3(OH)_4^{8+}$ were obtained from selected sets of data by standard SIT-regression. In a second step, the equilibrium constants and ion interaction parameters for all other species in the hydrolysis model were obtained by a global least-squares-type fit (minimizing an objective function that is composed of the squares of the deviations of the calculated from the experimental quantities) to the complete set of experimental data, keeping the stability constants and ion interaction coefficients for $ZrOH^{3+}$ and for $Zr_3(OH)_4^{8+}$ fixed at the values derived in the first step. The global fit was based on a preselection of the dominant species, which always included $Zr(OH)_4(aq)$, $Zr_4(OH)_8^{8+}$, $Zr_4(OH)_{15}^{+}$, and $Zr_4(OH)_{16}(aq)$. Various other mono-, di-, tri-, and tetrameric species were added to improve the fit (although with hardly an objective base for their selection). If the fitted results were found to be insensitive to the stability constant of a given species, the species was removed from the list of considered species. The set of species resulting in the lowest overall objective function was considered as best fit and was used as hydrolysis model. In this way, BROWN et al. (2005) obtained their zirconium hydrolysis model, which consists of stability constants and ion interaction coefficients for $ZrOH^{3+}$, $Zr(OH)_2^{2+}$, $Zr(OH)_4(aq)$, $Zr(OH)_6^{2-}$, $Zr_3(OH)_4^{8+}$, $Zr_3(OH)_9^{3+}$, $Zr_4(OH)_8^{8+}$, $Zr_4(OH)_{15}^{+}$, and $Zr_4(OH)_{16}(aq)$.

Monomeric hydrolysis species: The stability constant selected by BROWN et al. (2005) for $ZrOH^{3+}$ is based on two studies in mixed $HClO_4/NaClO_4$ solutions (1 and 4 M) using potentiometry, spectrophotometry, and liquid ion exchange. SIT analysis of three data points resulted in

$$Zr^{4+} + H_2O(l) \Leftrightarrow ZrOH^{3+} + H^+$$

$$\log_{10}{}^*\beta_{1,1}^\circ(298.15) = 0.32 \pm 0.22$$

with $\Delta\varepsilon = -(0.18 \pm 0.08)$ kg · mol^{-1} and

$$\varepsilon(ZrOH^{3+}, ClO_4^-) = (0.57 \pm 0.13) \text{ kg} \cdot \text{mol}^{-1}$$

following from the value of $\Delta\varepsilon$ and from the selected $\varepsilon(Zr^{4+}, ClO_4^-) = (0.89 \pm 0.10)$ kg · mol^{-1} and $\varepsilon(H^+, ClO_4^-) = (0.14 \pm 0.02)$ kg · mol^{-1}.

The stability constant and SIT coefficient for $Zr(OH)_2^{2+}$ was obtained by BROWN et al. (2005) from the global fit to the hydrolysis data:

$$Zr^{4+} + 2\ H_2O(l) \Leftrightarrow Zr(OH)_2^{2+} + 2\ H^+$$

$$\log_{10}{}^*\beta_{2,1}^\circ(298.15) = 0.98 \pm 1.06$$

$$\varepsilon(Zr(OH)_2^{2+}, ClO_4^-) = (0.62 \pm 0.39) \text{ kg} \cdot \text{mol}^{-1}$$

BROWN et al. (2005) did not select any stability constant for $Zr(OH)_3^+$. Due to the apparently small stability field of this species, the global fit to the available hydrolysis data did not fully constrain its stability constant, i.e., the resulting uncertainty was too large to justify the selection of a value.

In the case of $Zr(OH)_4(aq)$, the global fit to the available hydrolysis data resulted in

$$Zr^{4+} + 4\ H_2O(l) \Leftrightarrow Zr(OH)_4(aq) + 4\ H^+$$

$$\log_{10}{}^*\beta_{4,1}^\circ(298.15) = -2.19 \pm 1.70$$

The formation of $Zr(OH)_5^-$ was proposed on the basis of an experimental observation that, at high pH, the solubility of zirconium hydroxide increases with pH. A later experiment suggested, however, that the observed solubility increase was rather due to a contamination with carbon dioxide that lead to the formation of Zr carbonate complexes. For this reason, BROWN et al. (2005) did not consider any stability constant for $Zr(OH)_5^-$.

Solubility experiments of Zr hydroxides in alkaline media showed that Zr solubility increases with increasing pH, which is compatible with the formation of the zirconate ion, ZrO_3^{2-}, or of $Zr(OH)_6^{2-}$. Since there is no evidence from the solubility experiments as to the true stoichiometry of this divalent anion, BROWN et al. (2005) assumed it to be $Zr(OH)_6^{2-}$, based on the absence of discrete zirconate ions in crystalline so-called zirconate phases. The solubility data were included by BROWN et al. (2005) in the global fit, leading to

$$Zr^{4+} + 6\ H_2O(l) \Leftrightarrow Zr(OH)_6^{2-} + 6\ H^+$$

$$\log_{10}{}^*\beta_{6,1}^\circ(298.15) = -29.0 \pm 0.70)$$

The ion interaction coefficient

$$\varepsilon(Zr(OH)_6^{2-}, Na^+) = -(0.10 \pm 0.10)\ kg \cdot mol^{-1}$$

was estimated by BROWN et al. (2005) from the NEA-selected interaction coefficients of fourteen twofold negative charged species.

Dimeric hydrolysis species: The presence of $Zr_2(OH)_7^+$ was reported in a study based on potentiometric and solubility data. BROWN et al. (2005), however, found the overall hydrolysis model applied in this study as incompatible with the presence of dimeric species and suggested that the proposed dimer is more likely the tetramer $Zr_4(OH)_{15}^+$.

Trimeric hydrolysis species: In very acid media, $Zr_3(OH)_4^{8+}$ becomes dominant. BROWN et al. (2005) reanalyzed experimental data from five studies that applied solvent extraction, spectroscopy, and potentiometry in chloride and perchlorate media. The SIT-regression lines for perchlorate and chloride media intersected at infinite dilution, supporting the experimental data, and BROWN et al. (2005) obtained

$$3\ Zr^{4+} + 4\ H_2O(l) \Leftrightarrow Zr_3(OH)_4^{8+} + 4\ H^+$$

$$\log_{10}{}^*\beta_{4,3}^\circ(298.15) = 0.4 \pm 0.3$$

with $\Delta\varepsilon_{4,3}(HClO_4) = -(0.22 \pm 0.05)\ kg \cdot mol^{-1}$ and $\Delta\varepsilon_{4,3}(HCl) = -(0.18 \pm 0.06)\ kg \cdot mol^{-1}$. From these values for $\Delta\varepsilon$ and the selected $\varepsilon(Zr^{4+}, Cl^-) = (0.33 \pm 0.09)\ kg \cdot mol^{-1}$, $\varepsilon(H^+, Cl^-) = (0.12 \pm 0.01)\ kg \cdot mol^{-1}$, $\varepsilon(Zr^{4+}, ClO_4^-) = (0.89 \pm 0.10)\ kg \cdot mol^{-1}$, and $\varepsilon(H^+, ClO_4^-) = (0.14 \pm 0.02)\ kg \cdot mol^{-1}$, BROWN et al. (2005) calculated

$$\varepsilon(Zr_3(OH)_4^{8+}, Cl^-) = (0.33 \pm 0.28)\ kg \cdot mol^{-1}$$

$$\varepsilon(Zr_3(OH)_4^{8+}, ClO_4^-) = (1.89 \pm 0.31)\ kg \cdot mol^{-1}$$

The ion interaction coefficient

$$\varepsilon(Zr_3(OH)_4^{8+}, NO_3^-) = (2.28 \pm 0.35)\ kg \cdot mol^{-1}$$

resulted from the global fit to the hydrolysis data.

The standard molar enthalpy of formation for $Zr_3(OH)_4^{8+}$

$$\Delta_f H_m°(Zr_3(OH)_4^{8+}, 298.15\ K) = -(2970.8 \pm 10.0)\ kJ \cdot mol^{-1}$$

selected by BROWN et al. (2005) is based on a reevaluation of measured enthalpies of dissolution of $ZrCl_4$(cr) in perchloric, hydrochloric, and nitric acid.

The trimer $Zr_3(OH)_9^{3+}$ was introduced by BROWN et al. (2005)—without any experimental evidence—just to improve the quality of the global fit to the experimental data. They obtained

$$3\ Zr^{4+} + 9\ H_2O(l) \Leftrightarrow Zr_3(OH)_9^{3+} + 9\ H^+$$

$$\log_{10}{}^*\beta_{9,3}°(298.15) = 12.19 \pm 0.08$$

and

$$\varepsilon(Zr_3(OH)_9^{3+}, ClO_4^-) = (0.93 \pm 0.35)\ kg \cdot mol^{-1}$$

from the global fit but stressed that this species has not yet been identified or proposed in the experimental literature and that additional experiments are needed to confirm its existence and its field of stability.

Tetrameric hydrolysis species: The stability constants and ion interaction coefficients for the tetramers $Zr_4(OH)_8^{8+}$, $Zr_4(OH)_{15}^{+}$, and $Zr_4(OH)_{16}$(aq) were all derived from the global fit to the available hydrolysis data, leading to

$$4\ Zr^{4+} + 8\ H_2O(l) \Leftrightarrow Zr_4(OH)_8^{8+} + 8\ H^+$$

$$\log_{10}{}^*\beta_{8,4}°(298.15) = 6.52 \pm 0.65$$

$$\varepsilon(Zr_4(OH)_8^{8+}, ClO_4^-) = (3.61 \pm 1.02)\ kg \cdot mol^{-1}$$

$$4\ Zr^{4+} + 15\ H_2O(l) \Leftrightarrow Zr_4(OH)_{15}^{+} + 15\ H^+$$

$$\log_{10}{}^*\beta_{15,4}°(298.15) = 12.58 \pm 0.24$$

$$\varepsilon(Zr_4(OH)_{15}^{+}, ClO_4^-) = (0.09 \pm 0.92)\ kg \cdot mol^{-1}$$

$$\varepsilon(Zr_4(OH)_{15}^{+}, NO_3^-) = -(0.02 \pm 1.46)\ kg \cdot mol^{-1}$$

$$4\ Zr^{4+} + 16\ H_2O(l) \Leftrightarrow Zr_4(OH)_{16}(aq) + 16\ H^+$$

$$\log_{10}{}^*\beta_{16,4}°(298.15) = 8.39 \pm 0.80$$

The standard molar enthalpy of formation for $Zr_4(OH)_{16}(aq)$ was derived by BROWN et al. (2005) from a heat of solution measurement of $ZrCl_4(cr)$ in aqueous solution. Their selected value is

$$\Delta_f H_m^\circ(Zr_4(OH)_{16}, aq, 298.15\ K) = -(6706.16 \pm 7.20)\ kJ \cdot mol^{-1}$$

Since several ion interaction coefficients of zirconium hydrolysis species with Cl^- are missing, we estimated

$$\varepsilon(ZrOH^{3+}, Cl^-) = (0.25 \pm 0.10)\ kg \cdot mol^{-1}$$

$$\varepsilon(Zr(OH)_2^{2+}, Cl^-) = (0.15 \pm 0.10)\ kg \cdot mol^{-1}$$

$$\varepsilon(Zr_3(OH)_9^{3+}, Cl^-) = (0.25 \pm 0.10)\ kg \cdot mol^{-1}$$

$$\varepsilon(Zr_4(OH)_8^{8+}, Cl^-) = (0.75 \pm 0.50)\ kg \cdot mol^{-1}$$

$$\varepsilon(Zr_4(OH)_{15}^{+}, Cl^-) = (0.05 \pm 0.10)\ kg \cdot mol^{-1}$$

according to HUMMEL (2009).

In a study that was carried out after the publication of BROWN et al. (2005), WALTHER et al. (2007) investigated the speciation of Zr in acidic solutions (pH_c=0-3) at total Zr concentrations between 1.5 x 10^{-3} and 10^{-2} M, with time-of-flight electrospray mass spectrometry (ESI-MS) and X-ray absorption spectroscopy (XANES, XAFS). The solutions were prepared by dissolving "zirconyl chloride hydrate" ("$ZrOCl_2 \cdot x\ H_2O(cr)$", which rather corresponds to $Zr(OH)_2(H_2O)_{x-1}Cl_2$, see discussion in Section 3 above) in hydrochloric acid of appropriate concentration.

The ESI-MS measurements were conducted using mild injection conditions (low flow rate and low electrostatic potential) to avoid the splitting of the (nanometric) droplets and other secondary effects. The good agreement of the obtained data with the EXAFS results and with independent published data is a convincing argument in favor of the non-invasiveness of the method. The authors conclude that the observed mass distributions faithfully reflect the complexes present in the solution.

Because of the large number of stable isotopes in natural Zr, it was possible to resolve unequivocally the very complex mass spectra and to assign to each peak an unambiguous stoichiometry. Typically, the measured masses consisted of polymeric Zr-hydroxo species with chloride ions and up to 20-25 water molecules in the solvation shell. The main results from this study can be summarized as follows:

1. At these relatively high Zr concentrations (1.5 x 10^{-3} - 10^{-2} M) and low pH the Zr hydroxo species are dominantly polymeric; nevertheless also monomers were detected.

2. A large number of polymeric species was identified. In general, the degree of polymerization was found to increase with increasing pH and the mean charge of the hydroxo species approached to -2 towards the solubility limit of amorphous $Zr(OH)_4$.

3. Overall, tetramers, pentamers and octamers (with a variable number of hydroxyls) are the dominating species.

4. No evidence was found for the presence of trimeric species. Hence, the existence of $Zr_3(OH)_4^{8+}$ and $Zr_3(OH)_9^{3+}$, two complexes proposed and selected by BROWN et al. (2005) is not confirmed by the ESI-MS data.

The X-ray spectroscopic data generally agree with the ESI-MS data. In particular, the Fourier transforms of solutions dominated by polymeric species ([Zr]= 10 mM) could only be fitted by splitting the first oxygen shell in two distances (4 O at 2.12 and 4 O at 2.26 A), in agreement with the structural parameters for the tetrameric units of "$ZrOCl_2 \cdot 8H_2O$". In addition, the fitting of Zr-Zr backscattering peaks could be fitted assuming CN ~ 1-2, as expected from the polymer structures. The broadening and in some cases disappearance of the Zr-Zr contribution was explained by the simultaneous presence of many different Zr species in the intermediate pH range (0.6-1.5) as indicated by the ESI-MS data (see Fig. 7 in original paper).

In summary, the work of WALTHER et al. (2007) provides valuable insight into the process of Zr polymerization at low pH and high Zr concentrations. The results disprove the existence of $Zr_3(OH)_4^{8+}$ and $Zr_3(OH)_9^{3+}$ and indicate the formation of a large variety of Zr hydroxo polymers (note, however, that the solubilities measured by ALTMAIER et al. (2008) of aged $Zr(OH)_4$ precipitates at pH < 3 in $CaCl_2$ and in NaCl solutions are consistent with the formation of $Zr_3(OH)_9^{3+}$, see Section 4.2 below). On the other hand, a thermodynamic model including all the species detected by ESI-MS would be highly impractical and not credible, due to the large number of unconstrained model parameters.

Despite the fact that $Zr_3(OH)_4^{8+}$ and $Zr_3(OH)_9^{3+}$ were not identified by WALTHER et al. (2007) we have decided to adopt the hydrolysis model by BROWN et al. (2005), as presented in this Section, for our database. BROWN et al. (2005) state in the preface of their review: *"The contribution of Bernd Grambow warrants a special mention. As is clear from the review, data on the hydrolysis of zirconium reported in the literature is highly contradictory. For example, the variation in a stability constant, at a particular ionic strength, may be as great as ten orders of magnitude. To overcome this difficulty, the original experimental data was reinterpreted in the present review to obtain a consistent hydrolysis model with common hypotheses. This model was critical in the interpretation*

and re-interpretation of the thermochemical data in all other sections of the book". Thus, for the sake of consistency with all the other zirconium data, the hydrolysis model by BROWN et al. (2005) cannot be disposed of. BROWN et al. (2005) continue in the preface: *"To our knowledge, this is the first time that a reevaluation has been undertaken in this way. Due to the complexity and contradictory nature of currently available hydrolysis data, we nevertheless feel that, at least in the low pH-region, the data selected in this review will be susceptible to amendments in the future"*. It is very important to keep this in mind when using these data.

4.2 Aqueous calcium zirconium hydroxide complexes

ALTMAIER et al. (2008) studied the solubility of Zr(IV), Th(IV), and U(IV) oxyhydroxide precipitates, which can be described as $MO_2 \cdot x\ H_2O$(pr) or as $M(OH)_4$(pr), in 0.1 - 4.5 M $CaCl_2$ solutions. In the case of Zr, solubilities decrease at pH 1 to 3 with a slope consistent with the formation of $Zr_3(OH)_9^{3+}$. At pH 3 to 9, Zr concentrations remain constant, due to the formation of neutral $Zr(OH)_4$(aq), or a multiple thereof. At pH > 9 solubilities increase, which, unlike the solubility increase observed in NaCl and $NaClO_4$ solutions at pH > 12, cannot be explained by the formation of $Zr(OH)_6^{2-}$. The data could best be interpreted by ALTMAIER et al. (2008) with the ternary calcium zirconium hydroxide complexes $Ca_2Zr(OH)_6^{2+}$ and $Ca_3Zr(OH)_6^{4+}$. The latter complex was identified by BRENDEBACH et al. (2007) in an EXAFS study. From an SIT regression of the solubility data, ALTMAIER et al. (2008) obtained $\log_{10}K_{s,(2,1,6)}°$(298.15 K) = 1.1 ± 0.2 for $Zr(OH)_4$(pr) + 2 OH^- + 2 Ca^{2+} ⇔ $Ca_2Zr(OH)_6^{2+}$ and $\log_{10}K_{s,(3,1,6)}°$(298.15 K) = 0.5 ± 0.2 for $Zr(OH)_4$(pr) + 2 OH^- + 3 Ca^{2+} ⇔ $Ca_3Zr(OH)_6^{4+}$ and $\log_{10}K_{s,(0,1,6)}°$(298.15 K) = -5.5 ± 0.2 for $Zr(OH)_4$(pr) + 2 OH^- ⇔ $Zr(OH)_6^{2-}$ in the Ca-free system. From their solubility product $\log_{10}K_{s,0}°$(298.15 K) = -60.3 ± 0.2 for $Zr(OH)_4$(pr) ⇔ Zr^{4+} + 4 OH^- then follow $\log_{10}\beta_{2,1,6}°$(298.15 K) = 61.4 ± 0.3 for the reaction 2 Ca^{2+} + Zr^{4+} + 6 OH^- ⇔ $Ca_2Zr(OH)_6^{2+}$, $\log_{10}\beta_{3,1,6}°$(298.15 K) = 60.8 ± 0.3 for the reaction 3 Ca^{2+} + Zr^{4+} + 6 OH^- ⇔ $Ca_3Zr(OH)_6^{4+}$ and $\log_{10}\beta_{0,1,6}°$(298.15 K) = 54.8 ± 0.3 for the reaction Zr^{4+} + 6 OH^- ⇔ $Zr(OH)_6^{2-}$ (note that the value for $\log_{10}\beta_{0,1,6}°$(298.15 K) selected by BROWN et al. 2005 and included in our database is 55.0 ± 0.7). For inclusion in our database, we used the dissociation constant of water to express the reactions in terms of H_2O(l) and H^+ instead of OH^-. Thus

$$2\ Ca^{2+} + Zr^{4+} + 6\ H_2O(l) \Leftrightarrow Ca_2Zr(OH)_6^{2+} + 6\ H^+$$

$$\log_{10}{}^*\beta_{2,1,6}°(298.15\ K) = -22.6 \pm 0.3$$

$$3\ Ca^{2+} + Zr^{4+} + 6\ H_2O(l) \Leftrightarrow Ca_3Zr(OH)_6^{4+} + 6\ H^+$$

$$\log_{10}{}^*\beta_{3,1,6}°(298.15\ K) = -23.2 \pm 0.3$$

From the Δε values of their SIT regressions, ALTMAIER et al. (2008) obtained

$$\varepsilon(Ca_2Zr(OH)_6^{2+}, Cl^-) = (0.1 \pm 0.1)\ kg \cdot mol^{-1}$$

$$\varepsilon(Ca_3Zr(OH)_6^{4+}, Cl^-) = (0.40 \pm 0.07)\ kg \cdot mol^{-1}$$

by using their experimentally determined $\varepsilon(OH^-, Ca^{2+}) = -(0.45 \pm 0.03)\ kg \cdot mol^{-1}$ and $\varepsilon(Ca^{2+}, Cl^-) = (0.12 \pm 0.01)\ kg \cdot mol^{-1}$ selected by NEA (e.g., BROWN et al. 2005). ALTMAIER et al. (2008) also measured the solubility of $Zr(OH)_4$(pr) in $Ca(ClO_4)_2$ solutions. The value

$$\varepsilon(Ca_3Zr(OH)_6^{4+}, ClO_4^-) = (0.89 \pm 0.12)\ kg \cdot mol^{-1}$$

was derived by ALTMAIER et al. (2008) from these experiments, while they estimated

$$\varepsilon(Ca_2Zr(OH)_6^{2+}, ClO_4^-) = (0.3 \pm 0.1)\ kg \cdot mol^{-1}$$

by analogy from known SIT coefficients for ions with the same charge. These interaction coefficients of $Ca_2Zr(OH)_6^{2+}$ and $Ca_3Zr(OH)_6^{4+}$ with Cl^- and ClO_4^- are included in our database, as well as $\varepsilon(OH^-, Ca^{2+})$.

For estimating the stability constant of $CaZr(OH)_6$(aq), which is negligible at Ca concentrations > 0.1 M, ALTMAIER et al. (2008) proceeded as follows (for this discussion, we neglect the uncertainties and keep in mind that the equilibrium constants refer to 298.15 K): From $\log_{10}\beta_{2,1,6}^\circ = 61.4$ and $\log_{10}\beta_{3,1,6}^\circ = 60.8$ follows $\log_{10}K_3^\circ = -0.6$ for the reaction $Ca_2Zr(OH)_6^{2+} + Ca^{2+} \Leftrightarrow Ca_3Zr(OH)_6^{4+}$. Furthermore, from $\log_{10}\beta_{0,1,6}^\circ = 54.8$ and $\log_{10}\beta_{2,1,6}^\circ = 61.4$ follows $\log_{10}\beta_2^\circ = 6.6$ for the reaction $Zr(OH)_6^{2-} + 2\ Ca^{2+} \Leftrightarrow Ca_2Zr(OH)_6^{2+}$. ALTMAIER et al. (2008) assumed a linear decrease of $\log_{10}K_n^\circ$ for the stepwise association of Ca^{2+} to $Zr(OH)_6^{2-}$

$$Ca_{n-1}Zr(OH)_6^{2n-4} + Ca^{2+} \Leftrightarrow Ca_nZr(OH)_6^{2n-2}$$

Thus,

$$\log_{10}K_1^\circ - \log_{10}K_2^\circ = \log_{10}K_2^\circ - \log_{10}K_3^\circ = \log_{10}K_2^\circ + 0.6$$

In addition

$$\log_{10}\beta_2^\circ = \log_{10}K_1^\circ + \log_{10}K_2^\circ = 6.6$$

From these two equations then follows that $\log_{10}K_1^\circ(298.15\ K) = 4.6$ and $\log_{10}K_2^\circ(298.15\ K) = 2.0$. Combining $\log_{10}K_1^\circ(298.15\ K)$ with $\log_{10}\beta_{0,1,6}^\circ(298.15\ K) = 54.8 \pm 0.3$ leads to the estimate by ALTMAIER et al. (2008) for

$$Ca^{2+} + Zr^{4+} + 6\ OH^- \Leftrightarrow CaZr(OH)_6(aq)$$

$$\log_{10}\beta_{1,1,6}^\circ(298.15\ K) = 59.4 \pm 0.3$$

We include this estimate in the supplemental data of our database, rewriting the equilibrium in terms of H^+ and $H_2O(l)$ instead of OH^-. Hence

$$Ca^{2+} + Zr^{4+} + 6\ H_2O(l) \Leftrightarrow CaZr(OH)_6(aq) + 6\ H^+$$

$$log_{10}{}^*\beta_{1,1,6}{}^\circ(298.15\ K) = -24.6 \pm 0.3^{1}$$

4.3 Crystalline and amorphous zirconium oxides and dioxides

The most stable zirconium oxide solid is ZrO_2 and its monoclinic low-temperature ($T < 1147^\circ C$) polymorph is the mineral baddeleyite, which appears to be the solubility-limiting phase in low-temperature natural waters. BROWN et al. (2005) accepted data from a solubility study of amorphous and of well-crystallized ZrO_2. Since the measured solubilities were very similar, datasets of both phases were included in the overall fit procedure for the hydrolysis model, from which BROWN et al. (2005) obtained

$$ZrO_2(\text{baddeleyite}) + 4\ H^+ \Leftrightarrow Zr^{4+} + 2\ H_2O(l)$$

$$\log_{10}K_{s,0}^\circ(298.15\ K) = -7.0 \pm 1.6$$

The value for the formation enthalpy of baddeleyite selected by BROWN et al. (2005)

$$\Delta_f H_m^\circ(\text{baddeleyite}, 298.15\ K) = -(1100.6 \pm 1.3)\ kJ \cdot mol^{-1}$$

is the weighted average of two values that were determined by oxygen bomb calorimetry. BROWN et al. (2005) reevaluated data from two studies of the low-temperature heat capacity of baddeleyite. They fitted data in the temperature range from 50 to 301 K by least squares analysis and calculated the standard molar heat capacity for baddeleyite

$$C_{p,m}^\circ(\text{baddeleyite}, 298.15\ K) = (55.96 \pm 0.79)\ J \cdot K^{-1} \cdot mol^{-1}$$

from the regression equation.

In the initial phase of precipitation from Zr solutions, the solids formed are often amorphous and gelatinous oxyhydroxides. BROWN et al. (2005) referred to those as $Zr(OH)_4$(am, fresh), but they remarked that this is rather a name than a real composition. They included datasets from three

---

1 Note that the uncertainty was not reported in THOENEN (2012).

solubility studies in the overall fit procedure for the hydrolysis model and selected the average of the two largest solubility constants[2]. Hence

$$Zr(OH)_4(am, fresh) + 4\ H^+ \Leftrightarrow Zr^{4+} + 4\ H_2O(l)$$

$$\log_{10}K_{s,0}°(298.15\ K) = -3.24 \pm 0.10$$

All these data for baddeleyite and $Zr(OH)_4$(am, fresh) are included in our database. The solubility product measured by ALTMAIER et al. (2008) for $Zr(OH)_4$(s), $\log_{10}K_{s,0}°(298.15\ K) = -4.3 \pm 0.2$ is typical for an aged precipitate and lies in between the selected values for $Zr(OH)_4$(am, fresh) and ZrO_2(baddeleyite).

4.4 Gaseous zirconium oxides and dioxides

The thermodynamic data selected by BROWN et al. (2005) for ZrO(g) and ZrO_2(g) are not included in our database since these gases are not relevant in natural environments.

4.5 Zirconium hydride

BROWN et al. (2005) calculated standard molar Gibbs free energies of formation for ZrH(cr) and $ZrH_2(\varepsilon)$ from calorimetric measurements. These synthetic solids are not found in natural environments and are therefore not considered in our database.

5 Zirconium halogen compounds and complexes

5.1 Fluorine compounds and complexes

5.1.1 Aqueous zirconium fluoride complexes

There are several experimental studies on the formation of zirconium fluoride complexes. BROWN et al. (2005) accepted data from eight of these studies, some equilibrium constants, however, were recalculated using least squares techniques. Complexation was measured using solvent extraction, cation exchange resins, or potentiometry in either perchloric acid, perchloric acid/sodium perchlorate, or ammonium perchlorate at concentrations of 0.5, 1, 2, or 4 M. The equilibrium constants were reported for the stepwise formation of fluoride complexes according to

$$ZrF_{p-1}^{5-p} + HF(aq) \Leftrightarrow ZrF_p^{4-p} + H^+$$

with p ranging from one to six.

---

[2] Note that the explanations by BROWN et al. (2005) made it not entirely clear to us, how the solubility constants for different experimental datasets were extracted individually.

From an SIT regression of four data points concerning the formation of $ZrF_4(aq)$ in 0.5, 1, and 4 M perchlorate, BROWN et al. (2005) obtained

$$ZrF_3^+ + HF(aq) \Leftrightarrow ZrF_4(aq) + H^+$$

$$\log_{10}{}^*K_4^\circ(p = 4, 298.15\ K) = 2.18 \pm 0.12$$

with $\Delta\varepsilon = -(0.06 \pm 0.06)\ kg \cdot mol^{-1}$. Using this $\Delta\varepsilon$ and the selected $\varepsilon(H^+, ClO_4^-) = (0.14 \pm 0.02)\ kg \cdot mol^{-1}$, BROWN et al. (2005) found

$$\varepsilon(ZrF_3^+, ClO_4^-) = 0.20 \pm 0.06\ kg \cdot mol^{-1}$$

For the formation of ZrF_3^+, BROWN et al. (2005) considered four data points in 0.5, 2, and 4 M perchlorate, the SIT regression gave

$$ZrF_2^{2+} + HF(aq) \Leftrightarrow ZrF_3^+ + H^+$$

$$\log_{10}{}^*K_3^\circ(p = 3, 298.15\ K) = 2.99 \pm 0.22$$

with $\Delta\varepsilon = -(0.13 \pm 0.05)\ kg \cdot mol^{-1}$. From $\Delta\varepsilon$ and the selected values for $\varepsilon(ZrF_3^+, ClO_4^-)$ and $\varepsilon(H^+, ClO_4^-)$ then follows

$$\varepsilon(ZrF_2^{2+}, ClO_4^-) = (0.47 \pm 0.08)\ kg \cdot mol^{-1}$$

Seven data points were accepted by BROWN et al. (2005) for the formation of ZrF_2^{2+} in 1, 2, and 4 M perchlorate, the SIT regression resulted in

$$ZrF^{3+} + HF(aq) \Leftrightarrow ZrF_2^{2+} + H^+$$

$$\log_{10}{}^*K_2^\circ(p = 2, 298.15\ K) = 5.29 \pm 0.30$$

with $\Delta\varepsilon = -(0.02 \pm 0.06)\ kg \cdot mol^{-1}$. Combining this value for $\Delta\varepsilon$ with those selected for $\varepsilon(ZrF_2^{2+}, ClO_4^-)$ and $\varepsilon(H^+, ClO_4^-)$ leads to

$$\varepsilon(ZrF^{3+}, ClO_4^-) = 0.63 \pm 0.10\ kg \cdot mol^{-1}$$

Six data points for ZrF^{3+} in 1, 2, and 4 M perchlorate were included in the SIT regression, and BROWN et al. (2005) reported

$$Zr^{4+} + HF(aq) \Leftrightarrow ZrF^{3+} + H^+$$

$$\log_{10}{}^*K_1^\circ(p = 1, 298.15\ K) = 6.94 \pm 0.07$$

with $\Delta\varepsilon = -(0.12 \pm 0.01)\ kg \cdot mol^{-1}$, which leads to

$$\varepsilon(Zr^{4+}, ClO_4^-) = (0.89 \pm 0.10)\ kg \cdot mol^{-1}$$

by using the selected values for $\varepsilon(ZrF^{3+}, ClO_4^-)$ and $\varepsilon(H^+, ClO_4^-)$.

The stability constant for ZrF_5^- was determined by BROWN et al. (2005) from four data points in 0.5, 1, and 4 M perchlorate. According to the SIT regression

$$ZrF_4(aq) + HF(aq) \Leftrightarrow ZrF_5^- + H^+$$

$$\log_{10}{}^*K_5^\circ(p = 5, 298.15\ K) = 1.31 \pm 0.12$$

with $\Delta\varepsilon = -(0.00 \pm 0.02)\ kg \cdot mol^{-1}$. Combining this value for $\Delta\varepsilon$ with that selected for $\varepsilon(H^+, ClO_4^-)$ results in

$$\varepsilon(ZrF_5^-, Na^+) = -(0.14 \pm 0.03)\ kg \cdot mol^{-1}$$

For ZrF_6^{2-}, finally, BROWN et al. (2005) considered four data points in 0.5, 1, and 4 M perchlorate, their SIT analysis gave

$$ZrF_5^- + HF(aq) \Leftrightarrow ZrF_6^{2-} + H^+$$

$$\log_{10}{}^*K_6^\circ(p = 6, 298.15\ K) = 0.31 \pm 0.08$$

with $\Delta\varepsilon = -(0.13 \pm 0.05)\ kg \cdot mol^{-1}$, and

$$\varepsilon(ZrF_6^{-2}, Na^+) = -0.15 \pm 0.06\ kg \cdot mol^{-1}$$

following from this $\Delta\varepsilon$ and the selected $\varepsilon(ZrF_5^-, Na^+)$ and $\varepsilon(H^+, ClO_4^-)$.

For our database, we converted these stepwise stability constants of reactions expressed in terms of HF(aq) to overall stability constants of reactions of type $Zr^{4+} + q\ F^- \Leftrightarrow ZrF_q^{4-q}$ by using the selected $\log_{10}\beta^\circ(H^+ + F^- \Leftrightarrow HF(aq), 298.15\ K) = 3.18 \pm 0.02$ (GRENTHE et al. 1992, HUMMEL et al. 2002), resulting in:

$$Zr^{4+} + F^- \Leftrightarrow ZrF^{3+}$$

$$\log_{10}\beta_1^\circ(q = 1, 298.15\ K) = 10.12 \pm 0.07$$

$$Zr^{4+} + 2\ F^- \Leftrightarrow ZrF_2^{2+}$$

$$\log_{10}\beta_2^\circ(q = 2, 298.15\ K) = 18.55 \pm 0.31$$

$$Zr^{4+} + 3\ F^- \Leftrightarrow ZrF_3^+$$

$$\log_{10}\beta_3°(q = 3, 298.15\ K) = 24.72 \pm 0.38$$

$$Zr^{4+} + 4\ F^- \Leftrightarrow ZrF_4(aq)$$

$$\log_{10}\beta_4°(q = 4, 298.15\ K) = 30.11 \pm 0.40$$

$$Zr^{4+} + 5\ F^- \Leftrightarrow ZrF_5^-$$

$$\log_{10}\beta_5°(q = 5, 298.15\ K) = 34.60 \pm 0.42$$

$$Zr^{4+} + 6\ F^- \Leftrightarrow ZrF_6^{2-}$$

$$\log_{10}\beta_6°(q = 6, 298.15\ K) = 38.11 \pm 0.43$$

In addition to the values of $\varepsilon(Zr^{4+}, ClO_4^-)$, $\varepsilon(ZrF^{3+}, ClO_4^-)$, $\varepsilon(ZrF_2^{2+}, ClO_4^-)$, (ZrF_3^+, ClO_4^-), $\varepsilon(ZrF_5^-, Na^+)$, and $\varepsilon(ZrF_6^{-2}, Na^+)$ reported above, we also selected

$$\varepsilon(ZrF^{3+}, Cl^-) = 0.25 \pm 0.10\ kg \cdot mol^{-1}$$

$$\varepsilon(ZrF_2^{2+}, Cl^-) = 0.15 \pm 0.10\ kg \cdot mol^{-1}$$

$$\varepsilon(ZrF_3^+, Cl^-) = 0.05 \pm 0.10\ kg \cdot mol^{-1}$$

for our database by taking advantage of the estimation method by Hummel (2009).

There is one study that used calorimetry to determine the standard molar enthalpies of formation of zirconium fluoride complexes at 25˚C in 4.0 M $HClO_4$. The measured enthalpy changes for reactions of the type $ZrF_{p-1}^{5-p} + HF(aq) \Leftrightarrow ZrF_p^{4-p} + H^+$ are

$$\Delta_r H_m°(p = 1, 298.15\ K) = -(17.5 \pm 0.7)\ kJ \cdot mol^{-1}$$

$$\Delta_r H_m°(p = 2, 298.15\ K) = -(16.8 \pm 1.0)\ kJ \cdot mol^{-1}$$

$$\Delta_r H_m°(p = 3, 298.15\ K) = -(11.2 \pm 2.1)\ kJ \cdot mol^{-1}$$

$$\Delta_r H_m°(p = 4, 298.15\ K) = -(22.0 \pm 2.7)\ kJ \cdot mol^{-1}$$

The associated uncertainties were increased by BROWN et al. (2005) to account for the assumption that these enthalpy values are also valid at zero ionic strength[3]. For inclusion into our database, we

[3] Note that in the list of selected zirconium data (Table III-2 in BROWN et al. 2005) these reaction enthalpies were erroneously attributed to reactions of form $Zr^{4+} + q\ F^- \Leftrightarrow ZrF_q^{4-q}$, therefore, the reaction entropies listed in the same table are also incorrect. Moreover, the reaction enthalpies for $ZrF_{p-1}^{5-p} + HF(aq) \Leftrightarrow ZrF_p^{4-p} + H^+$ in HUMMEL et al.

expressed them in terms of reactions of type $Zr^{4+} + q\ F^- \Leftrightarrow ZrF_q^{4-q}$ by using the selected $\Delta_r H_m°(H^+ + F^- \Leftrightarrow HF(aq), 298.15\ K) = (12.2 \pm 0.3)\ kJ \cdot mol^{-1}$. Hence

$$\Delta_r H_m°(q = 1, 298.15\ K) = -(5.3 \pm 0.8)\ kJ \cdot mol^{-1}$$

$$\Delta_r H_m°(q = 2, 298.15\ K) = -(9.9 \pm 1.3)\ kJ \cdot mol^{-1}$$

$$\Delta_r H_m°(q = 3, 298.15\ K) = -(8.9 \pm 2.1)\ kJ \cdot mol^{-1}$$

$$\Delta_r H_m°(q = 4, 298.15\ K) = -(18.7 \pm 3.4)\ kJ \cdot mol^{-1}$$

5.1.2 Solid, liquid and gaseous zirconium fluorides

The synthetic solid $ZrF_4(\beta)$ is highly soluble and liquid $ZrF_4(l)$, as well as gaseous $ZrF_4(g)$, $ZrF_3(g)$, $ZrF_2(g)$, and $ZrF(g)$ are not relevant under low-temperature environmental conditions. Therefore, the corresponding data selected by BROWN et al. (2005) are not considered in our database.

5.2 Chlorine compounds and complexes

5.2.1 Aqueous zirconium chloride complexes

BROWN et al. (2005) examined five experimental studies dealing with zirconium chloride complexation in mixtures of perchloric and hydrochloric acid (2, 4, and 6.54 M) and re-interpreted all data using least-squares analysis. The data are consistent with the formation of $ZrCl^{3+}$, $ZrCl_2^{2+}$, $ZrCl_3^+$, and $ZrCl_4(aq)$. The mixed hydroxo-chloride complex $ZrOHCl^{2+}$ proposed in one study was considered to be very unlikely and was not accepted by BROWN et al. (2005). From their SIT analysis of four data points concerning the formation of $ZrCl^{3+}$ at all three ionic strengths follows

$$Zr^{4+} + Cl^- \Leftrightarrow ZrCl^{3+}$$

$$\log_{10}\beta_1°(298.15\ K) = 1.59 \pm 0.06$$

and $\Delta\varepsilon = -(0.14 \pm 0.02)\ kg \cdot mol^{-1}$. With the selected $\varepsilon(Zr^{4+}, ClO_4^-) = (0.89 \pm 0.10)\ kg \cdot mol^{-1}$, and $\varepsilon(Cl^-, H^+) = (0.12 \pm 0.01)\ kg \cdot mol^{-1}$ this value for $\Delta\varepsilon$ leads to

$$\varepsilon(ZrCl^{3+}, ClO_4^-) = (0.87 \pm 0.10)\ kg \cdot mol^{-1}$$

These data for $ZrCl^{3+}$ are included in our database.

(2002) have a wrong sign. As a consequence, the reaction enthalpies for reactions written in terms of F^- calculated by HUMMEL et al. (2002) are also incorrect.

In the case of $ZrCl_2^{2+}$, the SIT analysis of four data points at all three ionic strengths led BROWN et al. (2005) to

$$Zr^{4+} + 2\ Cl^- \Leftrightarrow ZrCl_2^{2+}$$

$$\log_{10}\beta_2^\circ(298.15\ K) = 2.17 \pm 0.24$$

with $\Delta\varepsilon = -(0.29 \pm 0.04)\ kg \cdot mol^{-1}$. From this value and those selected for $\varepsilon(Zr^{4+}, ClO_4^-)$ and $\varepsilon(Cl^-, H^+)$ follows

$$\varepsilon(ZrCl_2^{2+}, ClO_4^-) = (0.84 \pm 0.11)\ kg \cdot mol^{-1}$$

These data for $ZrCl_2^{2+}$ are also included in our database.

Following the discussion by HUMMEL et al. (2005) in their Chapter V.4 on weak complexes versus strong specific ion interaction, we used the value of $\varepsilon(ZrCl^{3+}, ClO_4^-)$ for

$$\varepsilon(ZrCl^{3+}, Cl^-) = \varepsilon(ZrCl^{3+}, ClO_4^-) = (0.87 \pm 0.10)\ kg \cdot mol^{-1}$$

and the value of $\varepsilon(ZrCl_2^{2+}, ClO_4^-)$ for

$$\varepsilon(ZrCl_2^{2+}, Cl^-) = \varepsilon(ZrCl_2^{2+}, ClO_4^-) = (0.84 \pm 0.11)\ kg \cdot mol^{-1}$$

It is important to keep in mind that in order to be consistent, these values for $\varepsilon(ZrCl^{3+}, Cl^-)$ and $\varepsilon(ZrCl_2^{2+}, Cl^-)$ should only be used in combination with $\varepsilon(Zr^{4+}, Cl^-) = \varepsilon(Zr^{4+}, ClO_4^-) = (0.89 \pm 0.10)\ kg \cdot mol^{-1}$.

BROWN et al. (2005) did not recommend any stability constants for $ZrCl_3^+$ and $ZrCl_4(aq)$ because of insufficient data for extrapolating the conditional constants to zero ionic strength.

5.2.2 Solid and gaseous zirconium chlorides

The data selected by BROWN et al. (2005) for the synthetic zirconium chloride solids $ZrCl_4(cr)$, $ZrCl_3(cr)$, $ZrCl_2(cr)$, and $ZrCl(cr)$ are not included in our database. $ZrCl_4(cr)$ is highly soluble. $ZrCl_3(cr)$, $ZrCl_2(cr)$, and $ZrCl(cr)$ are not relevant in aqueous environments because zirconium exists only in the +4 oxidation state.

The gaseous zirconium chlorides $ZrCl_4(g)$, $ZrCl_3(g)$, $ZrCl_2(g)$, and $ZrCl(g)$ are not relevant under low-temperature environmental conditions. The data selected by BROWN et al. (2005) are therefore not considered in our database.

5.3 Bromine compounds

The data selected by BROWN et al. (2005) for the synthetic zirconium bromide solids $ZrBr_4$(cr), $ZrBr_3$(cr), $ZrBr_2$(cr), and ZrBr(cr) are not included in our database. $ZrBr_4$(cr) is highly soluble. $ZrBr_3$(cr), $ZrBr_2$(cr), and ZrBr(cr) are not relevant in aqueous environments because zirconium exists only in the +4 oxidation state.

The data selected by BROWN et al. (2005) for the gaseous zirconium bromides $ZrBr_4$(g), $ZrBr_3$(g), $ZrBr_2$(g), and ZrBr(g) are not included in our database, because these gases are not relevant under low-temperature environmental conditions.

5.4 Iodine compounds

BROWN et al. (2005) selected thermodynamic data for the synthetic zirconium iodide solids ZrI_4(cr), ZrI_3(cr), ZrI_2(cr), and ZrI(cr). None of these solids occur naturally. In aqueous solutions, zirconium exists only in the +4 oxidation state. Therefore, ZrI_3(cr), ZrI_2(cr), ZrI(cr) are not relevant in aqueous environments and are not considered in our database. ZrI_4(cr) is hygroscopic and highly soluble and is also not considered.

BROWN et al. (2005) also selected thermodynamic data for the gaseous zirconium iodides ZrI_4(g), ZrI_3(g), ZrI_2(g), and ZrI(g). Since these gases are not relevant under low-temperature environmental conditions they are not part of our database.

6 Zirconium chalcogen compounds and complexes

6.1 Sulphur compounds and complexes

6.1.1 Zirconium sulphide compounds

Values for the Gibbs free energy of formation for the synthetic high-temperature zirconium sulphides ZrS_3(cr) , ZrS_2(cr), and $ZrS_{1.5}$(cr) were calculated by BROWN et al. (2005) using thermochemically measured enthalpies of formation and estimated entropies. These high-temperature solids are not considered in our database.

6.1.2 Zirconium sulphite compounds

BROWN et al. (2005) calculated a value for the standard molar Gibbs free energy of formation for the synthetic solid $Zr(SO_3)_2$(cr), which is not found in natural environments. This value is based on estimates for the standard molar enthalpy of formation and for the standard molar entropy and is not included in our database.

6.1.3 Zirconium sulphate compounds and complexes

6.1.3.1 Zirconium sulphate complexes

Solvent extraction and ion exchange techniques were employed in five experimental studies of zirconium sulphate complexes in perchloric acid media at three different ionic strengths (2, 2.33, and 4 M). The experimental data were reevaluated by BROWN et al. (2005) with least squares analysis providing stability constants for $ZrSO_4^{2+}$, $Zr(SO_4)_2(aq)$, and $Zr(SO_4)_3^{2-}$. SIT regression of the conditional constants (five data points) for the formation of $ZrSO_4^{2+}$ resulted in

$$Zr^{4+} + HSO_4^- \Leftrightarrow ZrSO_4^{2+} + H^+$$

$$\log_{10}{}^*\beta_1^\circ(298.15\ K) = 5.06 \pm 0.08$$

with $\Delta\varepsilon = -(0.19 \pm 0.02)$ kg · mol^{-1}. BROWN et al. (2005) obtained

$$\varepsilon(ZrSO_4^{2+}, ClO_4^-) = (0.39 \pm 0.13) \text{ kg} \cdot \text{mol}^{-1}$$

from $\Delta\varepsilon$ and the selected $\varepsilon(Zr^{4+}, ClO_4^-) = (0.89 \pm 0.10)$ kg · mol^{-1}, $\varepsilon(HSO_4^-, H^+) = -(0.17 \pm 0.05)$ kg · mol^{-1} (see below), and $\varepsilon(H^+, ClO_4^-) = (0.14 \pm 0.02)$ kg · mol^{-1}. Note that this value for $\varepsilon(ZrSO_4^{2+}, ClO_4^-)$ is, probably by oversight, not listed in the NEA compilation of selected ion interaction coefficients (BROWN et al. 2005, Table B-4). Nevertheless, it is included in our database. For $Zr(SO_4)_2(aq)$, the SIT regression (five data points) by BROWN et al. (2005) gave

$$Zr^{4+} + 2\ HSO_4^- \Leftrightarrow Zr(SO_4)_2(aq) + 2\ H^+$$

$$\log_{10}{}^*\beta_2^\circ(298.15\ K) = 7.58 \pm 0.20$$

with $\Delta\varepsilon = -(0.26 \pm 0.02)$ kg · mol^{-1}. BROWN et al. (2005) made use of this $\Delta\varepsilon$ together with the selected $\varepsilon(Zr^{4+}, ClO_4^-)$ and $\varepsilon(H^+, ClO_4^-)$ to derive $\varepsilon(HSO_4^-, H^+) = -(0.17 \pm 0.05)$ kg · mol^{-1}, assuming that there is no interaction of the neutral $Zr(SO_4)_2(aq)$ with any ion. From three data points for $Zr(SO_4)_3^{2-}$, finally, BROWN et al. (2005) obtained

$$Zr^{4+} + 3\ HSO_4^- \Leftrightarrow Zr(SO_4)_3^{2-} + 3\ H^+$$

$$\log_{10}{}^*\beta_3^\circ(298.15\ K) = 8.4 \pm 0.5$$

with $\Delta\varepsilon = (0.02 \pm 0.12)$ kg · mol^{-1}. With the value just derived for $\varepsilon(HSO_4^-, H^+)$ and those selected for $\varepsilon(Zr^{4+}, ClO_4)$ and $\varepsilon(H^+, ClO_4^-)$, this $\Delta\varepsilon$ leads to $\varepsilon(Zr(SO_4)_3^{2-}, H^+) = -(0.05 \pm 0.22)$ kg · mol^{-1}.

For inclusion in our database, the formation reactions of the Zr sulphate complexes were expressed in terms of SO_4^{2-} instead of HSO_4^-, and the stability constants derived above were converted by means of $\log_{10}{}^*\beta^\circ(H^+ + SO_4^{2-} \Leftrightarrow HSO_4^-, 298.15\ K) = 1.98 \pm 0.09$ leading to

$$Zr^{4+} + SO_4^{2-} \Leftrightarrow ZrSO_4^{2+}$$

$$\log_{10}\beta_1°(298.15\ K) = 7.04 \pm 0.09$$

$$Zr^{4+} + 2\ SO_4^{2-} \Leftrightarrow Zr(SO_4)_2(aq)$$

$$\log_{10}\beta_2°(298.15\ K) = 11.54 \pm 0.21$$

$$Zr^{4+} + 3\ SO_4^{2-} \Leftrightarrow Zr(SO_4)_3^{2-}$$

$$\log_{10}\beta_3°(298.15\ K) = 14.3 \pm 0.5$$

As the values for $\varepsilon(ZrSO_4^{2+}, Cl^-)$ and $\varepsilon(Zr(SO_4)_3^{2-}, Na^+)$ cannot be obtained from experiments in perchloric acid media, we estimated them according to HUMMEL (2009). The estimates

$$\varepsilon(Zr(SO_4)_3^{2-}, Na^+) = -(0.10 \pm 0.10)\ kg \cdot mol^{-1}$$

$$\varepsilon(ZrSO_4^{2+}, Cl^-) = (0.15 \pm 0.10)\ kg \cdot mol^{-1}$$

are included in our database.

BROWN et al. (2005) derived the standard molar enthalpies of formation for $ZrSO_4^{2+}$ and $Zr(SO_4)_2(aq)$ as follows: An experimental determination of the enthalpies of complexation of zirconium by sulphate in 2 M perchloric acid resulted in

$$\Delta_r H_m°(Zr^{4+} + HSO_4^- \Leftrightarrow ZrSO_4^{2+} + H^+, 298.15\ K) = (13.0 \pm 0.5)\ kJ \cdot mol^{-1}$$

and

$$\Delta_r H_m°(ZrSO_4^{2+} + HSO_4^- \Leftrightarrow Zr(SO_4)_2(aq) + H^+, 298.15\ K) = (8 \pm 1)\ kJ \cdot mol^{-1}$$

Assuming that the enthalpies of reaction at zero ionic strength are within the error intervals of the enthalpies measured in 2 M $HClO_4$, BROWN et al. (2005) employed these measured values together with the selected $\Delta_f H_m°(Zr^{4+}, 298.15\ K) = -(608.5 \pm 5.0)\ kJ \cdot mol^{-1}$ and $\Delta_f H_m°(HSO_4^-, 298.15\ K) = -(886.9 \pm 1.0)\ kJ \cdot mol^{-1}$ (the standard molar enthalpy of formation for H^+ is by definition zero) to get

$$\Delta_f H_m°(ZrSO_4^{2+}, 298.15\ K) = -(1480.9 \pm 5.1)\ kJ \cdot mol^{-1}$$

$$\Delta_f H_m°(Zr(SO_4)_2, aq, 298.15\ K) = -(2359.8 \pm 5.2)\ kJ \cdot mol^{-1}$$

These values are also included in our database.

6.1.3.2 Zirconium sulphate solids

BROWN et al. (2005) calculated standard molar Gibbs free energies of formation for the synthetic solid $Zr(SO_4)_2$(cr), and for the mineral $Zr(SO_4)_2 \cdot 4H_2O$(cr) (zircosulphate) from standard molar enthalpies of formation and standard molar entropies. Since these phases are extremely soluble in water, they are not included in our database.

6.2 Selenium and tellurium compounds

$Zr(SeO_3)_2$(cr): BROWN et al. (2005) selected only a value for the standard molar enthalpy of formation of this synthetic solid, which is therefore not considered in our database.

Zircon tellurium compounds: BROWN et al. (2005) selected thermodynamic data for the synthetic solids $ZrTe_{1.843}$(cr), $ZrTe_2$(cr), Zr_5Te_4(cr), and $ZrTe_3O_8$(cr). As Te is not part of our database, these phases are omitted.

7 Group 15 compounds and complexes

7.1 Zirconium nitrogen compounds and complexes

7.1.1 Zirconium nitride compounds

Thermodynamic data for the synthetic phase ZrN(cr), which does not occur in natural environments, were selected by BROWN et al. (2005) based on calorimetric measurements. It is doubtful, whether this phase forms at low temperatures and it is therefore omitted from our database.

7.1.2 Zirconium nitrate complexes

Experimental data on zirconium nitrate complexation are limited and only available at two different ionic strengths (2 and 4 M mixed nitrate/perchlorate solutions). The nitrate complexes appear to be weak. The best constrained stability constant is that for $ZrNO_3^{3+}$. The experimental data were re-analyzed by BROWN et al. (2005) using least squares techniques to provide conditional stability constants. In the case of $ZrNO_3^{3+}$, SIT analysis by BROWN et al. (2005) of three such constants, obtained by cation exchange resin, and liquid ion exchange methods, resulted in

$$Zr^{4+} + NO_3^- \Leftrightarrow ZrNO_3^{3+}$$

$$\log_{10}\beta_1^\circ(298.15\ \mathrm{K}) = 1.59 \pm 0.08$$

with $\Delta\varepsilon = -(0.08 \pm 0.04)$ kg $\cdot$ mol^{-1}. From this $\Delta\varepsilon$ and the selected $\varepsilon(Zr^{4+}, ClO_4^-) = (0.89 \pm 0.10)$ kg $\cdot$ mol^{-1} and $\varepsilon(NO_3^-, H^+) = (0.07 \pm 0.01)$ kg $\cdot$ mol^{-1} BROWN et al. (2005) calculated

$$\varepsilon(ZrNO_3^{3+}, ClO_4^-) = (0.88 \pm 0.11)\ kg \cdot mol^{-1}$$

These data for $ZrNO_3^{3+}$ are included in our database, as well as

$$\varepsilon(ZrNO_3^{3+}, Cl^-) = (0.25 \pm 0.10)\ kg \cdot mol^{-1}$$

which we estimated according to HUMMEL (2009).

For the stability constant of $Zr(NO_3)_2^{2+}$, BROWN et al. (2005) relied on a liquid ion exchange, and a cation exchange resin experiment in 2 M mixed nitrate/perchlorate solutions. They extrapolated the average of the conditional constants for

$$Zr^{4+} + 2\ NO_3^- \Leftrightarrow Zr(NO_3)_2^{2+}$$

to zero ionic strength with a value for $\Delta\varepsilon$ calculated from the selected values for $\varepsilon(Zr^{4+}, ClO_4^-)$ and $\varepsilon(NO_3^-, H^+)$ and from the estimate

$$\varepsilon(Zr(NO_3)_2^{2+}, ClO_4^-) \approx \varepsilon(ZrCl_2^{2+}, ClO_4^-) = (0.84 \pm 0.11)\ kg \cdot mol^{-1}$$

and selected the resulting

$$\log_{10}\beta_2^\circ(298.15\ K) = 2.64 \pm 0.17$$

These values for $\log_{10}\beta_2^\circ$ and $\varepsilon(ZrCl_2^{2+}, ClO_4^-)$ are also included in our database accompanied by

$$\varepsilon(Zr(NO_3)_2^{2+}, Cl^-) = (0.15 \pm 0.10)\ kg \cdot mol^{-1}$$

which we estimated according to HUMMEL (2009).

Stability constants for $Zr(NO_3)_3^+$ and $Zr(NO_3)_4(aq)$ were not recommended by BROWN et al. (2005), because the conditional constants could not be reliably extrapolated to zero ionic strength.

7.2 Zirconium phosphorous compounds

$Zr(HPO_4)_2 \cdot H_2O(cr)$: The solubility of zirconium phosphate was measured by HEVESY & KIMURA (1925) in hydrochloric acid solutions (6.01 and 10.00 m HCl). The composition of the solid used in the experiments was found to be $ZrH_4P_2O_9$, which the authors interpreted as $ZrO(H_2PO_4)_2$ resulting from the reaction of zirconyl ions, ZrO^{2+}, with phosphate ions. Since it was later shown that zirconyl ions do not exist in solution, the solid used in the experiments was more likely $Zr(HPO_4)_2 \cdot H_2O(cr)$. Using the SIT, BROWN et al. (2005), obtained from the solubility data

$$Zr(HPO_4)_2 \cdot H_2O(cr) + 4\ H^+ \Leftrightarrow Zr^{4+} + 2\ H_3PO_4(aq) + H_2O(l)$$

$$\log_{10}K_{s,0}^\circ(298.15\ K) = -22.8 \pm 3.1$$

The value

$$\Delta_f H_m°(Zr(HPO_4)_2 \cdot H_2O, cr, 298.15\ K) = -(3466.1 \pm 1.6)\ kJ \cdot mol^{-1}$$

selected by BROWN et al. (2005) is the average of data obtained by adiabatic calorimetry. For the following reasons, the data selected by BROWN et al. (2005) for $Zr(HPO_4)_2 \cdot H_2O$(cr) are included in our database as supplemental data only, serving as placeholders: $Zr(HPO_4)_2 \cdot H_2O$(cr) is a synthetic phase and does not occur in natural environments. The solubilities were only measured by dissolution of the solid. As BROWN et al. (2005) mention, the applicability of the SIT at such high concentrations of HCl may be questionable.

$Zr(HPO_4)_2(\alpha)$: The data selected by BROWN et al. (2005) for this synthetic solid, which is not found in natural environments, are based on thermochemical measurements. Since it is unclear whether this solid forms in low-temperature environments we did not include it in our database.

$Zr(HPO_4)_2(\beta)$: Since BROWN et al. (2005) selected only a value for the enthalpy of formation for this synthetic phase, it is not considered in our database.

$Zr(HPO_4)_2 \cdot 2H_2O$(cr): Since BROWN et al. (2005) selected only a value for the enthalpy of formation for this synthetic phase, it is not considered in our database.

ZrP_2O_7(cr): BROWN et al. (2005) selected only values for the heat capacity and entropy for this synthetic solid, which is therefore not included in our database.

$NaZr_2P_3O_{12}$(cr): The data selected by BROWN et al. (2005) for this synthetic solid, which does not occur in natural environments, are based on calorimetry. Since it is unlikely that this phase is formed in low-temperature environments it is not considered in our database.

7.3 Zirconium arsenic compounds

BROWN et al. (2005) selected only standard molar formation enthalpies for $Zr(HAsO_4)_2(\alpha)$, $Zr(HAsO_4)_2(\beta)$, and $Zr(HAsO_4)_2 \cdot H_2O$(cr). Therefore, these phases are omitted from our database.

8 Group 14 compounds and complexes

8.1 Carbon compounds and complexes

8.1.1 Zirconium carbides

The thermodynamic data for ZrC(cr) selected by BROWN et al. (2005) are based on thermochemical data. Carbides are formed neither at low temperatures nor in aqueous environments. For these reasons, ZrC(cr) is not included in our database.

8.1.2 Zirconium carbonate complexes

There are only a few experimental studies dealing with Zr-carbonate complexes and BROWN et al. (2005) were able to derive reliable thermodynamic constants only for $Zr(CO_3)_4^{4-}$. This species appears to be dominant when carbonate concentrations exceed the concentration of dissolved Zr. Based on the experimental data, BROWN et al. (2005) identified $Zr(CO_3)_2(aq)$, $Zr(CO_3)_3^{2-}$, and $ZrOH(CO_3)_3^{3-}$ as other probable carbonate complexes and remarked that considering only $Zr(CO_3)_4^{4-}$ as Zr carbonate complex may not be sufficient to describe the complexity of the Zr carbonate complexation, especially in dilute solutions.

A conditional constant for the reaction

$$Zr^{4+} + 4\ CO_3^{2-} \Leftrightarrow Zr(CO_3)_4^{4-}$$

was derived by BROWN et al. (2005) from a re-evaluation of solubility data of amorphous $Zr(OH)_4$ in NH_4NO_3 (I = 1 M) at 20˚C by taking into account the new hydrolysis model (discussed in Section 4.1 above). Since the solubility was measured at a single ionic strength, the usual linear SIT extrapolation procedure was not possible. Instead, BROWN et al. (2005) calculated a value for

$$\Delta\varepsilon = \varepsilon(Zr(CO_3)_4^{4-}, NH_4^+) - \varepsilon(Zr^{4+}, NO_3^-) - 4\ \varepsilon(CO_3^{2-}, NH_4^+)$$

estimating the unknown interaction parameters by analogy with homovalent pairs of ions:

$$\varepsilon(Zr(CO_3)_4^{4-}, NH_4^+) \approx \varepsilon(U(CO_3)_4^{4-}, Na^+) = -(0.09 \pm 0.20)\ kg \cdot mol^{-1}$$

$$\varepsilon(Zr^{4+}, NO_3^-) \approx \varepsilon(Th^{4+}, NO_3^-) = (0.33 \pm 0.35)^{4} kg \cdot mol^{-1}$$

$$\varepsilon(CO_3^{2-}, NH_4^+) \approx \varepsilon(CO_3^{2-}, K^+) = (0.02 \pm 0.10)\ kg \cdot mol^{-1}$$

Using the resulting $\Delta\varepsilon$, BROWN et al. (2005) obtained the thermodynamic constant at infinite dilution and at 20˚C, which they assumed to be valid also at 25˚C. Thus, they selected

$$\log_{10}\beta_4^\circ(298.15\ K) = 42.9 \pm 1.0$$

which is also selected for our database.

Note that $\varepsilon(Zr(CO_3)_4^{4-}, NH_4^+) \approx \varepsilon(U(CO_3)_4^{4-}, Na^+) = -(0.09 \pm 0.20)\ kg \cdot mol^{-1}$ was erroneously listed by BROWN et al. (2005) in their Table B-5 as $\varepsilon(Zr(CO_3)_4^{4-}, Na^+)$, which is also a reasonable estimate, since all three pairs of ions are homovalent. We therefore included

---

[4] Note that the value selected in a later NEA review by RAND et al. (2009) and included in our database is slightly different: $\varepsilon(Th^{4+}, NO_3^-) = (0.31 \pm 0.12)\ kg \cdot mol^{-1}$.

$$\varepsilon(Zr(CO_3)_4^{4-}, Na^+) = -0.09 \pm 0.20 \text{ kg} \cdot \text{mol}^{-1}$$

in our database.

8.2 Silicon compounds

$ZrSiO_4$(cr), zircon: BROWN et al. (2005) selected thermodynamic data for zircon from various thermochemical measurements. Since zircon is a high-temperature mineral mainly formed in igneous rocks, these data are not included in our database.

Calcium zirconium silicate compounds: Based on thermochemical measurements (enthalpies of formation and heat capacities), BROWN et al. (2005) selected thermodynamic data for $Ca_2ZrSi_3O_{12}$(cr) and $Ca_3ZrSi_2O_9$(cr). Since it is not known whether these synthetic solids (they are not found in natural environments) form at low temperatures they are not included in our database.

Strontium zirconium silicate compounds: BROWN et al. (2005) selected a value for the standard molar formation enthalpy of $Sr_6ZrSi_5O_{18}$(cr). As no other data were given, this solid (not found in natural environments) is not included in our database. BROWN et al. (2005) also calculated a value for $\Delta_f G_m°(SrZrSi_2O_7, cr, 298.15 K)$ from calorimetric data (heat capacity, entropy, enthalpy of formation). Since nothing is known about the formation of this synthetic solid (not found in natural environments) at low temperatures it is not included in our database.

Sodium zirconium silicate compounds: The $\Delta_f G_m°$ values selected by BROWN et al. (2005) for Na_2ZrSiO_5(cr), $Na_2ZrSi_2O_7$(cr) (parakeldyshite), and $Na_4Zr_2Si_3O_{12}$(cr), were calculated from thermochemical data. It is unlikely that these solids are formed under low-temperature conditions, therefore they are not included in our database. The $\Delta_f G_m°$ values for the minerals, $Na_2ZrSi_3O_9 \cdot 2H_2O$(cr) (catapleiite), $Na_2ZrSi_4O_{11}$(cr) (vlasovite), and $Na_2ZrSi_6O_{15} \cdot 3H_2O$(cr) (elpidite) selected by BROWN et al. (2005) were derived from dissolution experiments at 50˚C by AJA et al. (1995 and 1997) that could not be reversed. BAUSSY et al. (1974) synthesized these minerals from amorphous silica, amorphous ZrO_2 gels, and from hydrated Na_2CO_3 under hydrothermal conditions at a constant pressure of 700 bars. Formation temperatures were 340 - 450˚C for catapleiite, 350 - 500˚C for elpidite, and > 500˚C for vlasovite. Thus, it is very unlikely that these minerals are formed under low-temperature conditions and they are therefore excluded from our database.

Cesium zirconium silicate compounds: BROWN et al. (2005) selected a calorimetrically determined value for the formation enthalpy of $Cs_2ZrSi_2O_7$(cr). No other data were given, therefore, $Cs_2ZrSi_2O_7$(cr) is not considered in our database.

Table 1.1: Zirconium data selected by NEA (BROWN et al. 2005) but not included in TDB Version 12/07. For explanations see text.

Gases	$Zr(g)$ [a], $ZrO(g)$ [ad], $ZrO_2(g)$ [ad], $ZrF_4(g)$ [bd], $ZrF_3(g)$ [a], $ZrF_2(g)$ [a], $ZrF(g)$ [a], $ZrCl_4(g)$ [ad], $ZrCl_3(g)$ [ad], $ZrCl_2(g)$ [ad], $ZrCl(g)$ [a], $ZrBr_4(g)$ [ad], $ZrBr_3(g)$ [b], $ZrBr_2(g)$ [b], $ZrBr(g)$ [b], $ZrI_4(g)$ [ac], $ZrI_3(g)$ [a], $ZrI_2(g)$ [a], $ZrI(g)$ [a]
Solids	$Zr(\beta)$ [b], $Zr(\omega)$ [b], $ZrH(cr)$ [a], $ZrH_2(\varepsilon)$ [a], $ZrF_4(\beta)$ [ad], $ZrCl_4(cr)$ [ad], $ZrCl_3(cr)$ [a], $ZrCl_2(cr)$ [a], $ZrCl(cr)$ [a], $ZrBr_4(cr)$ [bd], $ZrBr_3(cr)$ [b], $ZrBr_2(cr)$ [b], $ZrBr(cr)$ [b], $ZrI_4(cr)$ [ac], $ZrI_3(cr)$ [a], $ZrI_2(cr)$ [a], $ZrI(cr)$ [a], $ZrS_3(cr)$ [a], $ZrS_2(cr)$ [a], $ZrS_{1.5}(cr)$ [a], $Zr(SO_3)_2(cr)$ [a], $Zr(SO_4)_2(cr)$ [a], $Zr(SO_4)_2 \cdot 4H_2O(cr)$ [a], $Zr(SeO_3)_2(cr)$ [b], $ZrTe_{1.843}(cr)$ [a], $ZrTe_2(cr)$ [a], $Zr_5Te_4(cr)$ [a], $ZrTe_3O_8(cr)$ [b], $ZrN(cr)$ [ad], $Zr(HPO_4)_2(\alpha)$ [a], $Zr(HPO_4)_2(\beta)$ [b], $Zr(HPO_4)_2 \cdot 2H_2O(cr)$ [b], $ZrP_2O_7(cr)$ [b], $NaZr_2P_3O_{12}(cr)$ [a], $Zr(HAsO_4)_2(\alpha)$ [b], $Zr(HAsO_4)_2(\beta)$ [b], $Zr(HAsO_4)_2 \cdot H_2O(cr)$ [b], $ZrC(cr)$ [a], $ZrSiO_4(cr)$ [a], $Ca_2ZrSi_3O_{12}(cr)$ [a], $Ca_3ZrSi_2O_9(cr)$ [a], $SrZrSi_2O_7(cr)$ [a], $Sr_6ZrSi_5O_{18}(cr)$ [b], $Na_2ZrSiO_5(cr)$ [a], $Na_2ZrSi_2O_7(cr)$ [a], $Na_2ZrSi_3O_9 \cdot 2H_2O(cr)$ [a], $Na_2ZrSi_4O_{11}(cr)$ [a], $Na_2ZrSi_6O_{15} \cdot 3H_2O(cr)$ [a], $Na_4Zr_2Si_3O_{12}(cr)$ [a], $Cs_2ZrSi_2O_7(cr)$ [b]
Liquids	$Zr(l)$ [b], $ZrF_4(l)$ [bd]
Aqueous species	All included

[a] Single species data including $\Delta_f G_m^\circ$
[b] Single species data excluding $\Delta_f G_m^\circ$
[c] Reaction data including $\log_{10} K^\circ$
[d] Reaction data excluding $\log_{10} K^\circ$

Table 1.2: Selected zirconium data. All data included in TDB Version 12/07 are taken from BROWN et al. (2005) with the exception of those marked with an asterisk (*). Supplemental data are in italics. New or changed data with respect to TDB Version 01/01 (HUMMEL et al. 2002) are shaded.

		TDB Version 01/01				TDB Version 12/07				
Name	**Redox**	$\Delta_f G_m°$ [kJ · mol^{-1}]	$\Delta_f H_m°$ [kJ · mol^{-1}]	$S_m°$ [J · K^{-1} · mol^{-1}]	$C_{p,m}°$ [J · K^{-1} · mol^{-1}]	$\Delta_f G_m°$ [kJ · mol^{-1}]	$\Delta_f H_m°$ [kJ · mol^{-1}]	$S_m°$ [J · K^{-1} · mol^{-1}]	$C_{p,m}°$ [J · K^{-1} · mol^{-1}]	**Species**
Zr(cr)	0	0.0	0.0	39.0	-	0.0	0.0	39.08 ± 0.10	26.08 ± 0.05	Zr(cr)
Zr+4	IV	-557.7 ± 10.8	-	-	-	-528.5 ± 9.2	-608.5 ± 5.0	-491.0 ± 35.2	-	Zr^{4+}

		TDB Version 01/01		TDB Version 12/07			
Name	**Redox**	$\log_{10}\beta°$	$\Delta_r H_m°$ [kJ · mol^{-1}]	$\log_{10}\beta°$	$\Delta_r H_m°$ [kJ · mol^{-1}]	$\Delta_f H_m°$ [kJ · mol^{-1}]	**Reaction**
ZrOH+3	IV	0.3	-	0.32 ± 0.22	-	-	$Zr^{4+} + H_2O(l) \Leftrightarrow ZrOH^{3+} + H^+$
Zr(OH)2+2	IV	-	-	0.98 ± 1.06	-	-	$Zr^{4+} + 2\ H_2O(l) \Leftrightarrow Zr(OH)_2^{2+} + 2\ H^+$
Zr(OH)4	IV	-9.7	-	-2.19 ± 1.70	-	-	$Zr^{4+} + 4\ H_2O(l) \Leftrightarrow Zr(OH)_4(aq) + 4\ H^+$
Zr(OH)5-	IV	-16	-	-	-	-	$Zr^{4+} + 5\ H_2O(l) \Leftrightarrow Zr(OH)_5^- + 5\ H^+$
Zr(OH)6-2	IV	-	-	-29.0 ± 0.7	-	-	$Zr^{4+} + 6\ H_2O(l) \Leftrightarrow Zr(OH)_6^{2-} + 6\ H^+$
Zr3(OH)4+8	IV	-	-	0.4 ± 0.3	-	-2970.8 ± 10.0	$3\ Zr^{4+} + 4\ H_2O(l) \Leftrightarrow Zr_3(OH)_4^{8+} + 4\ H^+$
Zr3(OH)9+3	IV	-	-	12.19 ± 0.08	-	-	$3\ Zr^{4+} + 9\ H_2O(l) \Leftrightarrow Zr_3(OH)_9^{3+} + 9\ H^+$
Zr4(OH)8+8	IV	-	-	6.52 ± 0.65	-	-	$4\ Zr^{4+} + 8\ H_2O(l) \Leftrightarrow Zr_4(OH)_8^{8+} + 8\ H^+$
Zr4(OH)15+	IV	-	-	12.58 ± 0.24	-	-	$4\ Zr^{4+} + 15\ H_2O(l) \Leftrightarrow Zr_4(OH)_{15}^+ + 15\ H^+$
Zr4(OH)16	IV	-	-	8.39 ± 0.80	-	-6706.16 ± 7.20	$4\ Zr^{4+} + 16\ H_2O(l) \Leftrightarrow Zr_4(OH)_{16}(aq) + 16\ H^+$
CaZr(OH)6	IV	-	-	*(-24.6 ± 0.3)** [a]	-	-	$Ca^{2+} + Zr^{4+} + 6\ H_2O(l) \Leftrightarrow CaZr(OH)_6(aq) + 6\ H^+$
Ca2Zr(OH)6+2	IV	-	-	(-22.6 ± 0.3)*	-	-	$2\ Ca^{2+} + Zr^{4+} + 6\ H_2O(l) \Leftrightarrow Ca_2Zr(OH)_6^{2+} + 6\ H^+$
Ca3Zr(OH)6+4	IV	-	-	(-23.2 ± 0.3)*	-	-	$3\ Ca^{2+} + Zr^{4+} + 6\ H_2O(l) \Leftrightarrow Ca_3Zr(OH)_6^{4+} + 6\ H^+$
ZrF+3	IV	10.2 ± 0.1	(-5.3) [b]	10.12 ± 0.07	(-5.3 ± 0.8) [c]	-	$Zr^{4+} + F^- \Leftrightarrow ZrF^{3+}$

		TDB Version 01/01		TDB Version 12/07			
Name	**Redox**	**$\log_{10}\beta°$**	**$\Delta_r H_m°$** [kJ · mol^{-1}]	**$\log_{10}\beta°$**	**$\Delta_r H_m°$** [kJ · mol^{-1}]	**$\Delta_f H_m°$** [kJ · mol^{-1}]	**Reaction**
ZrF2+2	IV	18.5 ± 0.2	(-9.9)[b]	18.55 ± 0.31	(-9.9 ± 1.3)[c]	-	$Zr^{4+} + 2\ F^- \Leftrightarrow ZrF_2^{2+}$
ZrF3+	IV	24.7 ± 0.3	(-8.9)[b]	24.72 ± 0.38	(-8.9 ± 2.1)[c]	-	$Zr^{4+} + 3\ F^- \Leftrightarrow ZrF_3^{+}$
ZrF4	IV	30.1 ± 0.8	(-19)[b]	30.11 ± 0.40	(-18.7 ± 3.4)[c]	-	$Zr^{4+} + 4\ F^- \Leftrightarrow ZrF_4(aq)$
ZrF5-	IV	34.7 ± 1.1	-	34.60 ± 0.42	-	-	$Zr^{4+} + 5\ F^- \Leftrightarrow ZrF_5^-$
ZrF6-2	IV	38.4 ± 1.5	-	38.11 ± 0.43	-	-	$Zr^{4+} + 6\ F^- \Leftrightarrow ZrF_6^{2-}$
ZrCl+3	IV	1.5 ± 0.3	-	1.59 ± 0.06	-	-	$Zr^{4+} + Cl^- \Leftrightarrow ZrCl^{3+}$
ZrCl2+2	IV	-	-	2.17 ± 0.24	-	-	$Zr^{4+} + 2\ Cl^- \Leftrightarrow ZrCl_2^{2+}$
ZrSO4+2	IV	7.0 ± 0.1	-	7.04 ± 0.09	-	-1480.9 ± 5.1	$Zr^{4+} + SO_4^{2-} \Leftrightarrow ZrSO_4^{2+}$
Zr(SO4)2	IV	-	-	11.54 ± 0.21	-	-2359.8 ± 5.2	$Zr^{4+} + 2\ SO_4^{2-} \Leftrightarrow Zr(SO_4)_2(aq)$
Zr(SO4)3-2	IV	-	-	14.3 ± 0.5	-	-	$Zr^{4+} + 3\ SO_4^{2-} \Leftrightarrow Zr(SO_4)_3^{2-}$
ZrNO3+3	IV	-	-	1.59 ± 0.08	-	-	$Zr^{4+} + NO_3^- \Leftrightarrow ZrNO_3^{3+}$
Zr(NO3)2+2	IV	-	-	2.64 ± 0.17	-	-	$Zr^{4+} + 2\ NO_3^- \Leftrightarrow Zr(NO_3)_2^{2+}$
Zr(CO3)4-4	IV	-	-	42.9 ± 1.0	-	-	$Zr^{4+} + 4\ CO_3^{2-} \Leftrightarrow Zr(CO_3)_4^{4-}$

[a] Note that the uncertainty was not reported in THOENEN (2012)
[b] Corrected values, the original values given by HUMMEL et al. (2002) are incorrect (see text for discussion)
[c] Note that the values reported in Table III-2 by BROWN et al. (2005) are incorrect (see text for discussion)

		TDB Version 01/01			TDB Version 12/07			
Name	**Redox**	**$\log_{10}K_{s,0}°$**	**$\Delta_f H_m°$** [kJ · mol^{-1}]	**$C_{p,m}°$** [J · K^{-1} · mol^{-1}]	**$\log_{10}K_{s,0}°$**	**$\Delta_f H_m°$** [kJ · mol^{-1}]	**$C_{p,m}°$** [J · K^{-1} · mol^{-1}]	**Reaction**
Baddeleyite	IV	-1.9	-	-	-7.0 ± 1.6	-1100.6 ± 1.3	55.96 ± 0.79	$ZrO_2(cr) + 4\ H^+ \Leftrightarrow Zr^{4+} + 2\ H_2O(l)$
Zr(OH)4(am)(fr)	IV	-	-	-	-3.24 ± 0.10	-	-	$Zr(OH)_4(am, fr) + 4\ H^+ \Leftrightarrow Zr^{4+} + 4\ H_2O(l)$
Zr(HPO4)2:H2O(cr)	*IV*	-	-	-	*-22.8 ± 3.1*	*-3466.1 ± 1.6*	-	*$Zr(HPO_4)_2 \cdot H_2O(cr) + 4\ H^+ \Leftrightarrow Zr^{4+} + 2\ H_3PO_4(aq) + H_2O(l)$*

Table 1.3: Selected SIT ion interaction coefficients $\varepsilon_{j,k}$ [kg · mol^{-1}] for zirconium species. All data included in TDB Version 12/07 are taken from BROWN et al. (2005) unless indicated otherwise. Data estimated according to HUMMEL (2009) are shaded. Supplemental data are in italics.

j k → ↓	Cl^- $\varepsilon_{j,k}$	ClO_4^- $\varepsilon_{j,k}$	NO_3^- $\varepsilon_{j,k}$	Li^+ $\varepsilon_{j,k}$	Na^+ $\varepsilon_{j,k}$	K^+ $\varepsilon_{j,k}$
Zr+4	0.33 ± 0.09	0.89 ± 0.10	0.33 ± 0.35	0	0	0
ZrOH+3	0.25 ± 0.10	0.57 ± 0.13	-	0	0	0
Zr(OH)2+2	0.15 ± 0.10	0.62 ± 0.39	-	0	0	0
Zr(OH)4	0	0	0	0	0	0
Zr(OH)6-2	0	0	0	-	-0.10 ± 0.10	-
Zr3(OH)4+8	0.33 ± 0.28	1.89 ± 0.31	2.28 ± 0.35	0	0	0
Zr3(OH)9+3	0.25 ± 0.10	0.93 ± 0.35	-	0	0	0
Zr4(OH)8+8	0.75 ± 0.50	3.61 ± 1.02	-	0	0	0
Zr4(OH)15+	0.05 ± 0.10	0.09 ± 0.92	-0.02 ± 1.46	0	0	0
Zr4(OH)16	0	0	0	0	0	0
CaZr(OH)6	*0*	*0*	*0*	*0*	*0*	*0*
Ca2Zr(OH)6+2	(0.1 ± 0.1)[a]	(0.3 ± 0.1)[a]	-	0	0	0
Ca3Zr(OH)6+4	(0.40 ± 0.07)[a]	(0.89 ± 0.12)[a]	-	0	0	0
ZrF+3	0.25 ± 0.10	0.63 ± 0.10	-	0	0	0
ZrF2+2	0.15 ± 0.10	0.47 ± 0.08	-	0	0	0
ZrF3+	0.05 ± 0.10	0.20 ± 0.06	-	0	0	0
ZrF4	0	0	0	0	0	0
ZrF5-	0	0	0	-	-0.14 ± 0.03	-
ZrF6-2	0	0	0	-	-0.15 ± 0.06	-
ZrCl+3	(0.87 ± 0.10)[b]	0.87 ± 0.10	-	0	0	0
ZrCl2+2	(0.84 ± 0.11)[b]	0.84 ± 0.11		0	0	0
ZrSO4+2	0.15 ± 0.10	(0.39 ± 0.13)[c]	-	0	0	0
Zr(SO4)2	0	0	0	0	0	0
Zr(SO4)3-2	0	0	0	-	-0.10 ± 0.10	-
ZrNO3+3	0.25 ± 0.10	0.88 ± 0.11	-	0	0	0
Zr(NO3)2+2	0.15 ± 0.10	0.84 ± 0.11	-	0	0	0
Zr(CO3)4-4	0	0	0	-	-0.09 ± 0.20	-

[a] ALTMAIER et al. (2008)
[b] This work, to be used in combination with $\varepsilon(Zr^{4+}, Cl^-) = \varepsilon(Zr^{4+}, ClO_4^-) = (0.89 \pm 0.10)$ kg · mol^{-1}
[c] Data given by BROWN et al. (2005) in text but not in Table B-4

Table 1.4: Selected SIT ion interaction coefficients $\varepsilon_{j,k}$ [kg · mol^{-1}] for auxiliary species needed to derive data for zirconium.

j k → ↓	OH^- $\varepsilon_{j,k}$
Ca^{2+}	(-0.45 ± 0.03)[a]

[a] ALTMAIER et al. (2008)

9 References

AJA, S.U, WOOD, S.A. & WILLIAMS-JONES, A.E. (1995): The aqueous geochemistry of Zr and the solubility of some Zr-bearing minerals. Applied Geochemistry, 10, 603-620.

AJA, S.U, WOOD, S.A. & WILLIAMS-JONES, A.E. (1997): The solubility of some alkali-bearing Zr minerals in hydrothermal solutions. Materials Research Society Symposium Proceedings, 432, 69-74.

ALTMAIER, M., NECK, V. & FANGHÄNEL, TH. (2008): Solubility of Zr(IV), Th(IV) and Pu(IV) hydrous oxides in $CaCl_2$ solutions and the formation of ternary Ca-M(IV)-OH complexes. Radiochimica Acta, 96, 541-550.

BAUSSY, G., CARUBA, R., BAUMER, A. & TURCO, G. (1974): Minéralogie expérimentale dans le système ZrO_2-SiO_2-Na_2O-H_2O. Corrélations pétrogénétiques. Bulletin de la Société Française de Minéralogie et Cristallographie, 97, 433-444.

BROWN, P.L., CURTI, E. & GRAMBOW, B. (2005): Chemical Thermodynamics of Zirconium. Elsevier, Amsterdam, 512 pp.

BRENDEBACH, B., ALTMAIER, M., ROTHE, J., NECK, V. & DENECKE, M.A. (2007): EXAFS study of aqueous Zr^{IV} and Th^{IV} complexes in alkaline $CaCl_2$ solutions: $Ca_3[Zr(OH)_6]^{4+}$ and $Ca_4[Th(OH)_8]^{4+}$. Inorganic Chemistry, 46, 6804-6810.

CLEARFIELD, A. & VAUGHAN, P.A. (1956): The crystal structure of zirconyl chloride octahydrate and zirconyl bromide octahydrate. Acta Crystallographica, 9, 555-558.

CURTI, E. (2001): Nagra/PSI Thermochemical Database Update: Selection of Data for Zirconium. PSI Internal Report, TM-44-01-01, Paul Scherrer Institut, Villigen, Switzerland, 32 pp.

HUMMEL, W., BERNER, U., CURTI, E., PEARSON, F.J. & THOENEN, T. (2002): Nagra/PSI Chemical Thermodynamic Data Base 01/01. Nagra NTB 02-16, Nagra, Wettingen, Switzerland. Also published by Universal Publishers/upublish.com, Parkland, USA.

HEVESY, G. & KIMURA, K. (1925): The solubilities of the phosphates of zirconium and hafnium. Journal of the American Chemical Society, 47, 2540-2544.

HUMMEL, W., ANDEREGG, G., PUIGDOMÈNECH, I., RAO, L. & TOCHIYAMA, O. (2005): Chemical Thermodynamics of Compounds and Complexes of U, Np, Pu, Am, Tc, Se, Ni, and Zr with Selected Organic Ligands. Elsevier, Amsterdam, 1088 pp.

HUMMEL, W. (2009): Ionic strength corrections and estimation of SIT ion interaction coefficients. PSI Internal Report, TM-44-09-01, Paul Scherrer Institut, Villigen, Switzerland, 15 pp.

MUHA, G.M. & VAUGHAN, P.A. (1960): Structure of the complex ion in aqueous solutions of zirconyl and hafnyl oxyhalides. Journal of Chemical Physics, 33, 194-199.

THOENEN, T. (2012): The PSI/Nagra Chemical Thermodynamic Database 12/07: Compilation of updated and new data with respect to the Nagra/PSI Chemical Thermodynamic Data Base 01/01. PSI Internal Report, TM-44-12-06, Paul Scherrer Institut, Villigen, Switzerland, 35 pp.

WALTHER, C., ROTHE, J., FUSS, M., BÜCHNER, S., KOLTSOV, S. & BERGMANN, T. (2007): Investigation of polynuclear Zr(IV) hydroxyde complexes by nanoelectrospray mass-spectrometry combined with XAFS. Analytical and Bioanalytical Chemistry, 388, 409-431.

Acknowledgements

Within the scope of the quality assurance procedures of our database project this report has been read and commented on by U. Berner and W. Hummel.