Solubility and hydrolysis of Zr oxides: a review and supplemental data

By E. Curti1,* and C. Degueldre2

1 Waste Management Laboratory, Paul Scherrer Institut, CH-5232 Villigen, Switzerland
2 Laboratory for Materials Behaviour, Paul Scherrer Institut, CH-5232 Villigen, Switzerland

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Summary. Thermodynamic data for Zr(IV) have been reviewed in the context of a recent update of the Nagra/PSI thermochemical database, which is primarily used in safety assessment calculations for radioactive waste repositories in Switzerland. In spite of the important role of Zr in nuclear reactor technology and as fission product in radioactive waste, the thermodynamic properties of this element in aqueous solutions are poorly constrained and published data are frequently contradictory. Specifically, hydrolysis constants, which are critical to any geochemical calculation of Zr speciation in aqueous solutions, may vary by several orders of magnitude.

Published solubility and hydrolysis data for Zr oxides were reviewed and evaluated. Recent solubility measurements on crystalline ZrO2, obtained in our laboratory, were integrated in this analysis. These new data are the only ZrO2 solubility measurements obtained in a pH region relevant for environmental aqueous systems, where equilibrium concentrations decrease to nanomolar levels.

All solubility data of (hydrous) Zr oxides can be reproduced satisfactorily by a single set of hydrolysis constants, provided that only data measured from undersaturation are considered. This set includes the species Zr4+, Zr(OH)4−, Zr(OH)3 and Zr(OH)2. However, present experimental data are still not sufficient to establish a fully reliable database.

1. Introduction

93Zr is one of the long-lived fission products of concern in Swiss high-level radioactive waste [1]. Due to its slow decay, this radionuclide will persist over millions of years after repository closure. The rate of release from the repository will critically depend on the aqueous concentration imposed by a solubility-limiting phase. Moreover, zirconium is widely used in nuclear reactors as a fuel containment material (zircalloy cladding) and could play an important role in advanced nuclear fuels such as zirconia-based and “cermet” inert matrix fuels [2]. Zr(IV) is considered to be immobile in most low-temperature natural environments. This is confirmed by laboratory experience indicating that Zr oxides and silicates are almost insoluble in the pH region relevant for environmental systems. Yet, it proved impossible to find in the literature quantitative data supporting these qualitative statements. Usually, the qualification “insoluble” simply means “below the detection limit of the analytical method”, which in the case of the methods used to study the aqueous geochemistry of Zr is hardly below 10−6 M. Whether the solubility limit is 10−6 or 10−10 M may be irrelevant for the purposes of a specific laboratory investigation, but is of critical importance for safety assessment analyses of radioactive waste repositories.

The aim of this paper is to discuss published constants, evaluate new experimental data on the solubility of Zr oxides and to derive a consistent set of hydrolysis constants and solubility products in the system Zr-H2O. The effect of other ligands on complexation and solubility is discussed elsewhere [3, 4].

2. Analysis of hydrolysis data

2.1 Survey of published data

Table 1 summarises thermodynamic constants for Zr hydrolysis reactions from two frequently cited sources [5, 6]. The two sets of constants show large discrepancies. For instance, the solubility products of (hydrous) Zr oxides differ by more than 6 orders of magnitude.

The solubility data of Bilinski et al. [5] refer to precipitates separated from strongly oversaturated solutions in the pH range 1.5 to 6.5. The experiments involved the detection of colloid precipitation through optical measurements of the solution turbidity (tindallometry). Such precipitates form through condensation of dissolved polymers. The transformation (depolymerisation) into crystalline anhydrous oxide is very slow and may be kinetically hindered. It occurs through the stepwise removal of protons and hydroxo groups from coordinating water molecules [7]. The stable final product is monoclinic zirconia, or baddeleyite as mineral [8], with stoichiometric formula ZrO2.

In contrast to the data of Bilinski et al. [5], the solubility product specified by Baes and Mesmer [6] refers to crystalline ZrO2. Although determined with the help of calori-metric data, this solubility product reproduces equilibrium concentrations measured from undersaturation reasonably well (see the data reported in Fig. 1 except those from [5]).
The solubility curves depicted in Fig. 1 were computed using the set of constants proposed by Baes and Mesmer [6] (Table 1) and the specific ion interaction theory (SIT) for the extrapolation to the desired ionic strength and medium. Three curves were calculated for ionic strengths and media encompassing the experimental conditions used in the various studies (two constant ionic strength curves for 0.001 M and 1 M NaClO₄, and a curve from 1 to 15 M NaOH for comparison with the data of Sheka and Pevzner [10]).

The data of Kovalenko and Bagdasarov [9] deviate about 0.5 log units from the solubility curve calculated with the constants recommended by Baes and Mesmer [6]. This discrepancy may be related to the short ageing time (24 hours) of the solid used in these dissolution experiments. In contrast, the data of Sheka and Pevzner [10], who used a precipitate aged for 45 days at 30–40 °C, are in excellent agreement with the calculated solubility curve, in spite of the large ionic strength corrections needed in such highly alkaline solutions. Such agreement is expected, considering that our medium correction is equivalent to that applied by Baes and Mesmer [6]. Sheka and Pevzner [10] state explicitly (without further clarification) that they took precautions against CO₂ contamination. This excludes in principle contributions by Zr carbonate complexes in their solubility measurements. Even if some CO₂ contamination occurred, the very high hydroxide concentrations in their experiments (above 1 M) should have prevented any carbonate complex to become predominant over Zr(OH)₅⁺.

The data reported in Fig. 1 from Adair et al. [11] refer to experiments carried out from undersaturation with pure monolinolic zirconia at low and high pH. In spite of their poor reproducibility, these measurements are roughly consistent with the solubility curve predicted using the constants selected by Baes and Mesmer [6].

2.2 Integration of new solubility data for crystalline ZrO₂

The results of recent dissolution experiments carried out in our laboratory with pure monoclinic and yttrium-doped cubic zirconia [3, 12] will be also considered. The aim of these experiments was to determine solubilities of zirconia-based inert matrix fuel (IMF) in a realistic repository environment. IMF is proposed as an alternative form of nuclear fuel for operating light water reactors in order to efficiently burn excess Pu stockpiles [1, 13].

The experiments were carried out at pH 9 in solutions with different carbonate concentrations (deionised water, 5 × 10⁻³, 5 × 10⁻² and 5 × 10⁻¹ M NaHCO₃). A total carbonate concentration of 2 × 10⁻³ M was estimated for the experiments carried out in deionised water, assuming equilibrium with atmospheric carbon dioxide. Two different solids were used: (a) Y-stabilised cubic zirconia, produced in-house through a coprecipitation technique; (b) reactor-grade, HF-free monoclinic zirconia (Ceraç™). Both phases were sintered at about 2000 K for the purposes of the original work. Aliquots of crushed zirconia powder (2 g each) were introduced in dialysis bags and immersed in bot-

Table 1. Compilation of hydrolysis constants for Zr. The data in bold, recommended by Baes and Mesmer [6] were used to construct the solubility curves shown in Fig. 1. The constants of Bilinski et al. [5] are conditional constants obtained in dilute solutions at 20 °C.

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>Zr⁴⁺ + H₂O = Zr(OH)³⁺ + H⁺</td>
<td>log β₀</td>
<td>0.3⁺</td>
<td>—</td>
</tr>
<tr>
<td>Zr⁴⁺ + 2H₂O = Zr(OH)⁵⁺ + 2H⁺</td>
<td>log β₀</td>
<td>—</td>
<td>—2.77</td>
</tr>
<tr>
<td>Zr⁴⁺ + 3H₂O = Zr(OH)⁶⁺ + 3H⁺</td>
<td>log β₀</td>
<td>—</td>
<td>—4.33</td>
</tr>
<tr>
<td>Zr⁴⁺ + 4H₂O = Zr(OH)⁷⁺ (aq) + 4H⁺</td>
<td>log β₀</td>
<td>—</td>
<td>—9.7⁺</td>
</tr>
<tr>
<td>Zr⁴⁺ + 5H₂O = Zr(OH)⁸⁺ + 5H⁺</td>
<td>log β₀</td>
<td>—</td>
<td>—16.0⁺</td>
</tr>
<tr>
<td>Zr(OH)₅⁺ (s) + 4H⁺ = Zr⁴⁺ + 4H₂O or ZrO₂₃³⁻ (s) + 4H⁺ = Zr⁴⁺ + 2H₂O</td>
<td>log₁₀ Kₑₒ</td>
<td>—1.9</td>
<td>4.6</td>
</tr>
</tbody>
</table>

a: Based on Noren [16];
b: Estimated by Baes and Mesmer [6];
c: Based on Sheka and Pevzner [10].
Table 2. Dissolution of monoclinic and cubic ZrO$_2$ in pure water and in 0.005, 0.05, 0.5 M NaHCO$_3$ solutions open to atmospheric CO$_2$. The concentrations have been determined from ICP-MS analyses of the $^{90}$Zr and $^{91}$Zr peaks using natural isotopic abundances. The data plotted in Fig. 1 are highlighted in bold.

<table>
<thead>
<tr>
<th>Atomic mass</th>
<th>Reaction time/days</th>
<th>Monoclinic ZrO$_2$</th>
<th>Cubic ZrO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{90}$Zr</td>
<td>1</td>
<td>(4.1±0.5)×10$^{-8}$</td>
<td>(4.1±0.5)×10$^{-8}$</td>
</tr>
<tr>
<td>$^{90}$Zr</td>
<td>1</td>
<td>(4.2±0.9)×10$^{-8}$</td>
<td>(4.2±0.9)×10$^{-8}$</td>
</tr>
<tr>
<td>$^{91}$Zr</td>
<td>12</td>
<td>(2.5±0.1)×10$^{-8}$</td>
<td>(2.5±0.1)×10$^{-8}$</td>
</tr>
<tr>
<td>$^{91}$Zr</td>
<td>12</td>
<td>(2.6±0.2)×10$^{-8}$</td>
<td>(2.6±0.2)×10$^{-8}$</td>
</tr>
<tr>
<td>$^{90}$Zr</td>
<td>43</td>
<td>(9.3±0.4)×10$^{-8}$</td>
<td>(9.3±0.4)×10$^{-8}$</td>
</tr>
<tr>
<td>$^{90}$Zr</td>
<td>42.4</td>
<td>(9.4±0.5)×10$^{-8}$</td>
<td>(9.4±0.5)×10$^{-8}$</td>
</tr>
<tr>
<td>$^{91}$Zr</td>
<td>250</td>
<td>(5.5±0.4)×10$^{-8}$</td>
<td>(5.5±0.4)×10$^{-8}$</td>
</tr>
<tr>
<td>$^{91}$Zr</td>
<td>250</td>
<td>(5.5±0.6)×10$^{-8}$</td>
<td>(5.5±0.6)×10$^{-8}$</td>
</tr>
</tbody>
</table>

Fig. 2. Evolution of Zr concentration for deionised water equilibrated with monoclinic and cubic zirconia. The median and maximum Zr concentrations obtained from blanks (experiments performed without the solid phase) are also shown. The data indicate a slight decrease in Zr concentrations after an intermediate maximum, implying that equilibrium concentrations may be even lower than those measured after 250 days.

3. Data selection

A striking feature of the data plotted in Fig. 1 is that, as far as equilibrium is approached from undersaturation, crystalline and fresh precipitates yield similar solubilities. In contrast, approaching equilibrium from oversaturated solutions, as done by Bilinski et al. [5], leads to much higher Zr concentrations. This is due to the formation of polymers and colloidal suspensions typical of acidic Zr solutions. As pointed out by Solovkin and Tsvektova [14], depolymerization in acidic Zr solutions is strongly hindered and thus exceedingly slow. Such Zr solutions thus equilibrate very slowly upon base addition and can persist for long times. Since equilibration times of only 24 hours were involved in the experiments of Bilinski et al. [5] there is little doubt that their data do not represent equilibrium between solid and aqueous phase.

Based on the evidence discussed above, and considering that Zr equilibrium concentrations in environmental systems will be approached from undersaturation, the constants of Bilinski et al. [5] should not be used in geochemical calcu-
lations, as they represent a metastable state obtained under particular laboratory conditions.

We also reject the hydrolysis constants given in the review of Aja et al. [15], according to which the solubility of monoclinic ZrO₂ would attain the millimolar range in the neutral pH region (see Fig. 7 in [15]). Such predictions trace back to a largely overestimated solubility product for monoclinic zirconia, which is based on a non-referenced standard Gibbs free energy of −18.1 kJ mol⁻¹ (log₁₀ K₀,s = 3.1) for the reaction Zr(OH)₄ (aq) = ZrO₂ (cr) + 2H₂O (see Eq. (15) in [15]).

A closer look to the numbers given by Aja et al. [15] also reveals an erroneous formation constant for Zr(OH)₄ (aq), which probably arises from a mistake in the manipulation of the original data. In their Table 1, Aja et al. [15] list log₁₀ β₄ = 52.0 for this complex in 1.0 m NaClO₄ and refer this constant to Bilinski et al. [5]. The latter authors give for the specified medium the following conditional constants (see Table 2 in [5]):

\[
\begin{align*}
\log_{10} K_{s,0} &\approx 3.8 \quad \text{Zr(OH)₄} (s) + 4H⁺ = Zr⁴⁺ + 4H₂O \\
\log_{10} K_{s,4} &\approx -4.36 \quad \text{Zr(OH)₄} (s) = \text{Zr(OH)₄} (aq) \\
\log_{10} K_{a} &\approx -13.94 \quad \text{H₂O} = H⁺ + OH⁻
\end{align*}
\]

A linear combination of the above equilibria yields the required formation constant: \( \log_{10} \beta_4 = \log_{10} K_{s,4} - \log_{10} K_{s,0} - 4 \log_{10} K_a \approx 47.6. \) The value of 52.0 given by Aja et al. [15] differs from our result by exactly 4.4, suggesting that these authors omitted the \( \log_{10} K_{s,4} \) term in the preceding calculation. This omission leads to the relative predominance of the Zr-tetrahydroxocomplex over the other hydroxo species in the speciation diagram given in [15].

Although based on a few investigations carried out under extreme pH conditions and on rough estimation procedures, the constants proposed by Baes and Mesmer [6] seem to be appropriate as they yield predictions in good agreement with all available solubility data obtained from undersaturation. The new data of Pouchon et al. [3] are an independent consistency check, since they were not used to derive the constants used for the calculation of the solubility curve.

Note that the three hydroxo complexes Zr(OH)⁺, Zr(OH)₄ (aq) and Zr(OH)₃⁻⁰ are sufficient to reproduce all the selected solubility data. We decided to exclude the constants for the polymeric species Zr₃(OH)₈⁺ and Zr₆(OH)₁₆⁺⁺ from the updated database of our organisation [4], because these data are not well assessed and polymerisation of Zr species does not play a role in environmentally relevant aqueous solutions. Note also that there is no experimental confirmation for \( \log \beta_0^s = -9.7 \), since no adequate solubility data in the pH range between 3 and 9 are available.

As solubility-limiting solid we selected the monoclinic form of crystalline Zr oxide, which is demonstrably the stable form in low temperature aqueous systems [8], to which we associated the solubility product given by Baes and Mesmer [6].

4. Conclusions

Dissolution experiments carried out with Zr oxides of various crystallinity and degree of hydration yield results consistent with the hydrolysis and solubility constants selected by Baes and Mesmer [6]. Recent experiments provide the first independent confirmation for the very low Zr concentrations predicted by this solubility model at environmentally relevant pH values (pH = 9). High-pH data indicate predominance of the pentahydroxo complex in the alkaline region, but this needs to be confirmed by new experiments conducted under strict CO₂ exclusion.

Since solubility data for Zr oxides of widely different structure, crystallinity and water content fit a single solubility/speciation model, it is suggested that the same surface structure forms for all the different solids upon reaction with water. Similar phenomena have already been observed for tetravalent actinides. For instance, the solubilities of amorphous and crystalline forms of Th and U(IV) oxides become indistinguishable above pH ~ 5–6 [17].

References