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Chemical speciation of environmentally significant metals with inorganic ligands. Part 5: The $Zn^{2+} + OH^-$, CI^- , CO_3^{2-} , SO_4^{2-} , and PO_4^{3-} systems (IUPAC Technical Report)*

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Abstract: The numerical modeling of Zn^{II} speciation amongst the environmental inorganic ligands Cl⁻, OH⁻, CO₃²⁻, SO₄²⁻, and PO₄³⁻ requires reliable values for the relevant stability (formation) constants. This paper compiles and provides a critical review of these constants and related thermodynamic data. It recommends values of log₁₀ $\beta_{p,q,r}^{\circ}$ valid at $I_m = 0$ mol·kg⁻¹ and 25 °C (298.15 K), and reports the empirical reaction ion interaction coefficients, $\Delta \varepsilon$, required to calculate log₁₀ $\beta_{p,q,r}$ values at higher ionic strengths using the Brønsted–Guggenheim–Scatchard specific ion interaction theory (SIT). Values for the corresponding reaction enthalpies, $\Delta_r H$, are reported where available. There is scope for additional high-quality measurements for the Zn²⁺ + H⁺ + CO₃²⁻ system and for the Zn²⁺ + OH⁻ and Zn²⁺ + SO₄²⁻ systems at I > 0.

In acidic and weakly alkaline fresh water systems (pH < 8), in the absence of organic ligands (e.g., humic substances), Zn^{II} speciation is dominated by $Zn^{2+}(aq)$. In this respect, Zn^{II} contrasts with Cu^{II} and Pb^{II} (the subjects of earlier reviews in this series) for which carbonato- and hydroxido- complex formation become important at pH > 7. The speciation of Zn^{II} is dominated by $ZnCO_3(aq)$ only at pH > 8.4.

In seawater systems, the speciation at pH = 8.2 is dominated by $Zn^{2+}(aq)$ with $ZnCl^+$, $Zn(Cl)_2(aq)$, $ZnCO_3(aq)$, and $ZnSO_4(aq)$ as minor species. This behaviour contrasts with that for Cu^{II} and Pb^{II} for which at the pH of seawater in equilibrium with the atmosphere at 25 °C ($\log_{10} \{[H^+]/c^\circ\} \approx 8.2$) the MCO₃(aq) complex dominates over the MCl_n⁽²⁻ⁿ⁾⁺ species. The lower stability of the different complexes of Zn^{II} compared with those of Cu^{II} , Pb^{II}, and Cd^{II} is also illustrated by the percentage of uncomplexed M²⁺ in seawater, which is ca. 55, 3, 2, and 3.3 % of $[M^{II}]_T$, respectively.

Keywords: chemical speciation; environmental chemistry; inorganic ligands; IUPAC Analytical Chemistry Division; stability constants; zinc.

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CONTENTS

- 1. INTRODUCTION
- 2. SUMMARY OF RECOMMENDED VALUES
- 3. Zn^{II} SOLUTION CHEMISTRY
- 4. EVALUATION OF EQUILIBRIUM CONSTANTS (HOMOGENEOUS REACTIONS)
 - 4.1 The Zn^{2+} + OH⁻ system
 - 4.1.1 Formation of ZnOH⁺
 - 4.1.2 Formation of Zn(OH)₂(aq)
 - 4.1.3 Formation of $Zn(OH)_{3_{-}}^{-}$
 - 4.1.4 Formation of Zn(OH)
 - 4.1.5 Formation of Zn_2OH^{3+}
 - 4.2 The $Zn^{2+} + Cl^{-}$ system
 - 4.2.1 Formation of ZnCl⁺
 - 4.2.2 Formation of ZnCl₂(aq)
 - 4.2.3 Formation of $ZnCl_3^{-}$ and $ZnCl_4^{2-}$
 - 4.3 The $Zn^{2+} + CO_3^{2-}$ system
 - 4.3.1 Formation of ZnCO₃(aq)
 - 4.3.2 Formation of $Zn(CO_3)_2^{2}$
 - 4.3.3 Formation of $ZnHCO_3^{\mp}$ 4.3.4 Formation of $Zn_2CO_3^{2+}$
 - 4.4 The $Zn^{2+} + SO_4^{2-}$ system
 - 4.4.1 Formation of ZnSO₄(aq)
 - 4.4.2 Formation of $Zn(SO_4)_2^{2-1}$
 - 4.4.3 Formation of higher-order and mixed complexes
 - 4.5 The $Zn^{2+} + PO_4^{3-}$ system
- 5. EVALUATION OF EQUILIBRIUM CONSTANTS (HETEROGENEOUS REACTIONS)
 - 5.1 The Zn^{2+} + OH⁻ system and the solubility of zinc oxide and hydroxide
 - 5.2 The $Zn^{2+} + CO_3^{2-}$ system
 - 5.2.1 Solubility of $ZnCO_3(s)$ (smithsonite)
 - 5.2.2 Solubility of $Zn_5(OH)_6(CO_3)_2(s)$ (hydrozincite)

 - 5.3 The $Zn^{2+} + SO_4^{2-}$ system 5.4 The $Zn^{2+} + PO_4^{3-}$ system
- 6. EVALUATION OF ENTHALPY DATA (HOMOGENEOUS AND HETEROGENEOUS **REACTIONS**)
 - 6.1 The Zn^{2+} + OH⁻ system

 - 6.2 The $Zn^{2+} + Cl^{-}$ system 6.3 The $Zn^{2+} + CO_{3}^{2-}$ system 6.4 The $Zn^{2+} + SO_{4}^{2-}$ system
 - 6.4.1 Formation of ZnSO₄(aq)
 - 6.4.2 Formation of $Zn(SO_4)_2^{2-1}$
- SPECIATION IN MULTICOMPONENT SYSTEMS: $Zn^{2+} + OH^{-} + Cl^{-} + CO_3^{2-} + PO_4^{3-} + CO_3^{2-} + CO_3^{2-}$ 7. SO₄²⁻
 - 7.1 Fresh water in equilibrium with $CO_2(g)$
 - 7.2 Seawater and saline systems
 - 7.3 Summary

8. QUANTITIES, SYMBOLS, AND UNITS USED IN THIS TECHNICAL REPORT

- 8.1 Quantities, symbols, and units
- 8.2 Subscripts and superscripts
 - 8.2.1 Subscripts

8.2.2 Superscripts

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REFERENCES

APPENDIX 1A

Data evaluation criteria

APPENDIX 1B

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Calculation of the interaction coefficients between Zn^{2+} and ClO_4^{-} and NO_3^{-}
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APPENDIX 2

Graphical evaluation for the interaction coefficients between Zn^{2+} and ClO_4^- and NO_3^-

APPENDIX 3

Selected equilibrium constants

APPENDIX 4

SIT plots for $Zn^{2+}+L$ systems

1. INTRODUCTION

This review is the last in a series relevant to the speciation of heavy metal ions in environmental waters of low to moderate ionic strength. It identifies the best available equilibrium data for use in chemical speciation modeling of reactions of Zn^{2+} with the major inorganic ligands present in environmental systems: Cl⁻, OH⁻, CO₃²⁻, SO₄²⁻, and PO₄³⁻. These quantities were derived from a critical evaluation of the literature, followed by regression analyses of the accepted data using Brønsted–Guggenheim–Scatchard specific ion interaction theory (SIT) functions [97GRE]. The previous reviews in this series were on the Hg²⁺ [2005PBa], Cu²⁺ [2007PBa], Pb²⁺ [2009PBa], and Cd²⁺ [2011POW] complexation reactions with these ligands. The primary source of data is the IUPAC Stability Constants Database, *SC-Database* [2010PET], and reference citations are based on those adopted there; see also the additional note at the beginning of the "References" section. The protonation* reactions of CO₃²⁻ and PO₄³⁻ were also reviewed [2005PBa].

The reader is referred to the earlier reviews in this series [2005PBa, 2007PBa, 2009PBa, 2011POW] which provide core information that is not repeated in the present document. Those reviews specify (i) the nomenclature used to express stability constants, e.g., $\beta_{p,q,r}$, $*\beta_{p,q,r}$, K_n , and $*K_n$ (Appendix 1A in [2005PBa]); (ii) the principles of SIT [97GRE]; and (iii) the application of SIT to the determination of standard equilibrium constants, $\beta_{p,q,r}^{\circ}$, valid at $I_m = 0 \text{ mol} \cdot \text{kg}^{-1}$ (infinite dilution). In this review, the SIT relationship is used to effect regression of "accepted" stability constants

In this review, the SIT relationship is used to effect regression of "accepted" stability constants measured at finite ionic strengths to obtain the $\beta_{p,q,r}$ ° values. In summary, for the general reaction (omitting charges except for H⁺)

$$p\mathbf{M} + q\mathbf{L} + r\mathbf{H}_2\mathbf{O} \rightleftharpoons \mathbf{M}_p\mathbf{L}_q(\mathbf{OH})_r + r\mathbf{H}^+$$
(1)

the SIT relationship between the standard equilibrium constant $\beta_{p,q,r}^{\circ}$, and that determined in an ionic medium of ionic strength I_m , $\beta_{p,q,r}$, is

$$\log_{10} \beta_{p,q,r} - \Delta z^2 D - r \log_{10} a(\mathrm{H_2O}) = \log_{10} \beta_{p,q,r}^{\circ} - \Delta \varepsilon I_m$$
⁽²⁾

^{*}By common usage, the terms "proton" and "protonation" refer to the natural isotopic mixture of hydrogen, not isotopically pure 1 H⁺. Strictly speaking, the reaction is hydronation.

In this equation, Δz^2 is defined by

$$\Delta z^2 = (p z_{\rm M} + q z_{\rm L} - r)^2 + r - p(z_{\rm M})^2 - q(z_{\rm L})^2$$

The value of D is defined by the activity coefficient relationship on the molality scale for a single ion i

$$\log_{10} \gamma_m(i) = -z_i^2 A \sqrt{I_m} (1 + a_j B \sqrt{I_m})^{-1} + \Sigma_k \varepsilon(i,k) m_k$$

= $-z_i^2 D + \Sigma_k \varepsilon(i,k) m_k$ (3)

in which k represents the "swamping" electrolyte ions N⁺ or X⁻, $\varepsilon(i,k)$ is the aqueous SIT coefficient for short-range interactions between ions i and k, and $\Delta \varepsilon$ is the reaction SIT coefficient, which is given by

$$\Delta \varepsilon = \varepsilon \text{ (complex, N^+ or X^-)} + r\varepsilon (H^+, X^-) - p\varepsilon (M^{n+}, X^-) - q\varepsilon (L^{m-}, N^+)$$

The term $a_j B$ is set (with very occasional exceptions) at 1.5 kg^{1/2}·mol^{-1/2} [2005PBa]. For a 1:1 electrolyte, the term $\log_{10} a(H_2O)$ can be calculated from the solution osmotic coefficient [59ROB]. For NaClO₄ media at 25 °C, the following approximation holds: $\log_{10} a(H_2O) \approx -(0.01484 \pm 0.00018)$ ($I_m/mol\cdot kg^{-1}$) at $0 \le I_m/mol\cdot kg^{-1} \le 3.5$ [2009PBa].

The criteria by which published data ($\beta_{p,q,r}$ and $\Delta_r H$) are "accepted" or "rejected" for the critical evaluations, are repeated in Appendix 1A. The data that meet our selection criteria for use in the SIT regression analyses are listed in Tables A3-1 through A3-16 (Appendix 3). The values for $\log_{10} K_n$ (reported) are given on the molality (mol·kg⁻¹) or amount concentration (mol·dm⁻³) scales, as published. In most cases, the uncertainties assigned to $\log_{10} K_n$ (reported) by the original authors reflect analytical and numerical precision but not systematic errors. In determining the value of $\log_{10} K_n$ (accepted) or $\log_{10} \beta_{p,q,r}$ (accepted) for inclusion in the regression analysis, an additional uncertainty has been assigned to each value of $\log_{10} K_n$ (reported) that reflects our estimation of the precision and reliability of the experimental methods [97GRE, Appendix C]. The $\log_{10} K_n$ (accepted) values are listed in Tables A3-1 to A3-14 on the molality scale (to facilitate SIT analysis). The assigned uncertainty for each "accepted" datum (see [2005PBa]) represents a 95 % confidence level and is used to weight each value in the SIT regression analysis. The weighting of each datum was $1/u^2$ where u is the assigned uncertainty for each value as indicated in the Tables.

The application of SIT to the accepted equilibrium constant values (Tables A3-1 to A3-14) involves extrapolation of $\log_{10} \beta_{p,q,r} - \Delta z^2 D - r \log_{10} a(H_2O)$ to m_k (or I_m) = 0 mol·kg⁻¹ for a system with a large excess of a 1:1 electrolyte, using eq. 2. Where appropriate an initial SIT analysis was used to identify (and reject) outliers based on their deviation from the calculated confidence limits. The regressions (shown in Appendix 4) yield $\log_{10} \beta_{p,q,r}^{\circ}$ (or $\log_{10} K_n^{\circ}$) as the intercept at $I_m = 0$ mol·kg⁻¹ and the reaction SIT coefficient, $-\Delta \varepsilon(i,k)$, as the slope. The uncertainties reported for $\log_{10} \beta_{p,q,r}^{\circ}$ ($\log_{10} K_n^{\circ}$) and $\Delta \varepsilon$ represent the 95 % confidence level for the regression intercept and slope, respectively. In the case of reaction enthalpy data (Tables A3-15 and A3-16), the SIT regressions to $I_m = 0$ mol·kg⁻¹ [97GRE] involve the relationship ($\Delta_r H - \Psi(I_m) - rL_1$) = $\Delta_r H^{\circ} - RT^2 I_m \Delta \varepsilon_L$, where $\Psi(I_m) = 0.75\Delta(z^2)A_L\sqrt{I_m} (1 + 1.5\sqrt{I_m})^{-1}$. The regression of ($\Delta_r H - \Psi(I_m) - rL_1$) against I_m yields $\Delta_r H^{\circ}$ as the intercept and ($-RT^2\Delta\varepsilon_L$) as the slope. For a more detailed discussion of terms, see [2005PBa].

Reactions described herein generally refer to aqueous solution, e.g.

$$Zn^{2+}(aq) + 2H_2O \rightleftharpoons Zn(OH)_2(aq) + 2H^+(aq)$$

For simplicity, suffixes are not used unless a species has zero net charge, in which case the phase is specified, e.g., (aq) or (s). In this document, "amount concentration" is abbreviated to "concentration", the units being mol·dm⁻³ (= mol·L⁻¹, or M).

For each Zn²⁺-ligand combination, this review will, where possible,

- identify the most reliable stability constants;
- identify (and reject for specified reasons) unreliable stability constants;

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- establish correlations among the accepted data on the basis of ionic strength dependence, using the SIT functions;
- establish recommended values of $\beta_{p,q,r}^{\circ}$ and K_{s0}° and related constants at 25 °C (298.15 K) and $I_m = 0 \text{ mol} \cdot \text{kg}^{-1}$, and of $\Delta \varepsilon$; and
- identify, where data are available, the most reliable reaction enthalpy values $\Delta_r H$.

Using the derived values of $\beta_{p,q,r}^{\circ}$ and $\Delta \varepsilon$, this review also provides:

- examples of distribution diagrams for binary and multicomponent systems; and
- values of $\beta_{p,q,r}$ applicable to calculations in fresh and saline water systems.

2. SUMMARY OF RECOMMENDED VALUES

Tables 1–5 provide a summary of the standard equilibrium constants ($I_m = 0 \text{ mol}\cdot\text{kg}^{-1}$), SIT reaction coefficients ($\Delta \varepsilon$), and, where available, reaction enthalpies for the formation of Zn²⁺ complexes with the selected inorganic anions. The reader is referred to [2005PBa] for definition of the terms "Recommended" (R) and "Provisional" (P) used in these Tables. The term "Indicative" (I) implies a value that the present authors consider to be reasonable, or at least the best available, but which has not been substantiated by independent studies under the same or similar experimental conditions. The log₁₀ $\beta_{p,q,r}^{\circ}$, log₁₀ K_n° , and log₁₀ $*\beta_{p,q,r}^{\circ}$ values are for 298.15 K, 100 kPa, and infinite dilution ($I_m = 0 \text{ mol}\cdot\text{kg}^{-1}$).

Reaction	Constant	Evaluation
$\overline{Zn^{2+} + H_2O} \rightleftharpoons ZnOH^+ + H^+$	$log_{10} *K_{1}^{\circ} = -8.96 \pm 0.05$ $\Delta \varepsilon = (0.03 \pm 0.02) \text{ kg} \cdot \text{mol}^{-1}$ $\Delta_{r} H^{\circ} = (56.8 \pm 0.9) \text{ kJ} \cdot \text{mol}^{-1}$	R P R
$Zn^{2+} + 2H_2O \rightleftharpoons Zn(OH)_2(aq) + 2H^+$	$\begin{array}{l} \log_{10} *\beta_2^{\circ} &= -17.82 \pm 0.08 \\ \Delta \varepsilon &= (0.18 \pm 0.04) \ \mathrm{kg} \cdot \mathrm{mol}^{-1} \\ \Delta_{\mathrm{r}} H^{\circ} &= (109 \pm 4) \ \mathrm{kJ} \cdot \mathrm{mol}^{-1} \end{array}$	R P R
$Zn^{2+} + 3H_2O \rightleftharpoons Zn(OH)_3^- + 3H^+$	$\begin{array}{ll} \log_{10} *\beta_{3}^{\circ} &= -28.05 \pm 0.05 \\ \Delta \varepsilon &= (0.19 \pm 0.06) \ \text{kg} \cdot \text{mol}^{-1} \\ \Delta_{r} H^{\circ} &= (151 \pm 3) \ \text{kJ} \cdot \text{mol}^{-1} \end{array}$	R P R
$Zn^{2+} + 4H_2O \rightleftharpoons Zn(OH)_4^{2-} + 4H^+$	$\begin{array}{ll} \log_{10} *\beta_{4}^{\circ} &= -40.41 \pm 0.12 \\ \Delta \varepsilon &= (0.46 \pm 0.04) \ \mathrm{kg} \cdot \mathrm{mol}^{-1} \\ \Delta_{\mathrm{r}} H^{\circ} &= (188 \pm 6) \ \mathrm{kJ} \cdot \mathrm{mol}^{-1} \end{array}$	R P R
$2Zn^{2+} + H_2O \rightleftharpoons Zn_2OH^{3+} + H^+$	$\log_{10} *\beta_{2,1}^{\circ} = -7.9 \pm 0.2$ $\Delta \varepsilon = (0.3 \pm 0.1) \text{ kg} \cdot \text{mol}^{-1}$	P P
$ZnO(s) + 2H^+ \rightleftharpoons Zn^{2+} + H_2O$	$\begin{array}{l} \log_{10} {}^{*}\!K_{\rm s0}{}^{\circ} = 11.12 \pm 0.05 \\ \Delta \varepsilon &= (0.07 \pm 0.04) \ \rm kg \cdot mol^{-1} \\ \Delta_{\rm r} H^{\circ} &= -(86.7 \pm 1.7) \ \rm kJ \cdot mol^{-1} \end{array}$	R R R
ϵ -Zn(OH) ₂ (s) + 2H ⁺ \rightleftharpoons Zn ²⁺ + 2H ₂ O	$\log_{10} {}^{*}K_{s0}^{\circ} = 11.38 \pm 0.20$ $\Delta_{r}H^{\circ} = -(100 \pm 4) \text{ kJ} \cdot \text{mol}^{-1}$	P P
$ \begin{array}{l} \beta_1\text{-}Zn(OH)_2(s) + 2H^+ \rightleftharpoons Zn^{2+} + 2H_2O \\ \beta_2\text{-}Zn(OH)_2(s) + 2H^+ \rightleftharpoons Zn^{2+} + 2H_2O \\ \gamma\text{-}Zn(OH)_2(s) + 2H^+ \rightleftharpoons Zn^{2+} + 2H_2O \\ \delta\text{-}Zn(OH)_2(s) + 2H^+ \rightleftharpoons Zn^{2+} + 2H_2O \end{array} $	$log_{10} *K_{s0}^{\circ} = 11.72 \pm 0.04 log_{10} *K_{s0}^{\circ} = 11.76 \pm 0.04 log_{10} *K_{s0}^{\circ} = 11.70 \pm 0.04 log_{10} *K_{s0}^{\circ} = 11.81 \pm 0.04$	R R R R

Table 1 Recommended (R) and Provisional (P) values for the system $Zn^{2+} + OH^-$ at T = 298.15 K, p = 100 kPa, and $I_m = 0$ mol·kg⁻¹; $\Delta \varepsilon$ values for ClO_4^- medium.

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Table 2 Recommended (R) and Provisional (P) values for the $Zn^{2+} + Cl^{-}$ system at T = 298.15 K, p = 100 kPa, and $I_m = 0$ mol·kg⁻¹. $\Delta \varepsilon$ values for ClO_4^{-} medium.

Reaction	Constant	Evaluation
$Zn^{2+} + Cl^- \rightleftharpoons ZnCl^+$	$log_{10} K_1^{\circ} = 0.40 \pm 0.09$ $\Delta \varepsilon = -(0.14 \pm 0.02) \text{ kg} \cdot \text{mol}^{-1}$	R P
$Zn^{2+} + 2Cl^{-} \rightleftharpoons ZnCl_2(aq)$	$ \log_{10} \beta_2^{\circ} = 0.69 \pm 0.15 \Delta \varepsilon = -(0.20 \pm 0.04) \text{ kg} \cdot \text{mol}^{-1} $	R P
$Zn^{2+} + 3Cl^{-} \rightleftharpoons ZnCl_{3}^{-}$	$ \begin{split} \log_{10} \beta_3^{\circ} &= 0.48 \pm 0.54 \\ \Delta \varepsilon &= -(0.27 \pm 0.13) \; \text{kg} \cdot \text{mol}^{-1} \end{split} $	P P

Table 3 Recommended (R), Provisional (P), and Indicative (I) values for the $Zn^{2+} + CO_3^{2-}$ system at T = 298.15 K, p = 100 kPa, and $I_m = 0$ mol·kg⁻¹.

Reaction	Constant	Evaluation
$\overline{Zn^{2+} + CO_3^{2-}} \rightleftharpoons ZnCO_3(aq)$	$\log_{10} K_1^{\circ} = 4.75 \pm 0.05$	Р
$\operatorname{Zn}^{2+} + 2\operatorname{CO}_3^{2-} \rightleftharpoons \operatorname{Zn}(\operatorname{CO}_3)_2^{2-}$	$\log_{10}\beta_2 = 5.4 \pm 0.6$	\mathbf{I}^1
$Zn^{2+} + HCO_3^- \rightleftharpoons ZnHCO_3^+$	$ \begin{aligned} \log_{10} K_1^{\circ} &= 1.62 \pm 0.10 \\ \Delta \varepsilon &= 0.100 \pm 0.042 \ \rm kg \cdot mol^{-1} \end{aligned} $	P P
$ZnCO_3(s) + 2H^+ \rightleftharpoons Zn^{2+} + H_2O + CO_2(g)$	$\begin{array}{l} \log_{10} {}^{*}K_{\rm ps0} = 7.21 \pm 0.04 \\ \Delta \varepsilon = 0.09 \pm 0.02 \ \rm kg {\cdot} mol^{-1} \end{array}$	P P
$ZnCO_3(s) \rightleftharpoons Zn^{2+} + CO_3^{2-}$	$\log_{10} K_{\rm s0}^{\circ} = -10.93 \pm 0.04$	Р
$\begin{array}{l} 0.2 \mathrm{Zn}_5(\mathrm{OH})_6(\mathrm{CO}_3)_2(\mathrm{s}) + 2\mathrm{H}^+ \rightleftharpoons \mathrm{Zn}^{2+} + \\ 0.4 \mathrm{CO}_2(\mathrm{g}) + 1.6 \mathrm{H}_2\mathrm{O} \end{array}$	$\log_{10} * K_{\rm ps0}^{\circ} = 9.07 \pm 0.09$	Р

 ${}^{1}I_{m} = 0.68 \text{ mol}\cdot\text{kg}^{-1}$; synthetic sea water medium.

Table 4 Recommended (R), Provisional (P), and Indicative (I) values for the Zn²⁺ + SO₄²⁻ system at T = 298.15 K, p = 100 kPa, and $I_m = 0$ mol·kg⁻¹. $\Delta \varepsilon$ values for LiClO₄ medium.

Reaction	Constant ¹	Evaluation
$\overline{\text{Zn}^{2+} + \text{SO}_4^{2-}} \rightleftharpoons \text{ZnSO}_4(\text{aq})$	$\log_{10} K_1^{\circ} = 2.304 \pm 0.042$	R
	$\Delta \varepsilon$ = -(0.05 ± 0.03) kg·mol ⁻¹	Р
	$\Delta_r H^\circ = 6.0 \pm 0.5 \text{ kJ} \cdot \text{mol}^{-1}$	R
$Zn^{2+} + 2SO_4^{2-} \rightleftharpoons Zn(SO_4)^{2-}$	$\log_{10} \beta_2^{\circ} = 3.2 \pm 0.2$	Ι
	$\Delta \varepsilon$ = (0.09 ± 0.08) kg·mol ⁻¹	Ι

¹The uncertainties represent 95 % confidence limits of the regression intercept $(\log_{10} K^{\circ})$ and of the slope $(-\Delta \varepsilon)$, except for $\log_{10} K_1^{\circ}$, which is a weighted standard deviation; see text.

Table 5 Recommended (R) and Provisional (P) values for the $Zn^{2+} + PO_A^{3-}$ system at T = 298.15 K.

Reaction	Constant ¹	Evaluation
$\overline{\text{Zn}^{2+} + \text{HPO}_4^{2-}} \rightleftharpoons \text{ZnHPO}_4(\text{aq})$ $\overline{\text{Zn}^{2+} + \text{H}^+ + \text{PO}_4^{3-}} \rightleftharpoons \text{ZnHPO}_4(\text{aq})$	$\begin{array}{l} \log_{10} K = 2.44 \pm 0.20 \\ \log_{10} \beta_{1,1,1} = 14.08 \pm 0.20 \end{array}$	$\begin{array}{c} R^2 \\ P^3 \end{array}$

¹The uncertainties represent 95 % confidence limits.

 ${}^{2}I_{m} = 0.10 \text{ mol} \cdot \text{kg}^{-1}$; see text. For $I_{m} = 0.0$, $\log_{10} K = 3.3 \pm 0.4$ (Provisional). ${}^{3}I_{m} = 0.10 \text{ mol} \cdot \text{kg}^{-1}$; see text. For $I_{m} = 0.0$, $\log_{10} \beta_{1,1,1} = 15.64 \pm 0.4$ (Provisional).

3. Zn^{II} SOLUTION CHEMISTRY

 Zn^{II} has a comparatively low affinity for the oxygen donor ligands surveyed in this review: OH⁻, CO₃²⁻, SO₄²⁻, and PO₄³⁻, as reflected in its stability constants with these ligands. For example, the stability constants for the 1:1 Zn²⁺-hydroxido and Zn²⁺-carbonato complexes are respectively about 1 and 2 orders of magnitude lower than the corresponding values for the Cu^{2+} [2007PBa] and Pb²⁺ [2009PBa] complexes. Also, the Zn²⁺ complexes with the more polarisable ligand Cl⁻ are weak, and less stable than those of Cu^{2+} [2007PBa] and Pb²⁺ [2009PBa].

In contrast to Cu^{II} and Pb^{II}, Zn^{II} has a negligible tendency to form polymeric hydroxido- species in aqueous solution under environmental conditions. The species $Zn_4(OH)_4^{4+}$ ([75ZGa]) and $Zn_2(OH)_6^{2-}$ ([64SCb]) have been postulated but there is no supporting evidence for their formation, and they have not been accepted in this review.

Heterogeneous solubility equilibria for Zn^{2+} with the stated inorganic ligands are unlikely to have a significant impact on the chemical speciation of Zn^{II} in environmental systems, except possibly in heavily polluted natural waters (which are not under consideration in this document).

4. EVALUATION OF EQUILIBRIUM CONSTANTS (HOMOGENEOUS REACTIONS)

4.1 The Zn²⁺+ OH⁻ system

A speciation diagram for the Zn^{2+} + OH⁻ system at $[Zn^{II}]_T = 1 \times 10^{-6} \text{ mol} \cdot \text{dm}^{-3}$ (0.065 mg Zn dm⁻³), based on our Recommended values for the relevant stability constants at $I_m = 0$ mol·kg⁻¹ (Table 1), is shown in Fig. 1. Results outside the range $2 \le -\log_{10}\{[H^+]/c^\circ\} \le 12$ should be viewed with caution as activity coefficients may deviate significantly from unity. The SC-Database [2010PET] reports results from 101 investigations for the hydrolysis of Zn^{2+} . In addition, a number of studies are included in this review that are not listed in [2010PET].

The hydrolysis of Zn^{2+} has been studied at low ionic strength (with data extrapolated or corrected to $I_m = 0 \text{ mol} \cdot \text{kg}^{-1}$) for a wide range of temperatures, enabling stability constants at zero ionic strength and 25 °C to be determined with a high degree of certainty. However, less certain is the behaviour of the system $Zn^{2+} + OH^{-}$ with changes in ionic strength, because of the paucity of accepted data over a range of fixed ionic strengths. Thus, the reaction ion interaction coefficients determined herein should be viewed, at best, as Provisional. More hydrolysis data at fixed ionic strengths are required for a more definitive description of the hydrolysis reactions of Zn^{2+} .



Fig. 1 Speciation diagram for the $Zn^{2+} + OH^-$ system as obtained from the Recommended and Provisional stability constants at 25 °C and $I_m = 0 \text{ mol} \cdot \text{kg}^{-1}$ (Table 1) and calculated for $[Zn^{II}]_T = 10^{-6} \text{ mol} \cdot \text{dm}^{-3}$. Results outside the $-\log_{10}\{[H^+]/c^\circ\}$ range of 2 to 12 should be viewed with caution as activity coefficients may deviate from 1.0. No corrections were made for ionic strength-dependent changes in formation constants at high pH.

4.1.1 Formation of ZnOH⁺

Formation of the first monomeric hydrolysis species can be described by eq. 4

$$Zn^{2+} + H_2O \rightleftharpoons ZnOH^+ + H^+ \tag{4}$$

Stability constant data for this reaction have been reported over a wide range of temperatures. These data are presented in Table A3-1 together with our estimated uncertainties. The majority of these data were determined in dilute solutions, or in a relatively low ionic strength non-complexing medium, and were corrected by the original authors to $I_m = 0 \text{ mol} \cdot \text{kg}^{-1}$. The data are sourced from a number of studies that join smoothly across the temperature range 15 to 350 °C. The regression line for a plot of log $*K_1^{\circ}$ (reaction 4) against the inverse of the thermodynamic temperature (in Kelvin) yields the slope $-(\Delta_r H^{\circ}/2.303 \text{R})$ and the intercept ($\Delta_r S^{\circ}/2.303 \text{R}$), from which log $*K_1^{\circ}$ at 25 °C is calculated. This analysis does not determine a value for the reaction interaction coefficient, $\Delta \varepsilon(4)$. The data selected in this review include only those results within the experimental temperature range of each separate study. As is the case for all reactions considered in this review, the data do not include extrapolated values outside those ranges.

The stability constant determined from the temperature dependence of reaction 4 (Fig. A4-1) is

 $\log_{10} * K_1^{\circ}$ (eq. 4, 298.15 K) = -8.96 ± 0.05

and this value is recommended. This is the same value as selected by [86BAE] in their review of the hydrolysis of cations, but is considerably more negative than the value of -7.5 ± 0.4 selected by [2001ZHA].

Hanzawa et al. [97HAN] measured the hydrolysis of Zn^{2+} and the solubility of ZnO(s) from 25 to 225 °C. For temperatures from 185 to 225 °C they used an yttria-stabilised zirconia (YSZ) electrode. The electrode was found to be unreliable at temperatures below 175 °C and broke down above 250 °C, but was reported to give reliable results between these two temperatures. However, these high temperature results [97HAN] are inconsistent with those of other workers, and they are rejected in this review.

There have been many determinations of the stability constant for ZnOH⁺ at fixed ionic strength, but the majority of these data are inconsistent with the stability constant at zero ionic strength listed above. Of the relatively few data consistent with this value, only three in perchlorate media are considered reliable. These data were selected for a SIT analysis to determine the reaction interaction coefficient, $\Delta \varepsilon(4)$, and are listed in Table A3-1, along with references and our assigned uncertainties. In this analysis, the value for $\log_{10} *K_1^{\circ}$ was fixed at -8.96 as selected above. The weighted regression of these data (Fig. A4-2), used the expression

$$\log_{10} *K_1 + 2D - \log_{10} a(H_2O) = \log_{10} *K_1^{\circ} - \Delta \varepsilon I_n$$

derived from eqs. 2 and 4 ($\Delta z^2 = -2$) and yielded the value $\Delta \varepsilon(4) = (0.03 \pm 0.02) \text{ kg} \cdot \text{mol}^{-1}$ for NaClO₄ medium. This value is consistent with those obtained for the analogous reactions of Pb²⁺ [2009PBa] and Cd²⁺ [2011POW]. It is selected as a Provisional value.

Direct comparison is not possible between the stability constants for ZnOH⁺ in NaClO₄ medium selected in this study and those published for fixed ionic strengths in other media and for temperatures slightly above 25 °C. However, Chaberek et al. [52CCa] determined $\log_{10} *K_1 = -8.7$ at 30 °C in 0.1 mol·dm⁻³ KCl, and this is reasonably consistent with the value $\log_{10} *K_1 = -8.85$ calculated at 30 °C from $\log_{10} *K_1^{\circ}$ and $\Delta_r H^{\circ}$ selected in this review (Table 1) and assuming the value of $\Delta \varepsilon$ (4) valid for NaClO₄ media at 25 °C is also applicable in KCl media. In studies at 37 °C, Hacht and Berthon [87HBb] determined $\log_{10} *K_1 = -8.378$ in 0.15 mol·dm⁻³ NaCl and Childs [70CHc] determined a value of -9.03 in 0.15 mol·dm⁻³ KNO₃. With the above assumptions about $\Delta \varepsilon$ (4), we calculate $\log_{10} *K_1 = -8.93 \pm 0.10$ based on the value for I = 0 selected in this review (-8.62 ± 0.10 for 36 °C [62PEb]; Table A3-1); this result is consistent with that of Childs [70CHc].

4.1.2 Formation of Zn(OH)₂(aq)

The formation of $Zn(OH)_2(aq)$ can be described by reaction 5

$$Zn^{2+} + 2H_2O \rightleftharpoons Zn(OH)_2(aq) + 2H^+$$
(5)

Data determined as a function of temperature are listed in Table A3-2. These data are presented together with our estimated uncertainties. The data are sourced from a number of studies that join smoothly across the whole temperature range for which data are available (20 to 350) °C.

Bénézeth et al. [2002BPb] re-examined the solubility of zincite (ZnO(s)) using a technique (flowthrough cell with downstream acid injection) different from that used in their earlier investigation [99BPa]. In the 2002 study, they determined stability constants for ZnOH⁺ and Zn(OH)₃⁻ that were similar to their earlier values, but for Zn(OH)₂(aq) the values were substantially different, indicating that at pH 7 the solubility of ZnO(s) was higher than previously measured [99BPa]. The 2002 results are more consistent with other data available in the literature (see Table A3-2) and consequently the results for Zn(OH)₂(aq) reported in [99BPa] are rejected.

The stability constant determined at 25 $^{\circ}$ C from the temperature dependence of reaction 5 (Fig. A4-3) is

 $\log_{10} *\beta_2^{\circ}(\text{eq. 5, 298.15 K}) = -17.82 \pm 0.08$

This value is recommended. It is significantly more negative than those selected by [86BAE] (-16.9) and [2001ZHA] (-16.4 \pm 0.1), but is in very good agreement with that selected by Smith and Martell (-17.8) [76SMI].

A significant issue in determining the stability of $Zn(OH)_2(aq)$ is the small amount of hydrolysis that occurs before the onset of precipitation reactions, making it difficult to obtain an accurate estimate of the stability constant by conventional techniques such as potentiometry. Although there have been a number of determinations of the stability constant of $Zn(OH)_2(aq)$ at I > 0 [65SEb, 67GSd, 83YYa, 87FGa, 88FSa, 91MGb, 98MSe, 99PPa, 99PGa, 2000MSa, 2001PSb, 2002PLb, 2002HTc, 2008FAR], none is consistent with the value calculated at zero ionic strength in this review. Moreover, for the same

ionic strength, the reported stability constants can differ by several orders of magnitude. All of these values are rejected.

The selected stability constant for $Zn(OH)_2(aq)$ leads to a second stepwise constant of log $*K_2 = -8.86$. The value is slightly more positive than the selected first stepwise constant of log $*K_1 = \log *\beta_1 = -8.96$. This is unusual behaviour, but is likely due to a change in coordination from octahedral to tetrahedral at the second hydrolysis step. This hypothesis is supported by the crystal structures of ε -Zn(OH)₂(s) [64SCH] and γ -Zn(OH)₂(s) [69CHR], in which the Zn-atom is tetrahedrally coordinated.

In the absence of reliable experimental values at I > 0, a value for $\Delta \varepsilon(5)$ in NaClO₄ medium has been estimated by assuming that the interaction coefficient $\varepsilon(\text{Zn}(\text{OH})_2(\text{aq}),\text{Na}^+,\text{ClO}_4^-) = (0.25 \pm 0.03)$ [the average of the values found for $\varepsilon(\text{Zn}\text{CO}_3(\text{aq}),\text{Na}^+,\text{ClO}_4^-)$ and $\varepsilon(\text{Zn}\text{Cl}_2(\text{aq}),\text{Na}^+,\text{ClO}_4^-)$ (see below), where the uncertainty is chosen to span the range in the two values], the interaction coefficient $\varepsilon(\text{Zn}^{2+},\text{ClO}_4^-) = 0.351 \pm 0.005 \text{ kg} \cdot \text{mol}^{-1}$ as determined in this review (Appendix 1B) and that $\varepsilon(\text{H}^+,\text{ClO}_4^-) = (0.14 \pm 0.02) \text{ kg} \cdot \text{mol}^{-1}$ [97GRE]. The calculated value is $\Delta \varepsilon(5) = (0.18 \pm 0.04) \text{ kg} \cdot \text{mol}^{-1}$, and it is selected as Provisional.

4.1.3 Formation of Zn(OH)3⁻

The formation of $Zn(OH)_3^-$ can be described by reaction 6

$$Zn^{2+} + 3H_2O \rightleftharpoons Zn(OH)_3^- + 3H^+$$
(6)

The majority of determinations have used solubility measurements. Because of the substantial increase in solubility of $Zn(OH)_2(s)$ or ZnO(s) at higher pH, it is somewhat easier to determine reliable stability constants for the negatively charged hydrolysis species of Zn^{2+} than for the cationic species. At lower pH, where the cationic species dominate in solution, potentiometric measurements are severely limited by the low solubility of $Zn(OH)_2(s)$ or ZnO(s) and the small extent of hydrolysis before the onset of the precipitation reaction. For this reason, the majority of successful measurements for $ZnOH^+$ and $Zn(OH)_2(aq)$ have used solubility measurements at lower pH; from these, the stability constants for each species from a number of studies are in reasonable agreement for a particular temperature. In contrast, when determined from potentiometric measurements, the agreement is significantly poorer.

Selected values of $\log_{10} {}^*\beta_3$ determined as a function of temperature are listed in Table A3-3 and are presented together with our estimated uncertainties. The data are sourced from a number of studies that join smoothly across the whole temperature range for which data are available (12.5 to 350) °C. The stability constant determined at 25 °C from the temperature dependence of reaction 6 (Fig. A4-4) is

$$\log_{10} *\beta_3^{\circ}(\text{eq. 6, 298.15 K}) = -28.05 \pm 0.05$$

This value is recommended. It is in good agreement with values selected by [86BAE] (-28.4), [2001ZHA] (-28.2 ± 0.2), and [76SMI] (-28.1).

Data selected for the SIT analysis, to determine the reaction ion interaction coefficient, $\Delta\epsilon(6)$, are also listed in Table A3-3. In this analysis, the value for $\log_{10} *\beta_3^\circ$ was fixed at -28.05 as selected above. The weighted regression (Fig. A4-5) used the selected values for NaClO₄ media at 25 °C and the expression

$$\log_{10} *\beta_3 - 3\log_{10} a(H_2O) = \log_{10} *\beta_3^\circ - \Delta \epsilon I_m$$

derived from eqs. 2 and 6 ($\Delta z^2 = 0$). The regression yields $\Delta \varepsilon(6) = (0.19 \pm 0.06) \text{ kg} \cdot \text{mol}^{-1}$, which is selected as a Provisional value. It is consistent with that obtained for the analogous reaction interaction coefficient for Pb²⁺ [2009PBa] (0.26 \pm 0.05) \text{ kg} \cdot \text{mol}^{-1}.

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1

2259

4.1.4 Formation of $Zn(OH)_4^{2-}$ The formation of $Zn(OH)_4^{2-}$ can be described by reaction 7

$$Zn^{2+} + 4H_2O \rightleftharpoons Zn(OH)_4^{2-} + 4H^+$$
(7)

Data determined as a function of temperature are listed in Table A3-4. These data are presented together with our estimated uncertainties. The data are sourced from a number of studies that join smoothly across the whole temperature range for which data are available (12.5 to 350) °C. The stability constant at 25 °C determined from the temperature dependence of reaction 7 (Fig. A4-6) is

$$\log_{10} * \beta_4^{\circ}$$
(eq. 7, 298.15 K) = -40.41 ± 0.12

This value is recommended. It is in reasonable agreement with the values selected by [86BAE] (-41.2), [2001ZHA] (-41.3 ± 0.3), and [76SMI] (-40.5).

Data selected for the SIT analysis, to determine the reaction ion interaction coefficient, $\Delta \epsilon$ (7), are also listed in Table A3-4, along with references and our assigned uncertainties. In this analysis, the value for $\log_{10} *\beta_4^{\circ}$ was fixed at -40.41 as selected above. The weighted regression (Fig. A4-7) used the selected values for NaClO₄ media at 25 °C and the expression

$$\log_{10} *\beta_4 - 4D - 4\log_{10} a(H_2O) = \log_{10} *\beta_4^{\circ} - \Delta \varepsilon I_m$$

derived from eqs. 2 and 7 ($\Delta z^2 = 4$). The value calculated for $\Delta \epsilon$ (7) in NaClO₄ medium is (0.46 ± 0.04) kg·mol⁻¹ and is selected as a Provisional value.

Some data collected in chloride media, considering their likely uncertainties, also appear consistent with the data selected in this review. Matsuda and Ayabe [59MAc] determined a value of -40.3 in 2 mol·dm⁻³ KCl, and [2002PLb] a value of -39.71 in 0.1 mol·dm⁻³ KCl; in contrast, the value determined by Schorsch [64SCb], $\log_{10} *\beta_4 = -42.41$ in 3.0 mol·dm⁻³ NaCl, is significantly smaller. The value of [2002PLb] is almost identical to that determined by [2008FAR] in 0.1 mol·dm⁻³ NaClO₄ (-39.60 ± 0.10).

4.1.5 Formation of Zn₂OH³⁺

Formation of this dimeric hydrolysis species is described by reaction 8

$$2Zn^{2+} + H_2O \rightleftharpoons Zn_2OH^{3+} + H^+$$
(8)

Values accepted in this review are reported in Table A3-5, along with our assigned uncertainties. Schorsch [64SCb, 65SCc] determined the stability constant for Zn_2OH^{3+} in 2.0 and 3.0 mol·dm⁻³ KCl and NaCl solutions. Analysis of these data using SIT indicates that the expression $\log_{10} *\beta_{2,1} - 2D - \log_{10} a(H_2O)$ is constant for three of the four conditions studied, suggesting that $\Delta \varepsilon(8)$ may be near zero in chloride media. Assuming this to be the case, the value selected for the stability constant at zero ionic strength is

$$\log_{10} *\beta_{2,1}^{\circ}(\text{eq. 8, 298.15 K}) = -7.9 \pm 0.2$$

This value is considered to be Provisional. It is considerably more positive than those selected in previous reviews (-8.7 to -9.0) [76SMI, 86BAE, 2001ZHA]. The stability constants selected for M_2OH^{3+} (M = Cu²⁺, Pb²⁺, Cd²⁺) in the other reviews in this series [2007PBa, 2009PBa, 2011POW] are substantially more positive than the constants selected for the corresponding MOH⁺ species, lending credence to the selected Zn₂OH³⁺ value.

The stability of $Zn_2^2OH^{3+}$ has also been studied in perchlorate media (Table A3-5). All three studies were conducted at $I_c = 3.0 \text{ mol}\cdot\text{dm}^{-3} \text{ NaClO}_4$ ([75ZGa], [78BYa]), or LiClO₄ [62BIE]. The stability constants determined are in good agreement; namely, -8.6, -8.72, and -8.7, respectively. On the basis of these consistent results, and the stability constant determined at zero ionic strength above, the reaction ion interaction coefficient, $\Delta \varepsilon(8)$, in perchlorate media is calculated to be $(0.3 \pm 0.1) \text{ kg} \cdot \text{mol}^{-1}$, where the uncertainty has been estimated in this review. This value is consistent with the interaction

coefficient determined for formation of Cd_2OH^{3+} in perchlorate media [2011PBa] and is listed as Provisional.

4.2 The Zn²⁺+ Cl⁻ system

Four consecutive complexes have been reported according to the following reactions

$$Zn^{2+} + Cl^{-} \rightleftharpoons ZnCl^{+} \tag{9}$$

$$Zn^{2+} + 2 Cl^{-} \rightleftharpoons ZnCl_{2}(aq)$$
⁽¹⁰⁾

$$Zn^{2+} + 3 Cl^{-} \rightleftharpoons ZnCl_{3}^{-}$$
⁽¹¹⁾

$$Zn^{2+} + 4 Cl^{-} \rightleftharpoons ZnCl_{4}^{2-}$$
⁽¹²⁾

The aqueous chlorido- complexes of Zn(II) are very weak and require media of high $[Cl^-]_T$, high $[Cl^-]_T:[Zn^{2+}]_T$ ratios, and high ionic strength. The stability constants have been investigated mainly by various types of potentiometry. No polynuclear complexes have been reported in aqueous solution. While some authors [e.g., 1944SLa, 1964MKc] reported overall formation constants with an anomalous sequence of $\beta_1 > \beta_2 < \beta_3$, some [e.g., 1977SJe] found no evidence for the 1:2 complex, and others [e.g., 1988FSb] found evidence only for the 1:2 and 1:4 complexes. It seems obvious that it is difficult to distinguish between complex formation and ionic interactions.

The speciation diagram for the $Zn^{2+} + Cl^-$ system is shown in Fig. 2, based on the Recommended values for the stability constants at $I_m = 0$ mol·kg⁻¹ (Table 2) and represents conditions in which hydrolysis is suppressed ($-\log_{10} \{[H^+]/c^\circ\} < 7.5$). Results for values of $\log_{10} \{[Cl^-]/c^\circ\} > -2$ should be viewed with caution as activity coefficients no longer remain constant.



Fig. 2 Speciation diagram for the binary $Zn^{2+} + Cl^-$ system as obtained from the Recommended stability constants at 25 °C and $I_m = 0 \text{ mol} \cdot \text{kg}^{-1}$ (Table 2) and calculated for $[Zn^{II}]_T = 10^{-6} \text{ mol} \cdot \text{dm}^{-3}$, assuming $-\log_{10}\{[H^+]/c^\circ\} < 7.5$, and with no corrections made for ionic strength-dependent changes in formation constants.

4.2.1 Formation of ZnCl⁺

A substantial number of equilibrium constant values have been reported for the formation of ZnCl⁺, for different media (NaClO₄, LiClO₄, HClO₄, NaCl), ionic strengths and temperatures. Data selected for the SIT analysis, to determine the standard stability constant at zero ionic strength for reaction 9 and the reaction ion interaction coefficient $\Delta \epsilon$ (9), are listed in Table A3-6 along with our assigned uncertainties according to our estimate of the overall precision of the data. The selected data all refer to either NaClO₄ or LiClO₄ media and 25 °C.

The weighted linear regression shown in Fig. A4-8 indicates reasonable consistency between the values and leads to the Recommended standard constant

 $\log_{10} K_1^{\circ}$ (eq. 9, 298.15 K) = 0.40 ± 0.09

The ion interaction coefficient based on this regression is $\Delta \varepsilon(9) = -(0.14 \pm 0.02) \text{ kg} \cdot \text{mol}^{-1}$. The Recommended value is in good agreement with that of [98RSa] ($\log_{10} K_1^{\circ} = 0.46 \pm 0.04$) determined from measurements in NaNO₃ media with I_m ranging from 0.17 to 0.54 mol·kg⁻¹, but using a different extrapolation method to I = 0.

Results from several studies in NaClO₄ media at 25 °C have been rejected, as indicated in the footnote to Table A3-6 with annotations on each reference. The formation constant value reported by [56SLa] is very low and has been rejected as an outlier; the study was quoted in [96AEb] but, as in this work, it was not used in their analysis. In the study of [74BLb], the ligand concentrations used were so low that the proportion of complex formed hardly exceeded 1 %. This evaluated formation constant is therefore considered uncertain and is not taken into account in the present analysis. The data in [70FCa, 71FCb] seem to be the same as those reported later by the same authors [75FCa], hence only the values from one study [75FCa] were used in our analysis. The value reported by [73HHb] from a kinetic study is much larger than any other reported value and is discarded as an outlier.

4.2.2 Formation of ZnCl₂(aq)

Data selected for the SIT analysis, to determine the standard stability constant at zero ionic strength for reaction 10 and the reaction ion interaction coefficient $\Delta \varepsilon(10)$, are listed in Table A3-7 along with our assigned uncertainties. The selected data all refer to either NaClO₄ or LiClO₄ media and 25 °C. The weighted linear regression shown in Fig. A4-9 indicates reasonable consistency between the values and leads to the Recommended standard constant

 $\log_{10} \beta_2^{\circ}$ (eq. 10, 298.15 K) = 0.69 ± 0.15

The ion interaction coefficient based on this regression is $\Delta \varepsilon(10) = -(0.20 \pm 0.04) \text{ kg} \cdot \text{mol}^{-1}$.

4.2.3 Formation of $ZnCl_3^-$ and $ZnCl_4^{2-}$

The stability constants for ZnCl_3^- and ZnCl_4^{2-} can be determined only at high chloride concentrations, and therefore at high ionic strengths. For the 1:1 and 1:2 complexes, we used the data reported in all the studies selected to determine the standard constants of the complexes, since only interactions with the ClO_4^- ion are required. However, for the 1:3 complex, data from LiClO_4 -media were excluded because it is anticipated that the interaction coefficient between the anion ZnCl_3^- and Li^+ is different from the corresponding one with Na⁺.

The data are scattered, but a SIT analysis seems possible due to the comparatively consistent picture as a function of the ionic strength (see Fig. A4-10). We have assigned somewhat larger uncertainties to the reported data to reflect the weakness of the 1:3 complex.

Data selected for the SIT analysis, to determine the standard stability constant at zero ionic strength for reaction 11 and the reaction ion interaction coefficient $\Delta \varepsilon(11)$, are listed in Table A3-8 along with our assigned uncertainties. The selected data all refer to NaClO₄ media and 25 °C. The weighted linear regression shown in Fig. A4-10 indicates reasonable consistency between the values and leads to the Provisional standard constant

 $\log_{10} \beta_3^{\circ}$ (eq. 11, 298.15 K) = 0.48 ± 0.54

This regression gives $\Delta \varepsilon(11) = -(0.27 \pm 0.13) \text{ kg} \cdot \text{mol}^{-1}$.

Some authors have reported stability constants for the 1:4 complex based on their evaluations of emf data. However, the data are too scattered to be evaluated with confidence. It is therefore not possible to give even an indicative value for the formation constant of $ZnCl_4^{2-}$.

4.3 The $Zn^{2+} + CO_3^{2-}$ system

Homogeneous equilibria reported for the system $Zn^{2+} + CO_3^{2-} + H^+$ are

$$\operatorname{Zn}^{2+} + \operatorname{CO}_3^{2-} \rightleftharpoons \operatorname{ZnCO}_3(\operatorname{aq})$$
 (13)

$$\operatorname{Zn}^{2+} + 2\operatorname{CO}_3^{2-} \rightleftharpoons \operatorname{Zn}(\operatorname{CO}_3)_2^{2-}$$
(14)

$$\operatorname{Zn}^{2+} + \operatorname{HCO}_3^{-} \rightleftharpoons \operatorname{ZnHCO}_3^{+}$$
 (15)

$$2Zn^{2+} + CO_3^{2-} \rightleftharpoons Zn_2CO_3^{2+}$$
⁽¹⁶⁾

The *SC-Database* [2010PET] has only 12 references with original experimental data for the $Zn^{2+} + CO_3^{2-}$ system. Six of these references are for homogeneous equilibria and, of these, only in the case of equilibria 13 and 15 are there sufficient data for a SIT analysis. Figure 3 shows a speciation diagram for the $Zn^{2+} + CO_3^{2-} + H^+$ system based on the stability con-

Figure 3 shows a speciation diagram for the $Zn^{2+} + CO_3^{2-} + H^+$ system based on the stability constants recorded for $I_m = 0$ mol·kg⁻¹ and t = 25 °C in Tables 1 and 3. The calculations assume a CO₂ fugacity nearly identical to that of the Earth's atmosphere in 2013 ($f(CO_2) = 10^{-1.4}$ kPa). As for Cd²⁺, the stabilities of the 1:1 and 1:2 carbonato- and hydroxido- complexes are considerably lower than those for the corresponding complexes of Cu²⁺ and Pb²⁺. As such, the pH at which Zn²⁺ forms significant fractions of carbonato- and hydroxido- complexes is shifted to higher values of $-\log_{10}\{[H^+]/c^\circ\}$. Under the speciation conditions presented here, $Zn(CO_3)_2^{2-}$ is of very minor significance at $-\log_{10}\{[H^+]/c^\circ\} < 10^{-10}$



Fig. 3 Speciation diagram for the ternary $Zn^{2+} + H^+ + CO_3^{2-}$ system as obtained from the Recommended and Provisional stability constants at 25 °C and $I_m = 0 \text{ mol} \cdot \text{kg}^{-1}$ (Tables 1 and 3), calculated for $[Zn^{II}]_T = 10^{-8} \text{ mol} \cdot \text{dm}^{-3}$ and a CO₂ fugacity of 37.0 Pa. $\log_{10} K(CO_2(g) \rightleftharpoons CO_2(aq)) = -1.5$ [93MOR].

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10, and the concentrations of Zn^{2+} and $ZnCO_3(aq)$ are equal when $-\log_{10}\{[H^+]/c^\circ\} = 8.45$. This value is approximately 0.2 lower than the corresponding value for Cd^{2+} and approximately one unit higher than the corresponding values for Cu^{2+} and Pb^{2+} .

4.3.1 Formation of ZnCO₃(aq)

The only experimental values for formation of $ZnCO_3(aq)$, reaction 13 (Table A3-9), are those obtained by [76BHa] using 0.101 mol·kg⁻¹ KNO₃ as the supporting electrolyte and [90SBb] using a synthetic seawater medium consisting of a NaCl-NaClO₄ mixture at [Cl⁻]_T = 0.55 mol·kg⁻¹ and $I_m = 0.68$ mol·kg⁻¹. A SIT analysis using these two values shown in Table A3-9 provides the following formation constant estimate and ion interaction coefficient:

 $\log_{10} K_1^{\circ}$ (eq. 13, 298.15 K) = 4.76 ± 0.35

and $\Delta \varepsilon(13) = -(0.19 \pm 0.58) \text{ kg} \cdot \text{mol}^{-1}$. Complexation of Zn^{2+} by NO₃⁻ was not considered by [76BHa]. Consequently, the formation constant determined in this medium, and regarded by the original authors as approximate, may be somewhat underestimated. The results of [90SBb] accounted for formation of ZnCl⁺ using a formation constant for reaction 9 (log₁₀ $K_1 = -0.4$). Use of Table 2 to calculate the ZnCl⁺ and ZnCl₂(aq) formation constants gives log₁₀ $K_1 = -0.26$ and log₁₀ $\beta_2 = -0.30$ at $I_m = 0.68 \text{ mol} \cdot \text{kg}^{-1}$. The accepted value for the result of [90SBb] shown in Table A3-9 incorporates the small differences between the present selected ZnCl⁺ and ZnCl₂(aq) formation constant data used by [90SBb].

The authors of [90SBb] used their formation constant results at $I_m = 0.68 \text{ mol}\cdot\text{kg}^{-1}$ and activity coefficient expressions to estimate and compare $\log_{10} K_1^{\circ}$ values for ZnCO₃(aq) and CuCO₃(aq) at $I_m = 0 \text{ mol}\cdot\text{kg}^{-1}$. They found that $\log_{10} K_1^{\circ}$ (ZnCO₃(aq)) was 2.06 smaller than that for CuCO₃(aq). In conjunction with the Recommended [2007PBa] standard CuCO₃(aq) formation constant ($\log_{10} K_1^{\circ}$ (298.15 K) = 6.75 ± 0.03), $\log_{10} K_1^{\circ}$ (eq. 13, 298.15 K) is then estimated to be 4.69 ± 0.09.

Although [76BHa] regarded their $ZnCO_3(aq)$ formation constant in 0.101 mol·kg⁻¹ KNO₃ as approximate only, their work did provide estimates for the $ZnCO_3(aq)$ and $CdCO_3(aq)$ formation constants in the same medium and using the same experimental procedure (differential pulse polarography). They observed a 0.4 difference in $\log_{10} K_1$ values for $CdCO_3(aq)$ and $ZnCO_3(aq)$ [76BHa]. Assuming that the $\log_{10} K_1^{\circ}$ values and $\log_{10} K_1$ values for each element differ by a similar amount, then from the $\log_{10} K_1^{\circ}$ value for $CdCO_3(aq)$ formation [2007PBa] we estimate $\log_{10} K_1^{\circ}(eq. 13, 298.15 \text{ K}) = 4.8 \pm 0.2$ for $ZnCO_3(aq)$.

An unweighted average of the above estimates gives a Provisional value for the $\text{ZnCO}_3(\text{aq})$ formation constant at $I_m = 0 \text{ mol} \cdot \text{kg}^{-1}$ as $\log_{10} K_1^{\circ}(\text{eq. 13, 298.15 K}) = 4.75 \pm 0.06$, where the listed uncertainty reflects the range of the three averaged values.

4.3.2 Formation of $Zn(CO_3)_2^{2-}$

Only two values have been reported for $\log_{10} \beta_2$ (eq. 14, 298.15 K). That reported by [90SBb] (Table A3-9; $\log_{10} \beta_2 = 5.3 \pm 0.6$), was poorly defined due to the very small extent of $Zn(CO_3)_2^{2-}$ formation in their "synthetic seawater" solutions at $I_m = 0.68 \text{ mol} \cdot \text{kg}^{-1}$. The accepted value for $\log_{10} \beta_2$ (eq. 14, 298.15 K) incorporates the differences between the present selected ZnCl⁺ and ZnCl₂(aq) formation constant data and the data used by [90SBb]. This constant was also measured over a range of ionic strengths in mixtures of NaClO₄ and Na₂CO₃ [87FGa], but this result is rejected because formation of Zn(OH)₃⁻ was neglected even though it should be a major solution species within the range of hydroxide concentrations used (see [65SEb] and Table A3-3 of the present work).

The $\log_{10} \beta_2(\text{eq. 14})$ and $\log_{10} K_1(\text{eq. 13})$ results of [90SBb] can be combined to estimate a $\log_{10} K_2$ at $I_m = 0.68 \text{ mol} \cdot \text{kg}^{-1}$ for the isocoulombic equilibrium

$$ZnCO_{3}(aq) + CO_{3}^{2-} \rightleftharpoons Zn(CO_{3})_{2}^{2-}$$
(17)

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The resultant Indicative value, $\log_{10} K_2$ (eq. 17, 298.15 K) = 2.0 ± 0.6, suggests that significant formation of $Zn(CO_3)_2^{2-}$ is restricted to high levels of dissolved inorganic carbon and very high pH relative to most natural waters.

4.3.3 Formation of ZnHCO3+

Three investigations have provided results that can be used to evaluate the ionic strength dependence of equilibrium 15. The work of [78RBc] was performed over a range of ionic strengths between 0.03 and 0.20 mol·kg⁻¹. Results were used to directly estimate formation constants at $I_m = 0 \text{ mol·kg}^{-1}$. The work of [90SBb] was performed at $I_m = 0.68 \text{ mol·kg}^{-1}$ with $[Cl^-]_T = 0.55 \text{ mol·kg}^{-1}$. As for the evaluation of the ZnCO₃(aq) formation constant [90SBb], the accepted values given in Table A3-9 have been corrected for the difference in the assigned values for the ZnCl⁺ formation constant in [90SBb] and the ZnCl⁺ and ZnCl₂(aq) values recommended in the present study. A stability constant for ZnHCO₃⁺ formation (eq. 15) at $I_m = 3.503 \text{ mol·kg}^{-1}$ was derived from the result obtained by [85FGa] for the following equilibrium:

$$Zn^{2+} + H_2O + CO_2(g) \rightleftharpoons ZnHCO_3^+ + H^+$$
(18)

The formation constant for this equilibrium, corrected to the molal concentration scale, is

 $\log_{10} K$ (eq. 18, 298.15 K) = -7.63 ± 0.05

This result, combined with the [58FNa] equilibrium constant ($\log_{10} K_0 K_1 = 7.88$) for the reaction

$$\mathrm{H^{+}} + \mathrm{HCO}_{3}^{-} \rightleftharpoons \mathrm{CO}_{2}(\mathrm{g}) + \mathrm{H}_{2}\mathrm{O}$$

was used to produce the result shown in Table A3-9 for equilibrium 15 at $I_m = 3.503 \text{ mol} \cdot \text{kg}^{-1}$.

A SIT analysis (Fig. A4-11) using the data for $ZnHCO_3^+$ formation (Table A3-9) provides the following Provisional $\log_{10} K^\circ$ and reaction ion interaction coefficient estimates:

 $\log_{10} K^{\circ}(\text{eq. 15, 298.15 K}) = 1.62 \pm 0.10$

and $\Delta \varepsilon(15) = 0.100 \pm 0.042 \text{ kg} \cdot \text{mol}^{-1}$.

4.3.4 Formation of $Zn_2CO_3^{2+}$ A $Zn_2CO_3^{2+}$ formation constant was obtained by [85FGa] at $I_c = 3.0 \text{ mol}\cdot\text{dm}^{-3}$ for the equilibrium

$$2Zn^{2+} + H_2O + CO_2(g) \rightleftharpoons Zn_2CO_3^{2+} + 2H^+$$
(19)

The value [85FGa], corrected to the molal concentration scale at $I_m = 3.503 \text{ mol} \cdot \text{kg}^{-1}$, is

 $\log_{10} K$ (eq. 19, 298.15 K) = -13.40 ± 0.05

This value, combined with the equilibrium constants for the reactions H⁺ + HCO₃⁻ \rightleftharpoons CO₂(g) + H₂O (log₁₀ K₀K₁ = 7.88; [58FNa]), and H⁺ + CO₃²⁻ \rightleftharpoons HCO₃⁻ (log₁₀ K₂ = 9.56; [58FNa]), provides an estimate for the formation constant for reaction 16 at $I_m = 3.503 \text{ mol} \cdot \text{kg}^{-1}$

 $\log_{10} \beta_{21}$ (eq. 16, 298.15 K) = 4.04 ± 0.20

This value indicates that solution concentrations of $Zn_2CO_3^{2+}$ are very low compared to $ZnCO_3(aq)$, unless $[Zn^{2+}]_T >> 1 \ \mu mol \cdot kg^{-1}$.

4.4 The $Zn^{2+} + SO_4^{2-}$ system

Quantitative characterization of the chemical speciation of systems such as $Zn^{2+} + SO_4^{2-}$ that contain ions of relatively high charge is complicated by a number of factors. These include activity coefficient variation in the mixed $ClO_4^- + SO_4^{2-}$ media that are typically employed in such studies, and the formation of solvent-separated (outer sphere) complexes. These problems, which have been discussed in

detail in earlier parts of this series [2005PBa, 2007PBa], are evident in higher-than-expected uncertainties in the measured constants.

The stability constants for the formation of Zn^{2+} -sulfato complexes in homogeneous solution, reactions 20 and 21

$$Zn^{2+} + SO_4^{2-} \rightleftharpoons ZnSO_4(aq)$$
⁽²⁰⁾

$$\operatorname{Zn}^{2+} + 2\operatorname{SO}_4^{2-} \rightleftharpoons \operatorname{Zn}(\operatorname{SO}_4)_2^{2-}$$

$$\tag{21}$$

are, except for equilibrium 20 at very low ionic strengths [2010PET], poorly characterised. This is surprising because the required measurements should be relatively straightforward and the data are of importance in the industrial extraction and electroplating of Zn [70MAT] and in natural water systems [80MAN].

The speciation diagram for the $Zn^{2+} + SO_4^{2-}$ system, Fig. 4, is based on our Recommended value for K_1° (reaction 20) and the Indicative value of β_2° (reaction 21), given in Table 4. Because of the pronounced decrease in both of these stability constants with increasing I_m , the calculations are truncated at $[SO_4^{2-}]_T = 0.030 \text{ mol} \cdot \text{kg}^{-1}$, which corresponds approximately to the standard seawater concentration. Note, however, that even at this low I_m there may be significant activity coefficient effects and the results of the calculations should be viewed with caution.



Fig. 4 Speciation diagram for the ternary $Zn^{2+} + SO_4^{2-}$ system as obtained from the Recommended and Indicative stability constants at 25 °C and $I_m = 0$ mol·kg⁻¹ (Table 4), calculated for $[Zn^{II}]_T = 10^{-6}$ mol·dm⁻³. No corrections were made for ionic strength-dependent changes in formation constants.

4.4.1 Formation of $ZnSO_4(aq)$

Reaction 20 is the only interaction between Zn^{2+} and SO_4^{2-} that is likely to significantly affect the chemical speciation of Zn^{II} under typical natural water conditions. The stability constants for this equilibrium are summarised in Table A3-10. At low ionic strengths, an exceptional number of determinations (19 in all) have been accepted. The broad agreement among these values has enabled a stringent assessment to be made of the many other publications reporting data under these conditions. Rejected publications (33 in all) are listed, along with the reasons for rejection, in footnote 3 of Table A3-10.

The 19 accepted values (Table A3-10) of the association constant for $\text{ZnSO}_4(\text{aq})$ at $I_m = 0$ mol·kg⁻¹, give a weighted average of

 $\log_{10} K_1^{\circ}$ (eq. 20, 298.15 K) = 2.304 ± 0.042

with the weighting of each datum taken as $1/u^2$ where *u* is the assigned uncertainty. This value is recommended.

Of the accepted values, including recalculations, 11 are based on conductivity measurements. Although these studies are generally of high quality, long-recognised theoretical difficulties [71HPa, 2005BES] make commensurately accurate derivation of $\log_{10} K_1^{\circ}$ from such data problematic. Similar considerations apply to the interpretation of thermodynamic (activity coefficient and $\Delta_{dil}H$) data [72PIa]. Nevertheless, the values of $\log_{10} K_1^{\circ}$ obtained by these different techniques agree within the above uncertainty range. It is particularly notable that the conductometric results for $\log_{10} K_1^{\circ}$ are in good agreement with the values obtained from thermodynamic data [55BPb, 72PIa, 81WAC], ion chromatography [93AN], and UV–vis spectrometry [97CRc]. In contrast, the $\log_{10} K_1^{\circ}$ result obtained via the normally reliable potentiometric method [73FCa] is rejected because of the long extrapolation involved (the data were measured at $I_c \ge 0.5 \text{ mol}\cdot\text{dm}^{-3}$) and because it is inconsistent with the other studies (Table A3-10). The potentiometric result of Nair and Nancollas [58NNa], obtained from measurements at low I, has been accepted even though it is somewhat larger than most other studies (albeit still within $\pm 2\sigma$ of the Recommended value).

Stability constants obtained by Raman spectroscopy [84HAY, 91RUD, 99RUD] are rejected because the technique is inappropriate in the presence of solvent-separated complexes [2003RUD, 2006HEF]. While no modern dielectric or ultrasonic relaxation study of the $Zn^{2+} + SO_4^{2-}$ system has been reported, older (technologically limited) investigations [67FPb, 70BBa] have suggested the presence of such complexes. It is relevant to note here that constants reported for "inner and outer sphere" speciation models have been rejected throughout this series [2005PBa, 2007PBa, 2009PBa, 2011POW], as being an incomplete account of the equilibria involved. A full description of such equilibria requires quantification of the "outer-outer" sphere complexes, which are in general only detectable by relaxation methods [2004BCa, 2006MAR].

In contrast to the plethora of results at infinite dilution, there are few data for equilibrium 20 at finite *I* (Table A3-10). The majority of the accepted values have been determined by one group using Zn(Hg) potentiometry [71FCb, 73FCa, 75FCa] or calorimetry [74BRa] in LiClO₄ media. The constants and their reported uncertainties vary slightly among these potentiometric studies but do not constitute independent verification. Independent measurements at $I_c = 0.1 \text{ mol}\cdot\text{dm}^{-3}$ (NaTf) [98WBa] and $I_c = 1.0 \text{ mol}\cdot\text{dm}^{-3}$ (NaClO₄) [74MSc] are in only fair agreement with those of [71FCb, 73FCa, 74BRa, 75FCa]. Clearly, there is a need for further investigations of the Zn²⁺ + SO₄²⁻ system at finite ionic strengths.

The SIT regression (Fig. A4-12) of the accepted results in LiClO_4 media, with $\log_{10} K_1^{\circ}$ (eq. 20, 298.15 K) fixed at the above Recommended value, gives $\Delta \varepsilon (20) = -(0.05 \pm 0.03) \text{ kg} \cdot \text{mol}^{-1}$.

4.4.2 Formation of $Zn(SO_4)_2^{2-}$

While some $M^{2+} + SO_4^{2-}$ systems form higher-order complexes [2005CHE, 2006ARa, 2011POW], others, such as $Cu^{2+} + SO_4^{2-}$ [2007PBa] and Pb²⁺ + SO₄²⁻ [2009PBa], appear not to. Literature data for equilibrium 21 are summarized in Table A3-11. Superficially, these results provide evidence for the existence of $Zn(SO_4)_2^{2-}$. However, all these data were reported by one group [71FCb, 73FCa, 75FCa] as part of a dubious speciation scheme (see Section 4.4.3). The only independent reports of this complex are an approximate value of β_2° derived by Pitzer [72PIa] from a Debye–Hückel-based analysis of various thermodynamic data and a value measured by solvent extraction at $I_c = 1.0 \text{ mol} \cdot dm^{-3}$ (NaClO₄) [74MSc]. Both results are in only modest agreement with the values of [71FCb, 73FCa, 75FCa]. As for some other $M^{2+} + SO_4^{2-}$ systems [2007PBa, 2009PBa], the apparent "observation" of $Zn(SO_4)_2^{2-}$ may simply reflect changes in activity coefficients when there is significant replacement of the medium

anion (typically ClO_4^{-}) by SO_4^{2-} . Accordingly, pending further investigation, all the results in Table A3-11 are considered Indicative only.

The SIT regression of the data in LiClO₄ media (Fig. A4-13) yields $\log_{10} \beta_2^{\circ}$ (eq. 21, 298.15 K) = 3.2 ± 0.2 and $\Delta \epsilon$ (21) = 0.09 ± 0.08 kg·mol⁻¹.

4.4.3 Formation of higher-order and mixed complexes

The formation of higher-order complexes, $Zn(SO_4)_n^{(2n-2)-}$ with $3 \le n \le 5$ has been claimed by Fedorov et al. [71FCb, 73FCa, 75FCa]. However, there are no independent data to support the existence of these complexes in aqueous solution; the formation of species with n > 2 seems unlikely on charge grounds and also by analogy with better-studied related systems [2007PBa]. Thus, all stability constants for $Zn(SO_4)_n^{(2n-2)-}$ with n > 2 are rejected. Similar comments apply to the plethora of mixed $Zn^{2+} + X^- + SO_4^{2-}$ complexes (X = Cl or Br), also reported by Fedorov et al. [71FCb, 75FCa].

4.5 The $Zn^{2+} + PO_4^{3-}$ system

Difficulties in quantifying the speciation and stability constants in $M^{2+} + H^+ + PO_4^{3-}$ systems have been discussed in the earlier parts of this series [2005PBa, 2007PBa, 2009PBa, 2011POW]. In the *SC-Database* [2010PET] there are only nine references for the homogeneous system $Zn^{2+} + PO_4^{3-}$. The composition of the identified water-soluble phosphate complexes strongly depends on the pH range, the total concentrations, and their ratios $[M^{II}]_T: [PO_4^{3-}]_T$. As a consequence, in the presence of Zn^{II} the formation of eight differently protonated mono- and bis-complexes: $ZnH_2PO_4^+$, $Zn(H_2PO_4)_2(aq), Zn(H_2PO_4)(HPO_4)^-$, $ZnHPO_4(aq), Zn(HPO_4)_2^{2-}$, $Zn(HPO_4)_3^{4-}$, $Zn(HPO_4)(PO_4)^{3-}$, $Zn(OH)_2(HPO_4)^{2-}$, and even a dimeric species $Zn_2(HPO_4)_2(aq)$ have been proposed (Table A3-12).

The diverse set of experimental conditions and speciation models adopted by different authors, even at 25 $^{\circ}$ C, allows the assignment of only one Recommended value. The constants reported by [67SBc] and [74RMa] for reaction 22

$$\operatorname{Zn}^{2+} + \operatorname{HPO}_4^{2-} \rightleftharpoons \operatorname{Zn}\operatorname{HPO}_4(\operatorname{aq})$$
 (22)

 $(\log_{10} K = 2.40 \pm 0.05; I_m = 0.101 \text{ mol} \cdot \text{kg}^{-1} \text{ NaClO}_4)$ are in reasonable agreement with that determined by Sigel et al. [96SSa] $(\log_{10} K = 2.53 \pm 0.03; I_m = 0.101 \text{ mol} \cdot \text{kg}^{-1} \text{ NaNO}_3)$. On the basis of these results, we assign the Recommended value at 25 °C and $I_m = 0.101 \text{ mol} \cdot \text{kg}^{-1}$

 $\log_{10} K$ (eq. 22; 298.15 K) = 2.47 ± 0.20

From this value, and the protonation constant for PO_4^{3-} in $I_m = 0.10 \text{ mol} \cdot \text{kg}^{-1} \text{ NaNO}_3$ ($\log_{10} K_1 = 11.68 \pm 0.05 \text{ [67SBc]}$), we derive $\log_{10} \beta_{1,1,1}$ ($I_m = 0.101 \text{ mol} \cdot \text{kg}^{-1}$) = 14.08 ± 0.20 at 25 °C for reaction 23

$$\operatorname{Zn}^{2+} + \operatorname{H}^{+} + \operatorname{PO}_{4}^{3-} \rightleftharpoons \operatorname{Zn}\operatorname{HPO}_{4}(\operatorname{aq})$$
 (23)

Application of the SIT function to the selected data for reaction 22 at $I_m = 0.10 \text{ mol} \cdot \text{kg}^{-1}$, assuming ε (ZnHPO₄,NaClO₄) = 0 (for an uncharged species), and taking ε (Na⁺,HPO₄²⁻) = -0.15 ± 0.06 and ε (Zn²⁺,ClO₄⁻) = 0.351 ± 0.005 or ε (Zn²⁺,NO₃⁻) = 0.174 ± 0.001 (Appendix 1B) yields $\log_{10} K^{\circ}$ (22) = 3.3 ± 0.4, from which $\log_{10} K^{\circ}$ (23) = 15.64 ± 0.4 can be derived. These latter values can be taken as Provisional. The stability constants listed in Table A3-12 for the formation of the other phosphato complexes can, in the absence of independent confirmation, only be considered as Indicative.

5. EVALUATION OF EQUILIBRIUM CONSTANTS (HETEROGENEOUS REACTIONS)

5.1 The Zn²⁺ + OH⁻ system and the solubility of zinc oxide and hydroxide

There are a number of different phases of zinc oxide and hydroxide. These include ZnO(s), α -Zn(OH)₂(s), β_1 -Zn(OH)₂(s), β_2 -Zn(OH)₂(s), γ -Zn(OH)₂(s), δ -Zn(OH)₂(s), and ϵ -Zn(OH)₂(s). The hydroxide phases can be prepared by following different methods [86BAE], and the solubility of each, as well as active and inactive ZnO(s) and amorphous Zn(OH)₂, has been determined. However, many solubility studies have been performed where the solid phase was not characterised; results from such studies are not accepted in this review.

Solubility constant data have been reported for the acid dissolution reactions of ZnO(s) over a wide range of temperature. The majority of these data were determined in dilute solutions, or over a range of ionic strengths using a non-complexing medium, and were corrected by the original authors to $I_m = 0 \text{ mol} \cdot \text{kg}^{-1}$. These data are presented in Table A3-13 together with our estimated uncertainties. The data from different sources join smoothly across the whole experimental temperature range (25 to 300) °C. From these data, the standard equilibrium constant at 25 °C for reaction 24, $*K_{s0}^{\circ}$, can be calculated

$$ZnO(s) + 2H^+ \rightleftharpoons Zn^{2+} + H_2O$$
 (24)

The value determined at 25 °C from the temperature dependence of the solubility constant (Fig. A4-14)

$$\log_{10} * K_{s0}^{\circ}$$
 (eq. 24, 298.15 K) = 11.12 ± 0.05

is Recommended. It is in very good agreement with the values selected by [86BAE] (11.14) and by [2001ZHA] (11.2 \pm 0.2).

Schindler et al. [64SAa] determined the acid dissolution of ZnO(s) in both 0.2 mol·dm⁻³ NaClO₄ and 0.2 mol·dm⁻³ KNO₃. They obtained the same value, $\log_{10} *K_{s0} = 11.39 \pm 0.04$ for both media (where the uncertainty has been increased by this review to the 95 % uncertainty interval). Collat [58COb] measured the acid dissolution of ZnO(s) in 0.1 mol·dm⁻³ KNO₃ obtaining the value $\log_{10} *K_{s0} = 11.23 \pm 0.10$ (uncertainty assigned by this review). Using the ion interaction coefficient data for Zn²⁺ with ClO₄⁻ and NO₃⁻, as determined in Appendix 1B, together with those of H⁺ with the same two anions [97GRE] and the $\log_{10} *K_{s0}^{\circ}$ value determined above, gives $\log_{10} *K_{s0}$ values of 11.38 ± 0.05, 11.39 ± 0.05, and 11.34 ± 0.05 in 0.2 mol·dm⁻³ NaClO₄, 0.2 mol·dm⁻³ KNO₃, and 0.1 mol·dm⁻³ KNO₃, respectively. These values are in excellent agreement with those determined by [64SAa] and [58COb]. The calculated value of $\Delta \varepsilon$ (24) is (0.07 ± 0.04) kg·mol⁻¹ in NaClO₄ media and (0.04 ± 0.04) kg·mol⁻¹ in KNO₃ media.

The acid dissolution of ε -Zn(OH)₂(s) has also been studied over a range of temperature, although not as wide as that for ZnO(s). These data are also listed in Table A3-13 together with our estimated uncertainties. The data from different sources, which refer to the reaction

$$\varepsilon - Zn(OH)_2(s) + 2H^+ \rightleftharpoons Zn^{2+} + 2H_2O$$
⁽²⁵⁾

join smoothly across the whole experimental temperature range (12.5 to 75) °C. The solubility constant for reaction 25 at 25 °C has been determined from the temperature dependence of the accepted data (Fig. A4-15). The value determined,

 $\log_{10} * K_{s0}^{\circ}$ (eq. 25, 298.15 K) = 11.38 ± 0.20

is considered to be Provisional.

Schindler et al. [64SAa] studied the acid dissolution of ε -Zn(OH)₂(s) in 0.2 mol·dm⁻³ NaClO₄ and 0.2 mol·dm⁻³ KNO₃. They determined log₁₀ * K_{s0} = 11.75 ± 0.04 for both media (the uncertainty has been increased in this review to the 95 % interval). They obtained the same value as an earlier investigation in 0.2 mol·dm⁻³ NaClO₄ [63SAa]. Pinto et al. [63PEa] obtained log₁₀ * K_{s0} = 11.72 ± 0.04

(uncertainty assigned by this review) for the acid dissolution of ε -Zn(OH)₂(s) in 0.2 mol·dm⁻³ KNO₃, a value in excellent agreement with that of Schindler et al. [64SAa]. It is deduced that the value of $\Delta \varepsilon$ (25) is the same in both media, and also that $\Delta \varepsilon$ (24) = $\Delta \varepsilon$ (25) since the same solution species are involved for both equilibria. The calculated values for $\log_{10} * K_{s0}$ in 0.2 mol·dm⁻³ NaClO₄ or KNO₃, using $\Delta \varepsilon$ (25) and the value given above for zero ionic strength, are 11.65 ± 0.05 and 11.66 ± 0.05, respectively. These values are in good agreement with those determined by [63PEa] and [64SAa].

Schindler et al. [64SAa] also measured the solubility of β_1 -, β_2 -, γ -, and δ -Zn(OH)₂(s) in 0.2 mol·dm⁻³ NaClO₄ or KNO₃. The log₁₀ * K_{s0}° values determined for each of these phases (eq. 25) are listed in Table A3-13. The values of $\Delta \epsilon$ (25) for these phases is assumed to be the same as those determined for ZnO(s) and ϵ -Zn(OH)₂(s). The calculated solubility constants for these phases at zero ionic strength are therefore

 $log_{10} *K_{s0}^{\circ}(eq. 25 (β_1-Zn(OH)_2), 298.15 K) = 11.72 \pm 0.04$ log_{10} *K_{s0}^{\circ}(eq. 25 (β_2-Zn(OH)_2), 298.15 K) = 11.76 \pm 0.04 log_{10} *K_{s0}^{\circ}(eq. 25 (γ-Zn(OH)_2), 298.15 K) = 11.70 \pm 0.04 log_{10} *K_{s0}^{\circ}(eq. 25 (δ-Zn(OH)_2), 298.15 K) = 11.81 \pm 0.04

These values are Recommended. They are in very good agreement with the values determined by [64SAa] at zero ionic strength ($\log_{10} *K_{s0}^{\circ} = 11.76 \pm 0.03$, 11.80 ± 0.03 , 11.74 ± 0.03 , and 11.85 ± 0.03 , respectively).

5.2 The $Zn^{2+} + CO_3^{2-}$ system

5.2.1 Solubility of $ZnCO_3(s)$ (smithsonite)

Solubility constants have been reported [69SRa, 2000PKa] for the acid dissolution of $ZnCO_3(s)$ (smithsonite) over a range of ionic strength in NaClO₄ at 25 °C. Equilibrium constants for reaction 26

$$ZnCO_3(s) + 2H^+ \rightleftharpoons Zn^{2+} + H_2O + CO_2(g)$$
⁽²⁶⁾

were expressed in the form $\log_{10} {}^*K_{ps0} = \log_{10} \{ [Zn^{2+}]p_{CO_2}[H^+]^{-2}(c^{\circ}/p^{\circ}) \}$. The results of [69SRa] for $I_m = 0.202 \text{ mol} \cdot \text{kg}^{-1} \text{ NaClO}_4$ and those of [2000PKa] for $I_m = 1.0, 2.0, \text{ and } 3.0 \text{ mol} \cdot \text{kg}^{-1} \text{ NaClO}_4$, are broadly consistent. However, since the $\log_{10} {}^*K_{ps0}$ ionic strength dependence observed by [2000PKa] is highly coherent and appears to be offset from the results of [69SRa] by about 0.1 units, only the results of [2000PKa] have been used in the SIT analysis shown in Fig. A4-16. The Provisional equilibrium constant and reaction ion interaction coefficient produced by analysis of the [2000PKa] data shown in Table A3-14 are

$$\log_{10} {}^*K_{\text{ps0}}^{\circ}(\text{eq. 26, 298.15 K}) = 7.21 \pm 0.04$$

and $\Delta \varepsilon(26) = 0.09 \pm 0.02 \text{ kg} \cdot \text{mol}^{-1}$.

The Provisional equilibrium constant for equilibrium 26 can be combined with the CODATA value for the equilibrium $CO_2(g) + H_2O \rightleftharpoons 2H^+ + CO_3^{2-} (\log_{10} K^\circ = -18.143; [82WAG])$ to produce a standard equilibrium constant of

 $\log_{10} K_{s0}^{\circ}$ (eq. 27, 298.15 K) = -10.93 ± 0.04

for the smithsonite solubility reaction written as

$$ZnCO_3(s) \rightleftharpoons Zn^{2+} + CO_3^{2-}$$
⁽²⁷⁾

This value is Provisional.

5.2.2 Solubility of $Zn_5(OH)_6(CO_3)_2(s)$ (hydrozincite)

In addition to an analysis of smithsonite solubility, [69SRa] determined an equilibrium constant for the hydrozincite reaction 28 at $I_m = 0.202 \text{ mol} \cdot \text{kg}^{-1}$ and 298.15 K

$$0.2Zn_5(OH)_6(CO_3)_2(s) + 2H^+ \rightleftharpoons Zn^{2+} + 0.4CO_2(g) + 1.6H_2O$$
 (28)

More recently, Preis and Gamsjäger [2001PRE] conducted a detailed study of the solubility of hydrozincite. They obtained data at 298.15 K for $I_m = 1.0$, 2.0, and 3.0 mol·kg⁻¹ NaClO₄ as well as at $I_m = 1.0 \text{ mol·kg}^{-1}$ NaClO₄ across the temperature range 288.15 to 338.15 K. Heat capacity data were also obtained.

The data at 298.15 K from [69SRa] and [2001PRE] (Table A3-14) were combined to derive an equilibrium constant for reaction 28 at zero ionic strength using a SIT analysis, as shown in Fig. A4-17. The derived solubility constant is

$$\log_{10} * K_{ps0}^{\circ}$$
 (eq. 28, 298.15 K) = 9.07 ± 0.09

and is regarded as Provisional. The derived interaction coefficient is $\Delta \varepsilon(28) = 0.12 \pm 0.05 \text{ kg} \cdot \text{mol}^{-1}$.

5.3 The Zn^{2+} + SO_4^{2-} system

Under conditions typically encountered in the natural environment, the equilibrium form of solid Zn^{II} sulfate will be the heptahydrate, $ZnSO_4 \cdot 7H_2O(s)$ [65LIN]. The solubility of this salt is high (>3 mol·dm⁻³ at 25 °C in water) and increases rapidly with temperature up to ~50 °C before becoming retrograde [65LIN]. It will not therefore have a significant influence on Zn^{II} speciation in natural waters. "Basic" Zn sulfates have also been reported [54DOa, 80MAN] but their solubility and stoichiometry in contact with saturated aqueous solutions have neither been well characterized nor confirmed by independent studies. As for related $M^{II} + SO_4^{-2-}$ systems [2005PBa, 2007PBa], the solubility of such mixed salts is unlikely to be sufficiently low to influence the speciation in typical natural water systems. They have, therefore, not been considered further in this review.

5.4 The Zn²⁺+ PO₄³⁻ system

The formation of insoluble phosphates, $Zn_3(PO_4)_2 \cdot nH_2O$, may influence both the availability of Zn in soil and the Zn levels in natural water systems [73NRa]. The only reliable data for the solubility constant of $Zn_3(PO_4)_2 \cdot 4H_2O(s)$, reaction 29

$$Zn_3(PO_4)_2 \cdot 4H_2O(s) \rightleftharpoons 2Zn^{2+} + 2PO_4^{3-} + 4H_2O$$
⁽²⁹⁾

were determined by Nriagu [73NRa] from solubility measurements in dilute phosphoric acid (pH = 3.4-4.6) at 25 °C. These indicated a low solubility for this solid. The resultant solubility constant is accepted as Provisional

$$\log_{10} K_{s0}^{\circ}$$
 (eq. 29; 298.15 K) = -35.3 ± 0.1

Zharovskii [51ZHa] determined the solubility of $Zn_3(PO_4)_2 \cdot 4H_2O(s)$, however, he considered neither the polymorphic nature of this compound, nor the effects of complex formation. The reported constant [51ZHa] ($log_{10} K_{s0}(29) = -32.04$, 19 °C, I = variable) is in poor agreement with that of [73NRa] but provides some support for the above Provisional value.

From measurements in alkaline solutions, Ziemniak et al. [92ZJa] reported $\log_{10} {}^*K_{s1}(30) = -5.8 \pm 0.3$ (pH = 10.2 – 11.7, *I* = variable, 25 °C) for reaction 30

$$ZnO(s) + H_2O + HPO_4^{2-} = Zn(OH)_2(HPO_4)^{2-}$$
(30)

6. EVALUATION OF ENTHALPY DATA (HOMOGENEOUS AND HETEROGENEOUS REACTIONS)

6.1 The $Zn^{2+} + OH^{-}$ system

The standard enthalpy changes for the formation of the monomeric Zn^{II} -hydroxido complexes (eqs. 4–7) were calculated from the temperature dependence of the stability constants, Sections 4.1.1 to 4.1.4 (Figs. A4-1, A4-3, A4-4, and A4-6):

 $\Delta_{\rm r} H^{\circ} (*K_1) = (56.8 \pm 0.9) \text{ kJ} \cdot \text{mol}^{-1}$ $\Delta_{\rm r} H^{\circ} (*\beta_2) = (109 \pm 4) \text{ kJ} \cdot \text{mol}^{-1}$

 $\Delta_{\rm r} H^{\circ} (*\beta_3) = (151 \pm 3) \, \rm kJ \cdot mol^{-1}$

 $\Delta_{\mathbf{r}} H^{\circ} (*\beta_{\Delta}) = (188 \pm 6) \text{ kJ} \cdot \text{mol}^{-1}$

These values, each assigned its 95 % confidence value, are Recommended.

Only $\log_{10} *K_1$ (ZnOH⁺) was found to have a linear dependence on T^{-1} . In this case, the van't Hoff equation could be used to determine the standard enthalpy change (from the slope of the regression line) and the entropy change (from the intercept). For the other three species, the enthalpy change has been determined from the gradient at T = 298.15 K of the temperature dependence of the respective stability constant.

There have been several literature reports of the enthalpy change for reaction 4. Perrin [62PEb], from measurements of the stability constant for ZnOH⁺ from 15 to 42 °C, derived a value of $\Delta_r H^{\circ}(*K_1) = 56.0 \text{ kJ} \cdot \text{mol}^{-1}$. Nikolaeva [69NIa] measured the temperature dependence for the formation of ZnOH⁺ and Zn₂OH³⁺ from 50 to 90 °C in Zn nitrate solutions. The value determined for $\Delta_r H^{\circ}(*K_1)$ was $65 \pm 9 \text{ kJ} \cdot \text{mol}^{-1}$. In a later study, Nikolaeva and Primanchuk [69NPe] determined the reaction enthalpy for ZnOH⁺ formation in Zn sulfate solutions, obtaining a value of $59 \pm 4 \text{ kJ} \cdot \text{mol}^{-1}$ (at 25 °C). It is not clear whether the enthalpies from either of the studies by Nikolaeva relate to values corrected to zero ionic strength. More recently, Burkov et al. [78BYa] studied the hydrolysis of Zn²⁺ in 3.0 mol·dm⁻³ NaClO₄ from 25 to 100 °C and found evidence for the formation of both ZnOH⁺ and Zn₂OH³⁺. From their measurements, they determined the reaction enthalpy $\Delta_r H(*K_1) = 48 \pm 8 \text{ kJ} \cdot \text{mol}^{-1}$. These values each provide support for the $\Delta_r H^{\circ}(*K_1)$ value selected in this study from the temperature dependence of $\log_{10} *K_1^{\circ}(\text{ZnOH}^+)$ over a much larger temperature interval, 15 to 350 °C.

temperature dependence of $\log_{10} *K_1^{\circ}(ZnOH^+)$ over a much larger temperature interval, 15 to 350 °C. No value is selected for the reaction enthalpy for the formation of Zn_2OH^{3+} . Burkov et al. [78BYa] reported $\Delta_r H(*\beta_{2,1}) = 61 \pm 2 \text{ kJ} \cdot \text{mol}^{-1}$ from the temperature dependence of $\log_{10} *\beta(Zn_2OH^+)$ in 3.0 mol·dm⁻³ NaClO₄. From the stability constants for Zn_2OH^{3+} reported by Nikolaeva [69NIa], we calculated $\Delta_r H(*\beta_{2,1}) = 33 \text{ kJ} \cdot \text{mol}^{-1}$ (Zn nitrate solutions of various ionic strength), a value which is not consistent with that determined by Burkov et al., even considering the difference in ionic strength. These values are both rejected.

The standard enthalpy change for the acid dissolution of ZnO(s) and ϵ - $Zn(OH)_2(s)$ (eqs. 24 and 25) was calculated from the temperature dependence of the respective solubility constants (Figs. A4-14 and A4-15). The values determined were

$$\Delta_{\rm r} H^{\circ}({}^{*}K_{\rm s0}, \operatorname{ZnO}({\rm s})) = -(86.7 \pm 1.7) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_{\rm r} H^{\circ}({}^{*}K_{\rm s0}, \varepsilon - \operatorname{Zn}({\rm OH})_{2}({\rm s})) = -(100 \pm 11) \text{ kJ} \cdot \text{mol}^{-1}$$

The enthalpy value $\Delta_r H^{\circ}(*K_{s0}, ZnO(s))$ is Recommended whereas the value $\Delta_r H^{\circ}(*K_{s0}, \varepsilon - Zn(OH)_2(s))$ is Provisional.

Shchukarev et al. [53SLa] determined the enthalpy of dissolution of ZnO(s) in a number of acids They found that in hydrohalic acids the reaction enthalpy was less exothermic than that in perchloric acid, most likely due to complexation between the halide ions and Zn^{2+} . In perchloric acid they deter-

mined a value of $\Delta_r H^{\circ}(*K_{s0}, ZnO(s)) = -88.7 \text{ kJ} \cdot \text{mol}^{-1}$, in good agreement with the value determined in this review. They also determined enthalpy values for the dissolution of "zinc hydroxide", however, it was not clear what phase was studied. As such, a comparison with the results determined in this review cannot be made. This is also the case for the enthalpy for dissolution of Zn hydroxide measured by Latysheva and Goryanina [62LGa].

6.2 The Zn²⁺ + Cl⁻ system

The enthalpy changes for the formation of the Zn(II) chlorido- complexes in aqueous solution are expected to be small, because their low stability suggests they are outer-sphere complexes. One calorimetric study on the formation of Zn^{II} chlorido- complexes has been reported [69GEa]. The stepwise reaction enthalpies determined in 3 mol·dm⁻³ NaClO₄ solution at 25 °C were $\Delta_r H(K_1) = 5.5 \pm 0.1$ kJ·mol⁻¹, $\Delta_r H(K_2) = 38 \pm 8$ kJ·mol⁻¹, and $\Delta_r H(K_3) = 0 \pm 8$ kJ·mol⁻¹. Other reported enthalpy data for Zn^{II} chlorido- complexes resulted from potentiometric and solvent extraction studies. There are large discrepancies between all of the reported data, and it is not considered possible to select any enthalpy data for the Zn^{II} chlorido- complexes.

6.3 The $Zn^{2+} + CO_3^{2-}$ system

The temperature dependence of equilibrium 26 was examined by [2000PKa] at $I_m = 1.00 \text{ mol}\cdot\text{kg}^{-1}$ NaClO₄ (Fig. A4-18) giving a value of, $\Delta_r H^{\circ}(26) = -(8.2 \pm 1.3) \text{ kJ}\cdot\text{mol}^{-1}$, which is regarded as Provisional. Values for the enthalpy of the formation reaction for ZnHCO₃⁺ (eq. 15) were obtained by [78RBc] over a range of temperature. Reported $\Delta_r H^{\circ}$ values increased with temperature: 0.54 kJ·mol⁻¹ (10 °C), 3.56 kJ·mol⁻¹ (25 °C), 7.32 kJ·mol⁻¹ (40 °C), 11.80 kJ·mol⁻¹ (55 °C), and 16.99 kJ·mol⁻¹ (70 °C). These values are regarded as Indicative only.

The temperature dependence of equilibrium 28 was examined by [2001PRE] at $I_m = 1.00 \text{ mol} \cdot \text{kg}^{-1}$ NaClO₄ who obtained a value of, $\Delta_r H^{\circ}(28) = -51.3 \text{ kJ} \cdot \text{mol}^{-1}$. This value is regarded as Provisional.

6.4 The $Zn^{2+} + SO_4^{2-}$ system

6.4.1 Formation of ZnSO₄(aq)

The enthalpy change associated with formation of $ZnSO_4(aq)$ has been extensively studied using a range of techniques (Table A3-15). These include titration calorimetry, both with [73POa, 78ARa] and without [69IEa] independent determination of K_1 , heats of dilution [70LAe, 72PIa], and the variation of K_1 with temperature, based on potentiometric [73FCa] or conductometric [81YYa, 2005BES] data. The problems associated with the quantification of $\Delta_r H_1(ZnSO_4(aq))$ are essentially the same as those discussed previously for CuSO₄(aq) [2007PBa] and so will not be considered in detail here. It is important to note that because of the strong correlation between K_1 , $\Delta_r H_1$ and the activity coefficient model adopted [73POa], independent determination of K_1 is more reliable than simultaneous evaluation of K_1 and $\Delta_r H_1$ [69IEa] using calorimetric data alone.

At infinite dilution (I = 0), there is excellent agreement amongst many of the publications reporting enthalpy data, which enabled a stringent selection to be made (Table A3-15; publications containing rejected values are listed in footnote 3). The seven accepted enthalpy results give an unweighted average of $\Delta_r H_1^{\circ} = 6.04 \pm 0.54 \text{ kJ} \cdot \text{mol}^{-1}$, while the unweighted average of the four accepted entropy results is: $\Delta_r S_1^{\circ} = 63.8 \pm 1.6 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, noting that some publications reporting $\Delta_r H_1^{\circ}$ did not report the corresponding $\Delta_r S_1^{\circ}$ values. Both of these values are Recommended. Using the thermodynamic relationships: $\Delta_r G^{\circ} = -\text{R}T \ln K^{\circ} = \Delta_r H^{\circ} - T\Delta_r S^{\circ}$ gives $\Delta_r G_1^{\circ} = -12.98 \pm 1.0 \text{ kJ} \cdot \text{mol}^{-1}$ and thus \log_{10}

 $K_1^{\circ} = 2.27 \pm 0.18$ (maximum error) at 25 °C, which agrees with, but is much less precise than, the value of $\log_{10} K_1^{\circ} = 2.30 \pm 0.04$ recommended in Section 4.4.1.

At finite I (Table A3-15), the majority of the values for $\Delta_r H_1$ and $\Delta_r S_1$ have been derived from potentiometric $K_1(T)$ data reported in one publication [73FCa]. Calorimetric data reported from the same laboratory [74BRA] at $I_c = 3.0 \text{ mol} \cdot \text{dm}^{-3}$ (LiClO₄) are in only fair agreement with the $K_1(T)$ results (Table A3-15). The real uncertainties in these $\Delta_r H_1$ and $\Delta_r S_1$ values are undoubtedly high: only graphical data were provided in [73FCa], and the $K_1(T)$ data on which they were based formed part of an implausible speciation model (Sections 4.4.1 and 4.4.3). Accordingly, pending further investigations, preferably by direct calorimetry, these values are regarded as Indicative only.

The SIT regression of the reaction enthalpy data for LiClO₄ media (Fig. A4-19) yields the Indicative values $\Delta_r H^{\circ}(\text{eq. 20, 298.15 K}) = (8.4 \pm 1.8) \text{ kJ} \cdot \text{mol}^{-1}$ which is consistent with (but less precise than) the above Recommended value. The value of $\Delta \varepsilon_L(20)$ is $(0.31 \pm 0.99) \times 10^{-4} \text{ kg} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$.

6.4.2 Formation of $Zn(SO_4)_2^{2-}$

All of the available enthalpy and entropy values (Table A3-16) for the formation of $Zn(SO_4)_2^{2-}$ (eq. 21) have been derived from potentiometric K(T) data and reported graphically in a single publication [73FCa]. The uncertainties in these results are high, not only due to the general unreliability of the K(T) approach but also because the reported β_2 values were part of a dubious speciation model involving many other higher-order complexes (Section 4.4.3). The values listed in Table A3-16 should therefore be regarded as Indicative only, and no SIT analysis is presented.

7. SPECIATION IN MULTICOMPONENT SYSTEMS: $Zn^{2+} + OH^- + CI^- + CO_3^{2-} + PO_4^{3-} + SO_4^{2-}$

This section presents results from speciation calculations for model aquatic systems. The required stability constants were calculated from the standard equilibrium constants in Tables 1–5, and from the previous critical evaluation for the protonation reactions of the ligands [2005PBa]. The standard equilibrium constants were corrected, as required, for ionic strength effects and water activity, $a(H_2O)$, according to eq. 2 and as described in Section 1. The calculation of $\log_{10} \beta_{p,q,r}$ at the required ionic strength (molality scale), its correction to the amount concentration (molarity) scale, and the speciation calculations were achieved using the program WinSGW. This program (www.WinSGW.se), incorporates the SIT functions (eq. 2) and generates the ionic strength-corrected values of $\log_{10} \beta_{p,q,r}$ for each datum in the calculation. In the calculations presented here, the changes in *I* and therefore in $\log_{10} \beta_{p,q,r}$ were small within the prescribed pH ranges.

7.1 Fresh water in equilibrium with CO₂(g)

To illustrate the speciation of Zn^{II} in representative fresh water in equilibrium with CO₂(g), the total concentration of Zn^{II} was set to 1 nmol·dm⁻³ and it was assumed that the system was in equilibrium with air having a CO₂ fugacity of 10^{-1.4} kPa. Total concentrations of inorganic anions were those typically found in fresh water [93MOR]: $[CI^-]_T = 0.23 \text{ mmol·dm}^{-3}$, $[SO_4^{2-}]_T = 0.42 \text{ mmol·dm}^{-3}$, and $[HPO_4^{2-}]_T = 0.7 \mu \text{mol·dm}^{-3}$. Furthermore, pH was allowed to vary between 7.0 and 9.0; in this range the ionic strength is approximately constant, ca. $I_c = 0.0015 \text{ mol·dm}^{-3}$ at pH = 7, and 0.007 mol·dm⁻³ at pH = 9, due to the increase in $[HCO_3^{-7}]$ and $[CO_3^{2-7}]$ at constant $f(CO_2)$.

The stability constants applicable at $I_c = 0.0015 \text{ mol}\cdot\text{dm}^{-3}$ for the major species are shown in Table 6. Note that although the calculations included all of the species critically evaluated in this review, Table 6 includes only those species that make a significant contribution to the speciation of Zn^{II} in the two media considered. The constants are shown for the equilibrium reactions in the format used in the speciation calculations, i.e., in terms of the component species H₂CO₃(aq) with [H₂CO₃(aq)]_T =

 $[CO_2(aq)] + [H_2CO_3(aq)]$. For calculations in fresh water media of low ionic strength: (i) the use of $\Delta \varepsilon$ (NaClO₄) values (rather than those for NaCl) has minimal effect, and (ii) the activity of water can be set equal to one.

Reaction	Medium ionic strength I_c /mol·dm ⁻³		
	$\frac{\log_{10} K^{\circ}}{(I_c = 0)}$	$\log_{10} K$ ($I_c = 0.0015$)	$log_{10} K$ ($I_c = 0.67$)
$\overline{Zn^{2+} + H_2O \leftrightarrows ZnOH^+ + H^+}$	-8.96	-9.00	-9.35
$Zn^{2+} + 2\tilde{H}_2O \rightleftharpoons Zn(OH)_2(aq) + 2H^+$	-17.82	-17.86	-18.31
$Zn^{2+} + H_2CO_3 = ZnCO_3(aq) + 2H^+$	-11.94	-11.83	-12.3
$H_2CO_3 \stackrel{\sim}{=} HCO_3^- + H^+$	-6.35	-6.32	-5.98
$H_2CO_3 = CO_3^{2-} + 2H^+$	-16.69	-16.58	-15.52
$Zn^{2+} + SO_4^{2-} \rightleftharpoons ZnSO_4(aq)$	2.30	2.15	0.84
$Zn^{2+} + Cl^{-} \leftrightarrows ZnCl^{+}$	0.40	0.32	-0.25
$Zn^{2+} + 2Cl^{-} \rightleftharpoons ZnCl_2(aq)$	0.69	0.58	-0.30
$Zn^{2+} + 3Cl^{-} \rightleftharpoons ZnCl_{3}^{-}$	0.48	0.37	-0.40

Table 6 Stability constants for species critical to the speciation of Zn^{II} in fresh water and seawater at T = 25 °C. Refer to [2009PBa] for the data for Mg²⁺ and Ca²⁺ complexes.

The results from the speciation calculation for fresh water are presented in a distribution diagram in Fig. 5. The speciation is very similar to that for the ternary $Zn^{2+} + H^+ + CO_3^{2-}$ system. The figure indicates that the predominant species are Zn^{2+} (pH ≤ 8.4) and $ZnCO_3(aq)$ (pH ≥ 8.4). Besides these two species, $ZnOH^+$ (ca. 5 % at pH = 9.0) and $Zn(OH)_2(aq)$ (ca. 6 % at pH = 9.0) are the only species formed to more than 5 % of $[Zn^{2+}]_T$. The carbonato-, hydrogencarbonato-, chlorido-, sulfato-, and phos-



Fig. 5 Speciation diagram for the Zn²⁺+ H⁺+ Cl⁻ + CO₂ + HPO₄²⁻ + SO₄²⁻ system with total concentrations $[Cl^-]_T = 0.23 \text{ mmol} \cdot dm^{-3}, [SO_4^{-2}]_T = 0.42 \text{ mmol} \cdot dm^{-3}, [HPO_4^{-2}_-]_T = 0.7 \mu \text{mol} \cdot dm^{-3}$ (fresh water medium) and $[Zn^{II}]_T = 1 \text{ nmol} \cdot dm^{-3}$. It was assumed that the system is in equilibrium with air having a CO₂ fugacity of 10^{-1.4} kPa. $\log_{10} K(CO_2(g) \rightleftharpoons CO_2(aq)) = -1.5$ [93MOR]. All other formation constants are according to Table 6 ($I_c = 0.0015 \text{ mol} \cdot dm^{-3}$).

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2275

phato- complexes do not contribute significantly to the speciation of Zn^{II} in fresh waters. The speciation diagram is much simpler than those for Cu^{II} [2007PBa] and Pb^{II} [2009PBa] in fresh water for which, in the pH range illustrated, hydroxido- and bis-carbonato- species are present at higher concentrations and at lower pH, and the formation of Cu^{II} and Pb^{II} ternary species M(CO₃)OH⁻ is also indicated.

7.2 Seawater and saline systems

Distinctive features of natural saline systems are: the higher pH (seawater), the much higher concentrations of Cl⁻, HCO₃⁻, CO₃²⁻, and SO₄²⁻, and the significant concentrations of Mg²⁺ and Ca²⁺ both of which form moderately stable complexes with CO₃²⁻ and SO₄²⁻ [2010PET]. Although the pH of surface seawater lies within a narrow band, ca. 8.2 ± 0.2 , it is informative to effect a calculation for a more generic saline system over a range of pH but approximating seawater composition. The calculations included all of the inorganic components of seawater with the exception of trace metals, fluoride, bromide, silicate, and borate. Thus, they included the competing reactions of Ca²⁺ and Mg²⁺ with the inorganic anions (see [2009PBa] for the relevant stability constants for Ca²⁺ and Mg²⁺ species). Weaker interactions, such as those between Na⁺ and CO₃²⁻ and SO₄²⁻, are considered as an implicit aspect of SIT when applied to measurements in NaClO₄ media and so do not require explicit inclusion in the speciation calculations. For saline media, a larger approximation arises in using SIT reaction parameters, $\Delta\varepsilon$, that were derived for NaClO₄ media rather than NaCl, although the overall uncertainty may be small (because the Δz^2D term is much more important than $\Delta\varepsilon I_m$ in eq. 2).

The increase in ionic strength in the range pH = 7 to 9 due to increasing $[HCO_3^{-1}]$ and $[CO_3^{2-1}]$ at constant $f(CO_2)$ was negligible in this medium and therefore had minimal effect on the stability constants. The stability constants calculated by WinSGW applicable at $I_c = 0.67 \text{ mol} \cdot \text{dm}^{-3}$ for the critical species are shown in Table 6.

The speciation diagram (Fig. 6) indicates that at pH < 7.0 the composition (mole fraction) is invariant with pH and is ca. 60 % Zn²⁺, 19 % ZnCl⁺, 9 % ZnCl₂(aq), and 8 % ZnSO₄(aq). In contrast, fresh water has ca. 93 % Zn²⁺ in this pH range (Fig. 5). In the presence of a high [Cl⁻]_T the formation of ZnCO₃(aq) is suppressed to a small extent relative to fresh water (50 % mol fraction at pH = 8.9, compared with pH = 8.4 for fresh water). Also at high [Cl⁻]_T the hydrolysis of Zn^{II} may be influenced by the formation of ternary Zn²⁺-OH⁻-Cl⁻ complexes, but reliable quantitative information for such ternary equilibria is not available.

The speciation diagram for Zn^{II} contrasts with those for Cu^{II} [2007PBa] and Pb^{II} [2009PBa] for which at the pH of seawater the MCO₃(aq) species dominates over the MCl_n⁽²⁻ⁿ⁾⁺ species. The much lower stability of the carbonato- (and chlorido-) complexes of Zn^{II} compared with those of Cu^{II} , Pb^{II}, and Cd^{II} is illustrated by the mole fraction of M²⁺ at the pH of surface seawater in equilibrium with the atmosphere at 25 °C (pH ca. 8.2 ± 0.2), which is ca. 54, 3.4, 1.1, and 3.3 %, respectively.



Fig. 6 Speciation diagram for the Zn²⁺ + H⁺ + Cl⁻ + CO₂ + HPO₄²⁻ + SO₄²⁻ system in a simulated seawater medium, $I_c = 0.67 \text{ mol}\cdot\text{dm}^{-3}$ including carbonato- and sulfato- complexes of Mg²⁺ and Ca²⁺. It was assumed that [Zn^{II}]_T = 1 nmol·dm⁻³ and that that the system is in equilibrium with air having a CO₂ fugacity of 10^{-1.4} kPa. log₁₀ $K(CO_2(g) \rightleftharpoons CO_2(aq)) = -1.5$ [93MOR]. All other formation constants are according to Table 6 ($I_c = 0.67 \text{ mol}\cdot\text{dm}^{-3}$).

7.3 Summary

The speciation calculations indicate that, in neutral/weakly acidic fresh water systems in equilibrium with atmospheric CO₂, $Zn^{2+}(aq)$ is the dominant Zn^{II} species (93 % of the total dissolved Zn species) in the absence of organic ligands such as humates. In weakly alkaline solutions, pH > 8.4, the speciation is dominated by the carbonato- species $ZnCO_3(aq)$. In saline systems, the formation of $ZnCl^+$ and $ZnCl_2(aq)$ is significant but at pH < 8.7 the species Zn^{2+} still dominates. At pH > 8.7 $ZnCO_3(aq)$ is the dominant species whereas only small amounts of $Zn(OH)_n^{(2-n)+}$ species are formed.

dominant species whereas only small amounts of $Zn(OH)_n^{(2-n)+}$ species are formed. Table 6 provides the critical constants in media at $I_c = 0.0015$ mol·dm⁻³ (simulating fresh water) and $I_c = 0.67$ mol·dm⁻³ (simulating seawater), calculated from those reported here for $I_m = 0$ mol·kg⁻¹. For reliable speciation calculations of Zn^{II} in environmental systems the accuracy of the equilibrium data ($I_m = 0$ mol·kg⁻¹) for formation of the complexes $ZnCO_3(aq)$, $ZnOH^+$, $Zn(OH)_2(aq)$, $ZnSO_4(aq)$, and $ZnCl_n^{(2-n)+}$ is crucial. This document provides critically evaluated, IUPAC-Recommended (or Provisional) standard equilibrium constant values for the formation of each of these species. However, for the formation of complexes within the $Zn^{2+} + CO_3^{2-}$ subsystem a lack of reliable equilibrium data is evident; this made it impossible to apply a rigorous (multi-data) SIT approach for the evaluation of Zn^{2+} -carbonato constants under standard conditions.

8. QUANTITIES, SYMBOLS, AND UNITS USED IN THIS TECHNICAL REPORT

8.1 Quantities, symbols, and units

Name	Symbol	Definition	SI Unit
amount of substance	п	(SI base unit)	mol
molar mass	М	$M_{\rm A} = m_{\rm A}/n_{\rm A}$ (= mass/amount)	kg•mol ⁻¹
molality	m, b	$m_{\rm B} = n_{\rm B}/M_{\rm A}(n - \sum_{\rm B} n_{\rm B})$	mol·kg ⁻¹
amount concentration	c, [species]	$c_{\rm B} = [\text{species B}] = n_{\rm B}/V$	$mol \cdot m^{-3}$ $(mol \cdot dm^{-3})^{a}$
ionic strength, molality basis	I _m	$I_m = \frac{1}{2} \sum m_i z_i^2$	mol·kg ⁻¹
ionic strength, amount concentration basis	I _c	$I_c = \frac{1}{2} \sum c_i z_i^2$	mol·m ⁻³ (mol·dm ⁻³) ^a
stepwise formation constant (equilibrium concentration product)	K _n	$K_n = [ML_n](c^\circ)/[ML_{n-1}][L]$ for the reaction: $ML_{n-1} + L \rightleftharpoons ML_n$	1
cumulative (overall) formation constant	β_n	$\beta_n = [ML_n](c^{\circ})^n / [M][L]^n$ for the reaction: M + nL \rightleftharpoons ML _n	1
stepwise (metal ion) hydrolysis constant	* <i>K</i> _n	$\label{eq:Kn} \begin{split} ^{*}K_{n} &= \\ [\mathrm{M}(\mathrm{H}_{2}\mathrm{O})_{6-n}(\mathrm{OH})_{n}][\mathrm{H}^{+}]/[\mathrm{M}(\mathrm{H}_{2}\mathrm{O})_{6-n+1}(\mathrm{OH})_{n-1}](c^{\circ}) \\ \text{for the reaction:} \\ \mathrm{M}(\mathrm{H}_{2}\mathrm{O})_{6-n+1}(\mathrm{OH})_{n-1} + \mathrm{H}_{2}\mathrm{O} \rightleftharpoons \mathrm{M}(\mathrm{H}_{2}\mathrm{O})_{6-n}(\mathrm{OH})_{n} + \mathrm{H}^{+} \\ \text{or: } \mathrm{M}(\mathrm{OH})_{n-1} + \mathrm{H}_{2}\mathrm{O} \rightleftharpoons \mathrm{M}(\mathrm{OH})_{n} + \mathrm{H}^{+} \end{split}$	1
cumulative (metal ion) hydrolysis	*β _n *β		1
constant	<i>r m,n</i>	for: $mM(H_2O)_6 + nH_2O \rightleftharpoons M_m(OH)_n + nH^+$	
solubility constant	K _{s0}	$K_{s0} = [M][X]^{p/(c^{\circ})^{p+1}}$ for the reaction: $MX_p(s) \rightleftharpoons M + pX$	1
solubility constant	K _{sn}	$K_{sn} = [MX_{p+q}](c^{\circ})^{q-1}/[X]^q \text{ (where } n = p + q)$ for the reaction: $MX_p(s) + qX \rightleftharpoons MX_{p+q}$	1
solubility constant	*K _{s0}	* $K_{s0} = [M](c^{\circ})^{p-1}/[H^+]^p$ for the reaction: $M(OH)_p(s) + pH^+ \rightleftharpoons M + pH_2O$	1

(continues on next page)

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Pure Appl. Chem., Vol. 85, No. 12, pp. 2249–2311, 2013

Name	Symbol	Definition	SI Unit
cumulative (overall) equilibrium concentration product	$\beta_{p,q,r}$	$\begin{split} \beta_{p,q,r} &= [\mathrm{M}_p \mathrm{L}_q(\mathrm{OH})_r] [\mathrm{H}^+]^r / [\mathrm{M}]^p [\mathrm{L}]^q (c^\circ)^{r-p-q+1} \\ \text{for the reaction:} \\ p\mathrm{M} + q\mathrm{L} + r\mathrm{H}_2\mathrm{O} \rightleftharpoons \mathrm{M}_p \mathrm{L}_q(\mathrm{OH})_r + r\mathrm{H}^+ \end{split}$	1
(molar) enthalpy	Н	H/n	J•mol ⁻¹
(molar) reaction enthalpy	$\Delta_{\rm r} H$	$\Delta_{\rm r} H = \Sigma H({\rm products}) - \Sigma H({\rm reactants})$	J•mol ^{−1}
activity coefficient, molality basis	γ_m	$RT\ln(\gamma_{m,\mathrm{B}}m_{\mathrm{B}}/m^{\mathrm{e}}) = \mu_{\mathrm{B}} - \mu_{\mathrm{B}}^{\mathrm{e}} = \lim_{m_{\mathrm{B}}\to 0} [\mu_{\mathrm{B}} - RT\ln(m_{\mathrm{B}}/m^{\mathrm{e}})]$	1
osmotic coefficient, molality basis	ϕ_m	$\phi_m = (\mu_{\rm A}^* - \mu_{\rm A})/RTM_{\rm A}\Sigma m_{\rm B}$	1
temperature (Celsius)	θ, t	$\theta / ^{\circ} C = T / K - 273.15$	°C
temperature, thermodynamic	Т	(SI base unit)	K

(Continued).

^aCommon units used in this report.

8.2 Subscripts and superscripts

8.2.1 Subscripts

A, B	general constituent
------	---------------------

m quantity expressed on a molality basis

c quantity expressed on an amount concentration basis

8.2.2 Superscripts

standard state for dissolved species $(I \rightarrow 0)$

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2278

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Pure Appl. Chem., Vol. 85, No. 12, pp. 2249–2311, 2013

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2285

APPENDIX 1A

Data evaluation criteria

Literature data have been accepted as reliable (designated "reported" in relevant Tables), and thus included in the regression analyses, when all, or in some cases most, of the following requirements have been met:

- full experimental details are reported (solution stoichiometry, electrode calibration method, temperature, ionic strength, error analysis);
- the equilibrium model is considered to be complete (including hydrolysis reactions);
- data were measured in an essentially non-complexing medium; and
- the experimental method and numerical analysis are considered to have minimal systematic errors.

References that contain data rejected from our analyses are recorded in the footnotes to relevant tables. Reasons for rejection of specific references (indicated by superscripts) include:

- (a) data for temperature(s) other than 25 °C cannot be corrected to 25 °C, or the temperature is not defined;
- (b) data are for a different medium and are not readily comparable with other data;
- (c) ionic strength has not been held constant, or the medium composition has changed excessively, or inadequate allowance has been made for activity coefficient changes;
- (d) inadequate description of, or inappropriate, experimental method;
- (e) the equilibrium model is incomplete or inappropriate;
- (f) electrode calibration details are missing;
- (g) incomplete experimental data;
- (h) inadequate numerical analysis of measurement data;
- (i) inadequate correction for competing equilibria;
- (j) value(s) appear to be in error when compared with results from more than one other reliable laboratory;
- (k) values are inconsistent with other thermodynamic data;
- (l) measurements of historical interest only: superseded by subsequent work;
- (m) the reference does not contain any original data;
- (n) translation into English not available; and
- (o) predicted values.

APPENDIX 1B

Calculation of the interaction coefficients between Zn²⁺ and ClO₄⁻ and NO₃⁻

Specific ion interaction coefficients of electrolyte solutions can be determined from the ionic strength dependence of their osmotic and mean activity coefficients. Stokes and Levien [46STO] measured the osmotic and mean activity coefficients of both Zn perchlorate and Zn nitrate solutions between 0.1 and $4.4 \text{ mol}\cdot\text{kg}^{-1}$ and 0.1 and 6.5 mol $\cdot\text{kg}^{-1}$, respectively.

The mean activity coefficient of a 1:2 electrolyte solution using SIT can be expressed [2005GAM] by

$$\log_{10} \gamma_{\pm} = -\frac{2A\sqrt{I_m}}{1+1.5\sqrt{I_m}} + \frac{4}{9}\varepsilon(N^{2+}, X^{-})I_m$$
(A1.1)

and similarly, the osmotic coefficient is given by

$$\varphi = 1 - \frac{2A\ln(10)}{1.5^3 I_m} \left[1 + 1.5\sqrt{I_m} - \frac{1}{1 + 1.5\sqrt{I_m}} - 2\ln\left(1 + 1.5\sqrt{I_m}\right) \right] + \frac{2\ln(10)}{9} \varepsilon(N^{2+}, X^-)I_m \quad (A1.2)$$

where A is the Debye–Hückel parameter, I_m is the ionic strength, and in the particular case under consideration, N²⁺ is Zn²⁺, and X⁻ is either ClO₄⁻ or NO₃⁻.

The data measured by Stokes and Levien [46STO] for Zn perchlorate and Zn nitrate are listed in Table A1-1. Equations A1.1 and A1.2 have been used in conjunction with the data in Table A1-1 to determine the interaction coefficients ε (Zn²⁺,ClO₄⁻) and ε (Zn²⁺,NO₃⁻). The interaction coefficients are determined by plotting log₁₀ $\gamma_{\pm} + 2D$ against I_m . However, eqs. A1.1 and A1.2 can have limited validity, particularly at higher ionic strength [2005GAM]. To overcome issues associated with departure from linearity, the Zn perchlorate data were only utilised up to a concentration of 2 mol·kg⁻¹ (an ionic strength of 6 mol·kg⁻¹). All of the Zn nitrate data were utilised (up to an ionic strength of 19.5 mol·kg⁻¹). Figures A2-1 and A2-2 show the relationship between the ionic strength and log₁₀ $\gamma_{\pm} + 2D$ for the Zn perchlorate and Zn nitrate mean activity coefficient data [46STO].

From the slope obtained in Figs. A2-1 and A2-2, the interaction coefficients are calculated to be: $\varepsilon(Zn^{2+},ClO_4^{-}) = 0.351 \pm 0.005$ and $\varepsilon(Zn^{2+},NO_3^{-}) = 0.174 \pm 0.001$ where the uncertainties represent 95 % confidence intervals.

Figures A2-3 and A2-4 show the relationship between the ionic strength and the function $\phi - 1 + 2A \ln(10)[X - 1/X - 2\ln(X)]/1.5^3I_m$, where $X = 1 + 1.5I_m^{\frac{1}{2}}$ for the Zn perchlorate and Zn nitrate osmotic coefficient data [46STO]. According to SIT, eq. A1.2, this relationship should be linear with a slope of $2\ln(10) \epsilon(N^{2+},X^{-})/9$.

From the slope obtained in Figs. A2-3 and A2-4, the interaction coefficients are calculated to be: $\varepsilon(\text{Zn}^{2+},\text{ClO}_4^-) = 0.351 \pm 0.010$ and $\varepsilon(\text{Zn}^{2+},\text{NO}_3^-) = 0.176 \pm 0.002$ where the uncertainties represent 95 % confidence intervals. These values are in excellent agreement with the values determined from the mean activity coefficients.

On the basis of the ion interaction coefficient values determined from the mean activity and osmotic coefficient data, the following mean values are selected for the ion interaction values

$$\varepsilon$$
(Zn²⁺,ClO₄⁻) = 0.351 ± 0.010; and
 ε (Zn²⁺,NO₃⁻) = 0.175 ± 0.003

where the 95 % confidence intervals were selected to cover the span of values calculated from both the mean activity and osmotic coefficient data. Allowing for the difference in ionic radius of Zn^{2+} and Ni^{2+} [97GRE], the value for $\varepsilon(Zn^{2+},ClO_4^{-})$ is consistent with that determined recently for $\varepsilon(Ni^{2+},ClO_4^{-})$ [2005GAM], using the same technique.

Zn	n perchlorat	e	Z	n nitrate	
Molality mol•kg ⁻¹	φ	γ_{\pm}	Molality mol·kg ⁻¹	φ	γ_{\pm}
0.1	0.893	0.573	0.1	0.862	0.532
0.15	0.911	0.560	0.15	0.868	0.507
0.2	0.928	0.556	0.2	0.873	0.490
0.3	0.966	0.565	0.3	0.890	0.475
0.4	1.010	0.588	0.4	0.909	0.470
0.5	1.056	0.620	0.5	0.934	0.474
0.6	1.105	0.661	0.6	0.958	0.481
0.7	1.157	0.710	0.7	0.982	0.490
0.8	1.212	0.769	0.8	1.009	0.503
0.9	1.269	0.838	0.9	1.037	0.519
1.0	1.328	0.916	1.0	1.064	0.536
1.2	1.450	1.111	1.2	1.120	0.576
1.4	1.578	1.367	1.4	1.180	0.626
1.6	1.708	1.695	1.6	1.238	0.682
1.8	1.843	2.126	1.8	1.296	0.746
2.0	1.984	2.694	2.0	1.355	0.819
2.5	(2.363)	(5.11)	2.5	1.506	1.047
3.0	(2.742)	(9.88)	3.0	1.664	1.363
3.5	(3.128)	(19.58)	3.5	1.817	1.781
4.0	(3.506)	(38.9)	4.0	1.960	2.313
4.4	(3.808)	(67.8)	4.5	2.098	3.00
			5.0	2.238	3.90
			5.5	2.372	5.05
			6.0	2.500	6.50
			6.5	2.614	8.25

Table A1-1 Mean activity coefficient and osmotic coefficient data of Zn perchlorate and Zn nitrate solutions [46STO].¹

¹The data given in parentheses were not used in the calculation of the interaction coefficients.

APPENDIX 2



Graphical evaluations for the interaction coefficients between $\rm Zn^{2+}$ and $\rm CIO_4^-$ and $\rm NO_3^-$

Fig. A2-1 Determination of the ion interaction coefficient between Zn^{2+} and ClO_4^- from a plot of $\log_{10} \gamma_{\pm} + 2D$ against ionic strength using the mean activity coefficient data of $Zn(ClO_4)_2$ solutions from [46STO].



Fig. A2-2 Determination of the ion interaction coefficient between Zn^{2+} and NO_3^- from a plot of $\log_{10} \gamma_{\pm} + 2D$ against ionic strength using the mean activity coefficient data of $Zn(NO_3)_2$ solutions from [46STO].



Fig. A2-3 Determination of the ion interaction coefficient between Zn^{2+} and ClO_4^- from a plot of $\phi - 1 + 2Aln(10)[X - 1/X - 2ln(X)]/1.5^3I_m$, where $X = 1 + 1.5I_m^{-\frac{1}{2}}$, against ionic strength using the osmotic coefficient data of $Zn(ClO_4)_2$ solutions from [46STO].



Fig. A2-4 Determination of the ion interaction coefficient between Zn^{2+} and NO_3^- from a plot of $\phi - 1 + 2A\ln(10)[X - 1/X - 2\ln(X)]/1.5^3I_m$, where $X = 1 + 1.5I_m^{1/2}$, against ionic strength using the osmotic coefficient data of $Zn(NO_3)_2$ solutions from [46STO].

APPENDIX 3

Selected equilibrium constants

Experimental methods are indicated by: **act**: activity (e.g., cryoscopy); **emf**: measurement of galvanic cell potentials; **sol**: solubility determination; **gl**: pH measurement by glass electrode; **con**: conductivity; **ic**: ion chromatography; **ise**: measurement of cell potentials using an ion selective electrode; **cal**: calorimetry; **vlt**: voltammetry; **sp**: (UV-visible) spectrophotometry; **dis**: distribution between "immiscible" solvents; K(T): temperature dependence of equilibrium constant; $\Delta_{dij}H$: enthalpy of dilution.

Table A3-1 Selected equilibrium constants for the reaction: $Zn^{2+} + H_2O \rightleftharpoons ZnOH^+ + H^+$ at zero ionic strength and in NaClO₄ at various temperatures.

	Ionic stren	gth				
Method	Amount conc./mol·dm ⁻³	Molality/ mol·kg ⁻¹	t/°C	$\log_{10} *K_1$ (reported)	$\log_{10} *K_1$ (accepted) ¹	Ref. ²
gl	dil	0 corr	15	-9.30 ± 0.02	-9.30 ± 0.10	62PEb
gl	dil	0 corr	20	-9.15 ± 0.04	-9.15 ± 0.10	62PEb
gl	dil	0 corr	25	-8.96 ± 0.03	-8.96 ± 0.10	62PEb
gl	var.	0 corr	25		-8.86 ± 0.10	31PRa ³
gl	dil	0 corr	25	-9.05 ± 0.14	-9.05 ± 0.14	60DFa
gl	dil	0 corr	25	-9.00	-9.00 ± 0.10	97HAN
gl	dil	0 corr	30	-8.79 ± 0.03	-8.79 ± 0.10	62PEb
gl	dil	0 corr	36	-8.62 ± 0.03	-8.62 ± 0.10	62PEb
gl	dil	0 corr	42	-8.46 ± 0.03	-8.46 ± 0.10	62PEb
gl	dil	0 corr	50	-8.05	-8.05 ± 0.10	97HAN
gl	dil	0 corr	75	-7.60	-7.60 ± 0.10	97HAN
sol	0.03^{4}	0 corr	100	-6.88 ± 0.10	-6.88 ± 0.10	99BPa
sol	0.03^{4}	0 corr	150	-5.99 ± 0.10	-5.99 ± 0.10	99BPa
sol	0.03 ⁴	0 corr	150	-6.08 ± 0.05	-6.08 ± 0.10	2002BPb
sol	0.03^{4}	0 corr	200	-5.29 ± 0.10	-5.29 ± 0.10	99BPa
sol	0.03^{4}	0 corr	200	-5.34 ± 0.06	-5.34 ± 0.10	2002BPb
sol	0.03^{4}	0 corr	250	-4.74 ± 0.10	-4.74 ± 0.10	99BPa
sol	0.03^{4}	0 corr	250	-4.71 ± 0.05	-4.71 ± 0.10	2002BPb
sol	0.03^{4}	0 corr	300	-4.27 ± 0.10	-4.27 ± 0.10	99BPa
sol	0.03^{4}	0 corr	300	-4.15 ± 0.07	-4.15 ± 0.10	2002BPb
sol	0.034	0 corr	350	-3.61 ± 0.07^5	-3.61 ± 0.10	2002BPb
gl	2.0 NaClO_4	2.212	25	-9.55^{6}	-9.51 ± 0.10	61SCa
gl	2.0 NaClO ₄	2.212	25	-9.45^{7}	-9.41 ± 0.10	57KLE
gl	4.0 NaClO ₄	4.950	25	-9.59^{8}	-9.50 ± 0.10	57KLE

¹Constant converted from molar (amount concentration) to molal units and including our assigned errors (see Section 1). ²References for rejected data: [2004BDa]^{b,j}, [2004DTa]^{b,j}, [2002PLb]^{a,i,j}, [2001PSb]^j, [2000MSa]^{b,j}, [99PGa]^{a,j}, [99PPa]^{a,b,j}, [98MSe]^{b,j}, [97HAN], [95STa]^{a,j}, [95MIL]^j, [91MGb]^{a,b,j}, [87HBb]^{a,b}, [83YYa]^{d,j}, [78BYa]^j, [78NAa]^{b,j}, [77BGb]^a, [75RMb]^{h,j}, [74JAb]^{b,j}, [70CHc]^{a,b}, [69NIa]^{a,b}, [67GSd]^{d,j}, [65SCc]^b, [64SCb]^b, [59BEa]^a, [58ACa]^j, [53SPd]^{a,d}, [52CCa]^{a,b}, [51DAa]^{d,j}, [40BCa]^{a,d,j}, [39HAa]^{d,j}, [33JEa]^{a,c}, [31KKa]^d, [13KUa]^{a,j}, [10WOa]^{d,j}.

 3 Value at zero ionic strength calculated by this review from data in [31PRa] at low ionic strength in (Zn²⁺,H⁺)Cl media.

 4 ZnO(s) (zincite) solubility in $I_m = 0.03$ mol·dm⁻³ sodium triflate or NaOH, values corrected by authors to I = 0.

⁵Calculated from the $\log_{10} *K_{s1}$ value reported by [2002BPb] and a $\log_{10} *K_{s0}$ value calculated from the regression given in Fig. A4-14 at 350 °C.

⁶This constant was initially quoted as being for $Zn(OH)_2(aq)$ in [64SMa] but was corrected in an erratum in [71SMa] as being for ZnOH⁺. The IUPAC database still relates to the earlier species.

⁷Using a p K_w value in 2 mol·dm⁻³ NaClO₄ of 13.91.

⁸Using a pK_w value in 4 mol·dm⁻³ NaClO₄ of 14.33.

	Ionic stren	gth				
Method	Amount conc./mol·dm ⁻³	Molality/ mol·kg ⁻¹	t/°C	$\log_{10} *\beta_2$ (reported)	$\log_{10} *\beta_2$ (accepted) ¹	Ref. ²
vlt	dil	0 corr	20	-18.44^{3}	-18.44 ± 0.10	73BRd
sol	dil	0 corr	20	-18.17	-18.17 ± 0.10	92ZJa ⁴
sol	dil	0 corr	25	-17.84	-17.84 ± 0.10	92ZJa ⁴
sol	dil	0 corr	50	-16.35	-16.35 ± 0.10	92ZJa ⁴
sol	dil	0 corr	75	-15.11	-15.11 ± 0.10	92ZJa ⁴
sol	dil	0 corr	100	-14.06	-14.06 ± 0.10	92ZJa ⁴
sol	dil	0 corr	100	-14.08	-14.08 ± 0.10	75KEa
sol	dil	0 corr	150	-12.42	-12.42 ± 0.10	92ZJa ⁴
sol	dil	0 corr	150	-12.78	-12.78 ± 0.10	75KEa
sol	0.03^{5}	0 corr	150	-12.66 ± 0.07	-12.66 ± 0.10	2002BPb
sol	dil	0 corr	200	-11.20	-11.20 ± 0.10	92ZJa ⁴
sol	dil	0 corr	200	-11.54	-11.54 ± 0.10	75KEa
sol	0.03^{5}	0 corr	200	-11.24 ± 0.05	-11.24 ± 0.10	2002BPb
sol	dil	0 corr	250	-10.27	-10.27 ± 0.10	92ZJa ⁴
sol	0.03^{5}	0 corr	250	-10.20 ± 0.05	-10.20 ± 0.10	2002BPb
sol	dil	0 corr	275	-9.90	-9.90 ± 0.10	92ZJa ⁴
sol	0.03 ⁵	0 corr	300	-9.41 ± 0.07	-9.41 ± 0.10	2002BPb
sol	0.03 ⁵	0 corr	350	-8.79 ± 0.07^{6}	-8.79 ± 0.10	2002BPb

Table A3-2 Selected equilibrium constants for the reaction: $Zn^{2+} + 2H_2O \rightleftharpoons Zn(OH)_2(aq) + 2H^+$ at zero ionic strength.

¹Constant converted from molar (amount concentration) to molal units and including our assigned errors (see Section 1). ²References for rejected data: [59ASa]^{b,d}, [65SEb]^j, [67GSd]^{d,j}, [75RMb]^{h,j}, [76MTa]^a, [78NAa]^{b,j}, [83YYa]^{d,j}, [87FGa]^j, [88FSa]^j, [91MGb]^{a,b,j}, [98MSe]^{b,j}, [99BPa]^l, [99PPa]^{a,b,j}, [99PGa]^{a,j}, [2000MSa]^{b,j}, [2001PSb]^j, [2002PLb]^{a,i,j}, [2002HTc]^{a,b,j}, [2004BDa]^{b,j}, [2008FAR]^j.

³Using a pK_w value of 14.151.

⁴Calculated from the $\log_{10} *\beta_{s2}$ values reported by [92ZJa] and the $\log_{10} *K_{s0}$ values calculated in this review. ⁵ZnO(s) (zincite) solubility in $I_m = 0.03 \text{ mol} \cdot \text{dm}^{-3}$ sodium triflate or NaOH, values corrected by authors to I = 0.

⁶Calculated from the $\log_{10} * K_{s2}^{m}$ value reported by [2002BPb] and the $\log_{10} * K_{s0}$ value calculated from the regression given in Fig. A3-9 at 350 °C.

Table A3-3 Selected equilibrium constants for the reaction: $Zn^{2+} + 3H_2O \rightleftharpoons Zn(OH)_3^- + 3H^+$ at zero ionic strength and in NaClO₄ at various temperatures.

	Ionic strength					
Method	Amount conc./mol·dm ⁻³	Molality/ mol·kg ⁻¹	t/°C	$\log_{10} *\beta_3$ (reported)	$\frac{\log_{10} *\beta_3}{(\text{accepted})^1}$	Ref. ²
sol	none	0 corr	12.5	-29.42	-29.42 ± 0.10	75RMb
sol	dil	0 corr	20	-28.39	-28.39 ± 0.10	92ZJa ³
sol	dil	0 corr	25	-27.97	-27.97 ± 0.10	92ZJa ³
sol	dil	0 corr	25	-27.77^{4}	-27.77 ± 0.10	54FSb
sol	var.	0 corr	25	-28.34^{5}	-28.34 ± 0.10	54DPb
sol	none	0 corr	25	-28.12	-28.12 ± 0.10	75RMb
sol	none	0 corr	50	-25.80	-25.80 ± 0.10	75RMb
sol	dil	0 corr	50	-26.13	-26.13 ± 0.10	92ZJa ³
sol	dil	0 corr	75	-24.59	-24.59 ± 0.10	92ZJa ³
sol	none	0 corr	75	-24.19	-24.19 ± 0.10	75RMb
sol	dil	0 corr	100	-23.29	-23.29 ± 0.10	92ZJa ³
sol	0.036	0 corr	100	-23.08 ± 0.10	-23.08 ± 0.10	99BPa

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Pure Appl. Chem., Vol. 85, No. 12, pp. 2249-2311, 2013

	Ionic strength					
Method	Amount conc./mol·dm ⁻³	Molality/ mol·kg ⁻¹	t/°C	$\log_{10} *\beta_3$ (reported)	$\log_{10} *\beta_3$ (accepted) ¹	Ref. ²
sol	dil	0 corr	100	-23.29^{7}	-23.29 ± 0.10	75KEa
sol	dil	0 corr	150	-21.22	-21.22 ± 0.10	92ZJa ³
sol	0.036	0 corr	150	-21.17 ± 0.10	-21.17 ± 0.10	99BPa
sol	dil	0 corr	150	-21.16^{8}	-21.16 ± 0.10	75KEa
sol	0.036	0 corr	150	-21.17 ± 0.03	-21.17 ± 0.10	2002BPb
sol	dil	0 corr	200	-19.66	-19.66 ± 0.10	92ZJa ³
sol	0.036	0 corr	200	-19.64 ± 0.10	-19.64 ± 0.10	99BPa
sol	dil	0 corr	200	-19.35 ⁹	-19.35 ± 0.10	75KEa
sol	0.036	0 corr	200	-19.66 ± 0.03	-19.66 ± 0.10	2002BPb
sol	dil	0 corr	200	-19.68 ± 0.19^9	-19.68 ± 0.10	88PLY
sol	dil	0 corr	250	-18.46	-18.46 ± 0.10	92ZJa ³
sol	0.036	0 corr	250	-18.52 ± 0.10	-18.52 ± 0.10	99BPa
sol	0.036	0 corr	250	-18.60 ± 0.07	-18.60 ± 0.10	2002BPb
sol	dil	0 corr	250	-18.50 ± 0.16^{10}	-18.50 ± 0.10	88PLY
sol	dil	0 corr	275	-17.97	-17.97 ± 0.10	92ZJa ³
sol	0.036	0 corr	300	-17.69 ± 0.10	-17.69 ± 0.10	99BPa
sol	0.036	0 corr	300	-17.92 ± 0.11	-17.92 ± 0.10	2002BPb
sol	dil	0 corr	300	-17.60 ± 0.25^{11}	-17.60 ± 0.10	88PLY
sol	dil	0 corr	350	-17.04 ± 0.50^{12}	-17.04 ± 0.10	88PLY
sp	0.10 NaClO_4	0.101	25	-27.79 ± 0.004	-27.78 ± 0.10	2008FAR
dis	0.10 NaClO_4	0.101	25	-28.00^{13}	-27.99 ± 0.20	62BOa
gl	3.0 NaClO ₄	3.503	25	-28.83 ± 0.09	-28.74 ± 0.20	65SEb

Table A3-3 (Continued).

¹Constant converted from molar (amount concentration) to molal units and including our assigned errors (see Section 4). ²References for rejected data: [83YYa]^{d,j}, [67GSd]^{d,j}, [53VTa]^{a,b,d}, [50BQa]^{a,j}, [49KKa]^{a,b,d}.

³Calculated from the $\log_{10} * K_{s3}$ values reported by [92ZJa] and the $\log_{10} * K_{s0}$ values calculated in this review for ZnO(s). ⁴Using a p K_w of 14.00.

⁵Using a pK_w of 14.00 and the $\log_{10} * K_{s0}$ value determined in this review for ZnO(s).

⁶ZnO(s) (zincite) solubility in $I_m = 0.03$ mol·dm⁻³ sodium triflate or NaOH, values corrected by authors to I = 0.

⁷Using a pK_w value of 12.259.

⁸Using a pK_{w} value of 11.693.

⁹Using a pK_w value of 11.307.

¹⁰Using a pK_w value of 11.183.

¹¹Using a pK_{w} value of 11.323.

¹²Using a pK_w value of 11.464.

¹³Using a pK_w value of 13.89 and a correction from 20 to 25 °C using the temperature dependence of log $*\beta_3^{\circ}$ as determined in this review.

	Ionic strength					
Method	Amount conc./mol·dm ⁻³	Molality/ mol·kg ⁻¹	t/°C	$\log_{10} * \beta_4$ (reported)	$\log_{10} *\beta_4$ (accepted) ¹	Ref. ²
sol	none	0 corr	12.5	-42.15	-42.15 ± 0.10	75RMb
sol	dil	0 corr	20	-40.45	-40.45 ± 0.10	92ZJa ³
sol	dil	0 corr	25	-39.98	-39.98 ± 0.10	92ZJa ³
sol	dil	0 corr	25	-40.50^{4}	-40.50 ± 0.10	54FSb
sol	var.	0 corr	25	-40.7^{5}	-40.71 ± 0.10	54DPb
sol	none	0 corr	25	-40.43	-40.43 ± 0.10	75RMb
ise	dil	0 corr	25	-40.85	-40.85 ± 0.10	54DIa
sol	dil	0 corr	25	-40.56	-40.56 ± 0.10	27DJa
sol	none	0 corr	50	-37.59	-37.59 ± 0.10	75RMb
sol	dil	0 corr	50	-37.88	-37.88 ± 0.10	92ZJa ³
sol	dil	0 corr	75	-36.11	-36.11 ± 0.10	92ZJa ³
sol	none	0 corr	75	-35.39	-35.39 ± 0.10	75RMb
sol	dil	0 corr	100	-34.61	-34.61 ± 0.10	92ZJa ³
sol	dil	0 corr	100	-34.97^{6}	-34.97 ± 0.10	75KEa
sol	dil	0 corr	150	-32.21	-32.21 ± 0.10	92ZJa ³
sol	dil	0 corr	150	-32.56^{7}	-32.56 ± 0.10	75KEa
sol	dil	0 corr	200	-30.40	-30.40 ± 0.10	92ZJa ³
sol	dil	0 corr	200	-30.59^{8}	-30.59 ± 0.10	75KEa
sol	dil	0 corr	200	-30.71 ± 0.11^{8}	-30.71 ± 0.10	88PLY
sol	dil	0 corr	250	-28.99	-28.99 ± 0.10	92ZJa ³
sol	dil	0 corr	250	-29.27 ± 0.13^9	-29.27 ± 0.10	88PLY
sol	dil	0 corr	275	-28.41	-28.41 ± 0.10	92ZJa ³
sol	dil	0 corr	300	-28.59 ± 0.13^{10}	-28.59 ± 0.10	88PLY
sol	dil	0 corr	350	-28.13 ± 0.09^{11}	-28.13 ± 0.10	88PLY
sp	0.10 NaClO ₄	0.101	25	-39.61 ± 0.006	-39.60 ± 0.10	2008FAR
dis	3.0 NaClO ₄	3.503	25	-40.80 ± 0.05^{12}	-40.52 ± 0.10	87FGa
gl	3.0 NaClO ₄	3.503	25	-41.10 ± 0.05^{12}	-40.83 ± 0.10	88FSa

Table A3-4 Selected equilibrium constants for the reaction: $Zn^{2+} + 4H_2O \rightleftharpoons Zn(OH)_4^{2-} + 4H^+$ at zero ionic strength and in NaClO₄ at various temperatures.

¹Constant converted from molar (amount concentration) to molal units and including our assigned errors (see Section 4). ²References for rejected data: [2002PLb]^{a,i,j}, [83YYa]^{d,j}, [67GSd]^{d,j}, [65SEb]^j, [64SCb]^{b,e}, [59MAc]^b, [51STa]^{a,b}, [50BQa]^{a,j}, [49KKa]^{a,b,d}, [40SFa]^{a,b}, [12KLa]^{a,d}, [04KUa]^{a,b,d}.

³Calculated from the $\log_{10} * K_{s4}$ values reported by [92ZJa] and the $\log_{10} * K_{s0}$ values calculated in this review for ZnO(s). ⁴Using a pK_w of 14.00.

⁵Using a p K_w of 14.00 and the $\log_{10} *K_{s0}$ value determined in this review for ZnO(s).

⁶Using a pK_w value of 12.259.

⁷Using a pK_w value of 11.693.

⁸Using a pK_w value of 11.307. ⁹Using a pK_w value of 11.183. ¹⁰Using a pK_w value of 11.183.

¹¹Using a pK_w value of 11.464.

¹²Using a pK_w value of 14.05.

	Ionic strength					
Method	Amount conc./mol·dm ⁻³	Molality/ mol·kg ⁻¹	t/°C	$\log_{10} * \beta_{2,1}$ (reported)	$\log_{10} * \beta_{2,1}$ (accepted) ¹	Ref. ²
gl	2.0 NaCl	2.086	25	-7.49	-7.49 ± 0.10	64SCb
gl	3.0 NaCl	3.200	25	-7.50	-7.50 ± 0.10	65SCc
gl	3.0 KCl	3.311	25	-7.47	-7.47 ± 0.10	65SCc
gl	3.0 LiClO_4	3.482	25	-8.7	-8.70 ± 0.10	62BIE
gl	3.0 NaClO_4	3.503	25	-8.6	-8.60 ± 0.10	75ZGa
gl	3.0 NaClO ₄	3.503	25	-8.72	-8.72 ± 0.10	78BYa

Table A3-5 Selected equilibrium constants for the reaction: $2Zn^{2+} + H_2O \rightleftharpoons Zn_2OH^{3+} + H^+$ in NaCl, KCl, and NaClO₄ media at 25 °C.

¹Constant converted from molar (amount concentration) to molal units and including our assigned errors. ²References for rejected data: [69NIa]^{a,b} and [64SCb]^b.

Table A3-6 Selected equilibrium constants for the reaction: $Zn^{2+} + Cl^- \rightleftharpoons ZnCl^+$ in $NaClO_4 HClO_4$ and in $LiClO_4$ solutions at 25 °C.

	Ionic stren	gth				
Method	Amount conc./mol·dm ⁻³	Molality/ mol·kg ⁻¹	t/°C	$\log_{10} K_1$ (reported)	$\log_{10} K_1$ (accepted) ¹	Ref. ²
emf	0.5 NaClO ₄	0.5133	25	-0.35	-0.35 ± 0.20	44SLa
emf	1.0 LiClO_4	1.0496	25	-0.13 ± 0.02	-0.15 ± 0.10	75FCa
pol	2.0 NaClO_4	2.2124	25	-0.49	-0.54 ± 0.25	57KLa
emf	2.0 LiClO_4	2.2038	25	-0.17 ± 0.02	-0.21 ± 0.10	75FCa
emf	3.0 NaClO_4	3.5034	25	-0.19 ± 0.07	-0.25 ± 0.10	44SLa
pot	3.0 NaClO_4	3.5034	25	-0.10 ± 0.1	-0.17 ± 0.25	74ASb
emf	3.0 LiClO_4	3.4815	25	0 ± 0.03	-0.06 ± 0.10	75FCa
pot	3.0 HClO_4^3	3.0000	25	-0.22	-0.22 ± 0.20	75LTa
emf	3.0 NaClO_4	3.5034	25	0.20	0.14 ± 0.20	77SJe
ise	3.0 NaClO_4	3.5034	25	-0.19	-0.26 ± 0.10	79FKd
emf	3.5 NaClO_4	4.2000	25	0.25	0.17 ± 0.20	77SJe
emf	4.0 LiClO_4	4.9056	25	0.30 ± 0.04	0.21 ± 0.15	64MKc
pot	4.0 NaClO_4	4.9496	25	0.01 ± 0.2	0.01 ± 0.25	74ASb
emf	4.0 LiClO_4	4.9056	25	0.15 ± 0.01	0.06 ± 0.10	75FCa
emf	4.0 NaClO_{4}	4.9496	25	0.34	0.25 ± 0.20	77SJe
ise	4.0 NaClO_4^{+}	4.9496	25	0.10	0.01 ± 0.10	79FKd

¹Constant converted from molar (amount concentration) to molal units and including our assigned errors.

²References for rejected data: [56SLa]^j, [61SMc]^j, [69MAa]^j, [69GEa]^m, [72MSC]^a, [73HHb]^j, [74BLb]^d. [70FCa], [71FCb] are earlier studies of [75FCa]; the results are very similar or included in [75FCa]. Therefore, only the values of [75FCa] were used. ³Reported on the molality scale.

	Ionic strength					
Method	Amount conc./mol·dm ⁻³	Molality/ mol·kg ⁻¹	t/°C	$\log_{10} \beta_2$ (reported)	$\log_{10}\beta_2$ (accepted) ¹	Ref. ²
emf	1.0 LiClO ₄	1.0496	25	-0.27 ± 0.04	-0.31 ± 0.15	75FCa
pol	2.0 NaClO ₄	2.2124	25	0.02	-0.07 ± 0.25	57KLa
emf	2.0 LiClO_4	2.2038	25	-0.10 ± 0.03	-0.18 ± 0.15	75FCa
emf	3.0 NaClO_4	3.5034	25	-0.60 ± 0.4	-0.74 ± 0.40	44SLa
pot	3.0 NaClO ₄	3.5034	25	0.20 ± 0.1	0.07 ± 0.25	74ASb
emf	3.0 LiClO_4	3.4815	25	-0.12 ± 0.04	-0.25 ± 0.15	75FCa
ise	3.0 NaClO_4	3.5034	25	-0.19	-0.32 ± 0.15	79FKd
emf	4.0 LiClO_4	4.9056	25	0.0 ± 0.4	-0.18 ± 0.25	64MKc
pot	4.0 NaClO_4	4.9496	25	0.50 ± 0.2	0.31 ± 0.25	74ASb
emf	4.0 LiClO_4	4.9056	25	0.57 ± 0.02	0.39 ± 0.15	75FCa
ise	4.0 NaClO ₄	4.9496	25	0.06	-0.13 ± 0.15	79FKd
emf	5.0 NaClO_4^{-3}	5.00	25	0.57 ± 0.01	0.57 ± 0.25	88FSb

Table A3-7 Selected equilibrium constants for the reaction: $Zn^{2+} + 2Cl^{-} \rightleftharpoons ZnCl_{2(aq)}$ in $NaClO_4$ and $LiClO_4$ solutions at 25 °C.

¹Constant converted from molar (amount concentration) to molal units and including our assigned errors.

²References for rejected data: [56SLa]^j, [61SMc]^j, [69MAa]^j, [69GEa]^m. [70FCa], [71FCb] are earlier studies of [75FCa]; the results are very similar or included in [75FCa]. Therefore, only the values of [75FCa] were used.

³Reported on the molality scale.

Table A3-8 Selected equilibrium constants for the reaction: $Zn^{2+} + 3Cl^{-} \rightleftharpoons ZnCl_{3}^{-}$ in $NaClO_{4}$ and in $LiClO_{4}$ solutions at 25 °C.

	Ionic strength					
Method	Amount conc./mol·dm ⁻³	Molality/ mol·kg ⁻¹	t/°C	$\log_{10} \beta_3$ (reported)	$\log_{10}\beta_3$ (accepted) ¹	Ref. ²
pol	2.0 NaClO_4	2.2124	25	-0.07	-0.20 ± 0.40	57KLa
emf	3.0 NaClO ₄	3.5034	25	0.15 ± 0.09	-0.06 ± 0.30	44SLa
pot	3.0 NaClO_4	3.5034	25	0.10 ± 0.1	-0.10 ± 0.3	74ASb
emf	3.0 NaClO_4	3.5034	25	0.32	0.12 ± 0.40	77SJe
ise	3.0 NaClO_4	3.5034	25	-0.22	-0.42 ± 0.30	79FKd
emf	3.5 NaClO_4	4.20	25	0.50	0.27 ± 0.40	77SJe
pot	4.0 NaClO_4	4.9496	25	0.70 ± 0.3	0.42 ± 0.30	74ASb
emf	4.0 NaClO_4	4.9496	25	0.71	0.43 ± 0.40	77SJe
ise	4.0 NaClO_4	4.9496	25	0.23	-0.05 ± 0.30	79FKd

¹Constant converted from molar (amount concentration) to molal units and including our assigned errors.

²References for rejected data: [56SLa]^j, [61SMc]^j, [64MKc]^b, [69MAa]^j, [69GEa]^m, [75FCa]^b. [70FCa], [71FCb] are earlier studies of 75FCa; the results are very similar or included in 75FCa. Therefore, only the values of [75FCa] were used.

	Ionic streng	th				
Method	Amount conc./mol·dm ⁻³	Molality/ mol•kg ⁻¹	t/°C	log ₁₀ K (reported)	$\log_{10} K$ (accepted) ¹	Ref. ²
$\overline{Zn^{2+} + CC}$	$D_3^{2-} \rightleftharpoons \operatorname{ZnCO}_3(\operatorname{aq})(K_1)$)				
vlt	0.10 KNO ₃	0.101	25.0	3.9	3.9 ± 0.3	76BHa
dis	0.68 NaCl/NaHCO3	0.68	25.0	3.30 ± 0.08	3.38 ± 0.15	90SBa
$Zn^{2+} + 2C$	$O_3^{2-} \rightleftharpoons Zn(CO_3)_2^{2-}$	3 ₂)				
dis	0.68 NaCl/NaHCO3	0.68	25.0	5.3 ± 0.6	5.4 ± 0.6	90SBa
$Zn^{2+} + HC$	$CO_3^- \rightleftharpoons ZnHCO_3^+$					
gl	0 corr	0 corr	25.0	1.40 ± 0.02	1.40 ± 0.15	78RBa
dis	0.68 NaCl/NaHCO3	0.68	25.0	0.85 ± 0.04	0.93 ± 0.10	90SBa
gl	3.0 NaClO ₄	3.503	25.0		0.25 ± 0.10	85FGa
$2Zn^{2+} + C$	$O_3^{2-} \rightleftharpoons Zn_2(CO_3)^{2+}$					
gl	3.0 NaClO_4^2	3.503	25.0		4.04 ± 0.2	85FGa

Table A3-9 Selected equilibrium constants for the system $Zn^{2+} + H^+ + CO_3^{2-}$ in various media at 25 °C.

¹Constant corrected from molar to molal units and including our assigned errors. ²References for rejected data: [87FGa]^e, [84FCa]^m, [85EFa]^d, [95VPa]^{a,k}.

Table A3-10 Selected equilibrium constants for the reaction: $Zn^{2+} + SO_4^{2-} \rightleftharpoons ZnSO_4$ in perchlorate media.

	Ionic med					
Method	Amount conc./mol·dm ⁻³	Molality/ mol•kg ⁻¹	t/°C	$\log_{10} K_1$ (reported) ¹	$\log_{10} K_1$ $(\text{accepted})^2$	Ref. ³
recalc (con)	0 corr	0 corr	18	2.30 ± 0.05^4	2.30 ± 0.10	27DAb, 38DAa
recalc (act)	0 corr	0 corr	25	2.27 ± 0.05	2.27 ± 0.10	31COW, 38DAa
con	0 corr	0 corr	25	2.31 ± 0.05	2.31 ± 0.10	380Ga
recalc (con)	0 corr	0 corr	25	2.28 ± 0.01	2.31 ± 0.20	380Ga, 51WYa
act (cry)	0 corr	0 corr	0	2.3 $\pm 0.2^4$	2.3 ± 0.2	55BPb
recalc (con)	0 corr	0 corr	25	2.38	2.38 ± 0.20	380Ga, 55ROB
emf (H)	0 corr	0 corr	25	2.38 ± 0.01	2.38 ± 0.10	58NNa
con	0 corr	0 corr	25	2.28	2.28 ± 0.10	61PFa
oth ⁵	0 corr	0 corr	25	2.34	2.34 ± 0.20	67FPb
recalc (con)	0 corr	0 corr	25	2.33 ± 0.01	2.33 ± 0.05	380Ga, 71HPa
recalc (act,	0 corr	0 corr	25	2.30	2.30 ± 0.10	72PIa
$\Delta_{\rm dil}H$)						
con	0 corr	0 corr	25	2.217 ± 0.007	2.22 ± 0.10	76KAa
$\Delta_{\rm dil}H$	0 corr	0 corr	25	2.309 ± 0.001	2.31 ± 0.05	81WAC
recalc (con)	0 corr	0 corr	25	2.210 ± 0.003	2.21 ± 0.10	81YYa
con	0 corr	0 corr	25	2.28	2.28 ± 0.10	86SDa
con	0 corr	0 corr	25	2.35	2.35 ± 0.10	89ADa
ic ⁶	0 corr	0 corr	22	2.29 ± 0.04^4	2.29 ± 0.10	93JAN
sp ⁷	0 corr	0 corr	25	2.34 ± 0.02	2.34 ± 0.20	97CRc
con	0 corr	0 corr	25	2.299 ± 0.002	2.30 ± 0.05	2005BES
sol	0.10 NaTf ^{8,9}	0.1^{8}	20	2.6 ± 0.1^9	2.6 ± 0.3	98WBa
ise ¹⁰	0.50 LiClO_4	0.513	25	0.93 ± 0.04^{11}	0.92 ± 0.20	73FCa
ise ¹⁰	1.0 LiClO_4	1.050	25	0.89 ± 0.04^{11}	0.87 ± 0.20	73FCa, 75FCa
dis	1.0 NaClO_{4}	1.051	25	0.69	0.67 ± 0.10	74MSc
ise ¹⁰	2.0 LiClO_4	2.204	25	0.76 ± 0.02^{11}	0.72 ± 0.20	73FCa, 75FCa

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	Ionic medi	ium				
Method	Amount conc./mol·dm ⁻³	Molality/ mol•kg ⁻¹	t/°C	$\log_{10} K_1$ (reported) ¹	$\log_{10} K_1 \\ (\text{accepted})^2$	Ref. ³
ise ¹⁰	3.0 LiClO ₄	3.482	25	0.70 ± 0.01^{11}	0.63 ± 0.20	71FCb, 73FCa, 75FCa
cal ise ¹⁰	3.0 LiClO ₄ 4.0 LiClO ₄	3.482 4.906	25 25	$\begin{array}{r} 0.21 \ \pm 0.06 \\ 0.61 \ \pm 0.01 \end{array}$	0.14 ± 0.20 0.53 ± 0.20	74BRa 75FCa

Table A3-1	0 (Continued).
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¹Uncertainties as given by the original authors or calculated by the present reviewer from the spread of values given by the original authors.

²Constant converted from molar to molal units; errors assigned by present reviewer (see text).

³References containing rejected data: [12NFa]¹, [27DAb]¹, [39HAa]¹, [56FSa]^{d,g,h}, [56KEb]^{b,i}, [58KEa]^{b,i}, [59RRc]^b, [67HEb]ⁿ, [68PRd]^{h,j}, [68PRd]^{h,j}, [69BYB]ⁿ, [69GAR]ⁿ, [69HEa]ⁿ, [69HEa]^{a,j}, [69NPe]^{d,j}, [69SMd]^j, [70BBa]^{b,g}, [73FCa, $I \rightarrow 0$ value]^{e,h,j}, [73POa]ⁿ, [74NIK]^m, [76NIK]^j, [75TAa]^j, [75YYa]^{d,h,j}, [77STd]^j, [84HAY]^{d,e}, [87KOM]^{c,e,h}, [90WAa]^{j,n}, [91PRI]^{e,h}, [93SHE]^g, [95VPa]^{a,e,g}, [96PAR]^b, [99RUD]^{c,d,e}, [2004AZa]^{c,g,i,j}.

⁴Constant converted to 25 °C by present reviewer assuming $\Delta_r H_1 = 6.0 \text{ kJ} \cdot \text{mol}^{-1}$ (Table 4).

⁵Ultrasonic absorption + calculations.

⁶Ion chromatography.

⁷Spectrophotometry using competitive equilibria.

⁸NaTf – sodium triflate (NaO₃SCF₃).

⁹Molality units.

 10 Zn(Hg) electrode.

¹¹Listed values and uncertainties differ slightly between [71FCb], [73FCa], and [75FCa]; data at other temperatures given in [73FCa].

Table A3-11 Selected equilibrium constants for the reaction: $Zn^{2+} + 2SO_4^{2-} \rightleftharpoons Zn(SO_4)_2^{2-}$ in perchlorate media at 25 °C.

	Ionic med	ium					
Method	Amount conc./mol·dm ⁻³	Molality/ mol•kg ⁻¹	t/°C	$\log_{10}\beta_2$ (reported) ¹	$\log_{10}\beta_2$ (accepted) ²	Ref. ³	
recalc (act, $\Delta_{w}H$)	0 corr	0 corr	25	2.9 ⁴	2.9 ± 0.3	72PIa	
ise ⁷	$\rightarrow 0$	$\rightarrow 0$	25	3.10 ± 0.10^5	3.1 ± 0.3	73FCa	
ise ⁷	0.5 LiClO_4	0.513	25	$1.97 \pm 0.06^{5,6}$	2.0 ± 0.2	73FCa	
ise ⁷	1.0 LiClO_{4}	1.050	25	$1.23 \pm 0.04^{5,6}$	1.2 ± 0.2	73FCa, 75FCa	
dis	1.0 NaClO_{4}	1.051	25	1.48	1.5 ± 0.1	74MSc	
ise ⁷	$2.0 \text{ LiClO}_{4}^{-1}$	2.204	25	1.18 ± 0.02^5	1.1 ± 0.2	73FCa, 75FCa	
ise ⁷	3.0 LiClO_4	3.482	25	$0.69 \pm 0.05^{5,6}$	0.6 ± 0.2	71FCb, 73FCa, 75FCa	
ise ⁷	4.0 LiClO_4	4.906	25	0.88 ± 0.04^{6}	0.8 ± 0.3	75FCa	

¹Uncertainties are as given by the original authors or calculated by the present reviewer from the spread of values given in the original publication.

²Constant converted from molar to molal units; errors assigned by present reviewer (see text).

³References containing rejected data: [56FSa]^{g,h}, [56KEb]^{b,h,j}, [58KEa]^b, [59RRc]^b, [69GAR]^{e,h,j}, [87KOM]^{c,e,h}.

⁴Note that $\log_{10} \beta_2$ is incorrectly listed as 1.70 in [2010PET].

⁵Data at other temperatures are given in [73FCa].

⁶Listed values and uncertainties differ slightly between [71FCb], [73FCa], and [75FCa]; higher-order complexes (up to β_5) also reported but are rejected (see text).

⁷Zn(Hg) electrode.

	Ionic medium	n				
Method	Amount conc./mol·dm ⁻³	Molality/ mol·kg ⁻¹	t/°C	$\log_{10} K$ (reported)	$\log_{10} K$ (accepted) ¹	Ref.
$\overline{Zn^{2+} + H}$	$_{2}PO_{4}^{-} \rightleftharpoons ZnH_{2}PO_{4}^{+}$					
gl	0.15 KNO ₃	0.151	37	1.15 ± 0.15	1.2 ± 0.2	70CHa
gl, ise	3.0 NaClO_4	3.503	25	0.37 ± 0.04	0.4 ± 0.2	94IUa
	·	$\rightarrow 0$		0.9 ± 0.2^2		
$Zn^{2+} + 2H$	$H_2PO_4^- \rightleftharpoons Zn(H_2PO_4)_2(aq)$					
gl, ise	3.0 NaClO_4	3.503	25	1.10 ± 0.03	1.1 ± 0.2	94IUa
	4	$\rightarrow 0$		2.0 ± 0.2^2		
$Zn^{2+} + H$	$_{2}PO_{4}^{-} + HPO_{4}^{2-} \rightleftharpoons Zn(H_{2})$	PO₄)(HPO₄) ⁻				
gl	0.15 KNO_{3}	0.151	37	4.0 ± 0.6	4.0 ± 0.6	70CHa
gl, ise	3.0 NaClO_{4}	3.503	25	2.47 ± 0.3^3	2.5 ± 0.5	94IUa
	+	$\rightarrow 0$		4.0 ± 0.5^2		
$Zn^{2+} + H$	$PO_4^{2-} \rightleftharpoons ZnHPO_4(aq)$					
gl	0.1 NaClO_4	0.101	25	2.40 ± 0.05	2.4 ± 0.2	67SBc
gl	$0.15 \text{ KNO}_{3}^{-1}$	0.151	37	2.35 ± 0.15	2.4 ± 0.2	70CHa
gl	0.10 NaClO_4	0.101	25	2.4	2.4 ± 0.2	74RMa
vlt	$0.01 \text{ NaClO}_{4}^{-7} + 0-0.025$ mol·dm ⁻³ Na ₂ PO ₄	0.01-0.085	25	4.16 ± 0.03		95VPa
gl	0.10 NaNO ₃	0.101	25	2.52 ± 0.03	2.5 ± 0.2	96SSa
$Zn^{2+} + 2F$	$\operatorname{HPO}_4^{2-} \rightleftharpoons \operatorname{Zn}(\operatorname{HPO}_4)_2^{2-}$					
gl, ise	3.0 NaClO_4	3.503	25	6.29 ± 0.02^2		94IUa
-	7	$\rightarrow 0$		7.1 ± 0.2^3		
$Zn^{2+} + H$	$PO_4^{2-} + PO_4^{3-} \Longrightarrow Zn(HPO)$	4)(PO ₄) ³ -				
gl, ise	3.0 NaClO_{4}	3.503	25	11.38 ± 0.03^2		94IUa
2,	4	$\rightarrow 0$		12.5 ± 0.2^3		
$Zn^{2+} + 3F$	$4PO_4^{2-} \Longrightarrow Zn(HPO_4)_2^{4-}$					
gl	$\begin{array}{c} 0.01 \text{ NaClO}_4 + 0-0.025 \\ \text{mol} \cdot \text{dm}^{-3} \text{ Na}_2 \text{PO}_4 \end{array}$	0.01–0.085	25	7.36 ± 0.07		95VPa
Zn(OH) ₂ ($(aq) + HPO_4^{2-} \rightleftharpoons Zn(OH)_2$	HPO4 ^{2–}				
sol	$0.0005-0.05 \text{ mol} \cdot \text{dm}^{-3}$ Na ₂ HPO ₄		25	0.9 ± 0.25		92ZJa

Table A3-12 Selected stability constants for the system $Zn^{2+} + H^+ + PO_4^{-3-}$.

¹Constant corrected from molar to molal units and including our assigned errors.

²Extrapolated to $I_m = 0$ by the authors using SIT and estimated ion interaction coefficients.

³Recalculated by the reviewers using the protonation constants for phosphate ion reported for 3 mol·dm⁻³ NaClO₄ in [69BSd] $(\log_{10} K_1 = 10.85, \log_{10} K_2 = 6.27, \log_{10} K_3 = 1.89).$

	Ionic medi	um				
Method	Amount conc./mol·dm ⁻³	Molality/ mol•kg ⁻¹	t/°C	$\log_{10} * K_{s0}^{\circ}$ (reported)	$\frac{\log_{10} *K_{\rm s0}^{\circ}}{(\rm accepted)^1}$	Ref. ²
$\overline{ZnO(s) + 2}$	$2H^+ \rightleftharpoons Zn^{2+} + H_2O$					
sol, gl	var.	0 corr	25	11.11 ³	11.11 ± 0.10	50FHa
gl	var.	0 corr	25	11.00	11.00 ± 0.10	60BBa
oth	var.	0 corr	25	11.17 ± 0.03	11.17 ± 0.10	64SAa
sol	var.	0 corr.	50	9.99 ± 0.05	9.99 ± 0.10	98WBa
sol	var.	0 corr.	75	8.99 ⁴	8.99 ± 0.10	98WBa
sol	var.	0 corr.	100	8.12 ± 0.03	8.12 ± 0.10	98WBa
sol	dil	0 corr.	100	8.04 ⁵	8.04 ± 0.10	75KEa
sol	var.	0 corr.	150	6.68 ± 0.03	6.68 ± 0.10	98WBa
sol	dil	0 corr.	150	6.60^{6}	6.60 ± 0.10	75KEa
sol	var.	0 corr.	200	5.55 ± 0.03	5.55 ± 0.10	98WBa
sol	dil	0 corr.	200	5.267	5.26 ± 0.10	75KEa
sol	var.	0 corr.	250	4.64 ± 0.03	4.64 ± 0.10	98WBa
sol	var.	0 corr.	300	3.88 ± 0.04	3.88 ± 0.10	98WBa
oth	0.20 NaClO_4	0.202	25	11.39 ± 0.02	11.38 ± 0.04	64SAa
oth	0.20 KNO ₃	0.201	25	11.39 ± 0.02	11.39 ± 0.04	64SAa
vlt	0.10 KNO ₃	0.101	25	11.23 ± 0.07	11.23 ± 0.10	58COb
ε-Zn(OH) ₂	$h(s) + 2H^+ \rightleftharpoons Zn^{2+} +$	2H,O				
sol	var.	0 corr	12.5	12.03	12.03 ± 0.10	75RMb
oth	var.	0 corr	25	11.53 ± 0.03	11.53 ± 0.10	64SAa
sol	var.	0 corr	25	11.24	11.24 ± 0.10	75RMb
ise	dil	0 corr	25	11.58	11.58 ± 0.10	72DSb
ise	dil	0 corr	50	9.93	9.93 ± 0.10	75RMb
ise	dil	0 corr	75	8.92	8.92 ± 0.10	75RMb
oth	0.20 NaClO_4	0.202	25	11.75 ± 0.02	11.74 ± 0.04	64SAa
oth	0.20 KNO ₃	0.201	25	11.75 ± 0.02	11.75 ± 0.04	64SAa
sol	0.20 KNO_3	0.201	25	11.72 ± 0.02	11.72 ± 0.04	63PEa
β_1 -Zn(OH	$)_{2}(s) + 2H^{+} \rightleftharpoons Zn^{2+} -$	+ 2H ₂ O				
oth	0.20 NaClO ₄	0.202	25	11.98 ± 0.02	11.97 ± 0.04	64SAa
oth	0.20 KNO ₃	0.201	25	11.98 ± 0.02	11.98 ± 0.04	64SAa
β ₂ -Zn(OH	$(s)_{2}(s) + 2H^{+} \rightleftharpoons Zn^{2+} -$	+ 2H ₂ O				
oth	0.20 NaClO ₄	0.202	25	12.02 ± 0.02	12.01 ± 0.04	64SAa
oth	0.20 KNO ₂	0.201	25	12.02 ± 0.02	12.02 ± 0.04	64SAa
γ-Zn(OH)	$r_{s}(s) + 2H^{+} \rightleftharpoons Zn^{2+} +$	2H ₂ O				
oth	0.20 NaClO	0.202	25	11.96 ± 0.02	11.95 ± 0.04	64SAa
oth	0.20 KNO_{2}^{4}	0.201	25	11.96 ± 0.02	11.96 ± 0.04	64SAa
δ.Zn(OH)	$(s) + 2H^+ \rightarrow Zn^{2+} +$	2H.O				
oth	0.20 NaClO.	0.202	25	12.07 ± 0.02	12.06 ± 0.04	64SAa
oth	0.20 KNO_{2}	0.201	25	12.07 ± 0.02 12.07 ± 0.02	12.07 ± 0.04	64SAa
	0.20 11103	0.201		12.07 ± 0.02	12.07 ± 0.01	010/10

Table A3-13 Selected solubility constant data for zinc oxide, ZnO(s), and various forms of zinc hydroxide, $Zn(OH)_2(s)$.

¹Constant corrected from molar to molal units and including our assigned errors.

²References for rejected data: [97HAN], [71PPd], [68GSd], [68SMf], [67GSd], [58ASd], [54DOa], [53SPd], [53VTa],

[50AFa], [39HAa], [38OKa], [31KKa], [31PRa], [25WIa], [23HEa], [00HEa].

³As reported in [53FIE].

⁴Reported in [2002BPb].

⁵Using a pK_w value of 12.259.

⁶Using a pK_{w} value of 11.693.

⁷Using a pK_w value of 11.307.

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Pure Appl. Chem., Vol. 85, No. 12, pp. 2249-2311, 2013

	Ionic medi	um				
Method	Amount conc./mol·dm ⁻³	Molality/ mol•kg ⁻¹	t/°C	$\frac{\log_{10} * K_{\rm ps0}}{\rm (reported)}$	$\log_{10} * K_{ps0}$ (accepted) ¹	Ref. ²
ZnCO ₂ (s)	$+ 2H^+ \Longrightarrow Zn^{2+} + CO$	$a(g) + H_2O$				
el	0.20 NaClO	0.202	25.0	7.574 ± 0.023	7.57 ± 0.10	69SRa
gl	1.0 NaClO_4^3	1.00	25.0	7.501	7.50 ± 0.05	2000PKa
gl	$1.0 \text{ NaClO}_{4}^{43}$	1.00	25.0	7.578	7.58 ± 0.05	2000PKa
gl	$1.0 \text{ NaClO}_{4}^{43}$	1.00	25.0	7.493	7.49 ± 0.05	2000PKa
gl	$1.0 \text{ NaClO}_{4}^{43}$	1.00	25.0	7.570	7.57 ± 0.05	2000PKa
gl	$2.0 \text{ NaClO}_{4}^{3}$	2.00	25.0	7.528	7.53 ± 0.05	2000PKa
gl	$2.0 \text{ NaClO}_{4}^{3}$	2.00	25.0	7.484	7.48 ± 0.05	2000PKa
gl	$3.0 \text{ NaClO}_{4}^{3}$	3.00	25.0	7.448	7.45 ± 0.05	2000PKa
gl	$3.0 \text{ NaClO}_{4}^{3}$	3.00	25.0	7.466	7.47 ± 0.05	2000PKa
gl	$1.0 \text{ NaClO}_{4}^{3}$	1.00	15.0	7.600	7.60 ± 0.05	2000PKa
gl	$1.0 \text{ NaClO}_{4}^{3}$	1.00	15.0	7.588	7.59 ± 0.05	2000PKa
gl	$1.0 \text{ NaClO}_{4}^{3}$	1.00	30.0	7.474	7.47 ± 0.05	2000PKa
gl	$1.0 \text{ NaClO}_{4}^{3}$	1.00	30.0	7.473	7.47 ± 0.05	2000PKa
gl	$1.0 \text{ NaClO}_{4}^{3}$	1.00	37.5	7.532	7.53 ± 0.05	2000PKa
gl	$1.0 \text{ NaClO}_{4}^{3}$	1.00	37.5	7.573	7.57 ± 0.05	2000PKa
gl	$1.0 \text{ NaClO}_{4}^{3}$	1.00	37.5	7.612	7.61 ± 0.05	2000PKa
gl	$1.0 \text{ NaClO}_{4}^{3}$	1.00	37.5	7.522	7.52 ± 0.05	2000PKa
gl	$1.0 \text{ NaClO}_{4}^{3}$	1.00	37.5	7.513	7.51 ± 0.05	2000PKa
gl	$1.0 \text{ NaClO}_{4}^{3}$	1.00	40.0	7.511	7.51 ± 0.05	2000PKa
gl	$1.0 \text{ NaClO}_{4}^{3}$	1.00	40.0	7.484	7.48 ± 0.05	2000PKa
gl	$1.0 \text{ NaClO}_{4}^{3}$	1.00	50.0	7.507	7.51 ± 0.05	2000PKa
gl	$1.0 \text{ NaClO}_{4}^{3}$	1.00	50.0	7.450	7.45 ± 0.05	2000PKa
gl	$1.0 \text{ NaClO}_{4}^{3}$	1.00	50.0	7.515	7.52 ± 0.05	2000PKa
gl	1.0 NaClO_4^{3}	1.00	50.0	7.440	7.44 ± 0.05	2000PKa
gl	$1.0 \text{ NaClO}_{4}^{3}$	1.00	65.0	7.419	7.42 ± 0.05	2000PKa
gl	1.0 NaClO_4^{3}	1.00	65.0	7.298	7.30 ± 0.05	2000PKa
gl	1.0 NaClO_4^{3}	1.00	65.0	7.307	7.31 ± 0.05	2000PKa
gl	1.0 NaClO_4^3	1.00	65.0	7.343	7.34 ± 0.05	2000PKa
0.27n (OF	$\frac{1}{10}$ (CO ₁) (s) + 2H ⁺ -	$-7n^{2+} + 0.4CC$). (a) ± 1 6]	0.6		
ol	0.20 NaClO_4	0.202	25.0	9.42 ± 0.04	9.41 ± 0.05	69SRa
8- 9]	1.0 NaClO_4	1.0	25.0	9.29 ³	9.29 ± 0.10	2001PRE
9]	2.0 NaClO_4	2.0	25.0	9.34 ³	9.34 ± 0.10	2001PRE
8- 9]	3.0 NaClO_4	3.0	25.0	9.33 ³	9.33 ± 0.10	2001PRE
51 0]	1.0 NaClO_4	1.0	15.0	9.54^3	9.54 ± 0.10	2001PRE
5- g]	1.0 NaClO_4	1.0	30.0	9.15 ³	9.15 ± 0.10	2001PRE
0- 0]	1.0 NaClO_4	1.0	37.5	9.043	9.29 ± 0.20	2001PRE
0- g]	1.0 NaClO_4	1.0	40.0	8.91 ³	8.91 ± 0.10	2001PRE
0- g]	1.0 NaClO_4	1.0	50.0	8.66 ³	8.66 ± 0.20	2001PRE
g	1.0 NaClO ₄	1.0	65.0	8.29 ³	8.29 ± 0.10	2001PRE

Table A3-14 Selected solubility constant data for the system $Zn^{2+} + H^+ + CO_3^{2-}$ in NaClO₄ media at various temperatures.

¹Constant corrected from molar to molal units and including our assigned errors.

²References for rejected data: [11AVa]¹, [18SMa]^h, [35KAa]^m, [52SAa]^{a,e,n}, [69HEa]^m.

³Reported on the molality scale.

	Ionic m	edium						
Method	Amount conc./ mol·dm ⁻³	Molality/ mol•kg ⁻¹	t/°C	$\Delta_r H/kJ \cdot mol^{-1}$ (reported) ¹	$\Delta_r H/$ kJ·mol ⁻¹ (accepted) ²	$\frac{\Delta_r S}{J \cdot K^{-1} \cdot \text{mol}^{-1}}$ (reported) ¹	$\Delta_r S/$ J·K ⁻¹ ·mol ⁻¹ (accepted) ²	Ref. ³
$\overline{Zn^{2+} + Sc}$	$D_4^{2-} \rightarrow ZnSO_4$	4(aq) (K1)						
cal ⁴	0 corr	0 corr	25	5.7 ± 0.8	5.7 ± 1.0	64 ± 2	64 ± 5	70LAe
cal ⁵	0 corr	0 corr	25	6.7 ± 0.1	6.7 ± 0.5			73HPa
cal ⁵	0 corr	0 corr	25	5.6 ± 0.4	5.6 ± 1.0			73AUS,
								73HPa
recalc ⁶	0 corr	0 corr	25	6.4 ± 0.2	6.4 ± 0.5			73POa
cal ⁷	0 corr	0 corr	25	6.20 ± 0.01^8	6.2 ± 0.1	65 ± 1^8	65 ± 1	81WAC
$K(T)^9$	0 corr	0 corr	25	6.6 ± 0.1^8	6.6 ± 1.0	65 ± 1^8	65 ± 5	81YYa
$K(T)^{10}$	0 corr	0 corr	25	5.05	5.1 ± 1.0	61	61 ± 5	2005BES
$K(T)^{11}$	0.5 LiClO ₄	0.513	25	4.3^{12}	4.3 ± 2.0	$30^{12,13}$	30 ± 10	73FC
$K(T)^{11}$	1.0 LiClO_4	1.050	25	3.5^{12}	3.5 ± 2.0	$26^{12,13}$	26 ± 10	73FCa
$K(T)^{11}$	2.0 LiClO_4	2.204	25	2.0^{12}	2.0 ± 2.0	$20^{12,13}$	20 ± 10	73FCa
$K(T)^{11}$	3.0 LiClO ₄	3.482	25	0.8^{12}	0.8 ± 2.0	7 ^{12,13}	7 ± 10	73FCa
cal ⁵	3.0 LiClO_4	3.482	25	3.0 ± 0.1	3.0 ± 2.0	15	15 ± 10	74BRa

Table A3-15 Selected reaction enthalpies and entropies for the formation of $ZnSO_4(aq)$ at 25 °C.

¹Reported values with the present reviewer's assigned uncertainties.

²Reported values or as calculated by the present reviewer.

³Rejected data: [58NNa, 59NNa]^j, [67HEb]^{k,n}, [69IEa]^{h,j}, [73FCa, $I \rightarrow 0$ value]^j, [76KAa]^j, [78ARa]^{b,j}, [69NPe]^k, [89ADa]^j. ⁴Recalculation using $\Delta_{dil}H$ data from various literature sources.

⁵Titration calorimetry using independently determined K_1 .

⁶Various recalculations of earlier calorimetric data, using independently determined K_1 .

⁷Using $\Delta_{dil}H$ data.

⁸Reported value and uncertainty rounded up by present reviewer.

⁹Using conductometric data from 0–45 °C.

¹⁰Using conductometric data from 5–35 °C.

¹¹Using potentiometric data from 15–65 °C.

¹²Estimated by present reviewer from graphical data in [73FCa].

 $^{13}\Delta_r S$ values in [73FCa] are incorrectly labeled as negative.

Table A3-16 Reaction	enthalpies and	entropies for th	ne formation of	of $Zn(SO_4)_2^{2-}$	at 25 °C.1
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	Ionic m	edium						
Method	Amount conc./ mol·dm ⁻³	Molality/ mol•kg ⁻¹	t/°C	$\Delta_r H/kJ \cdot mol^{-1}$ (reported) ¹	$\Delta_r H/kJ \cdot mol^{-1}$ (accepted) ²	$\frac{\Delta_r S}{J \cdot K^{-1} \cdot \text{mol}^{-1}}$ (reported) ^{1,3}	$\frac{\Delta_r S}{J \cdot K^{-1} \cdot mol^{-1}}$ (accepted) ²	Ref.
$\overline{Zn^{2+}+2s}$	$\mathrm{SO_4^{2-} \rightarrow Zn(S)}$	$O_4)_2^{2-}(\beta_2)$						
K(T)	$\rightarrow 0$	$\rightarrow 0$	25	9.8	10 ± 5	86	86 ± 20	73FCa
K(T)	0.5 LiClO_4	0.513	25	3.1	3.1 ± 2.5	45	45 ± 15	73FCa
K(T)	1.0 LiClO_4	1.050	25	2.8	2.8 ± 2.5	33	33 ± 15	73FCa
K(T)	2.0 LiClO_4	2.204	25	2.0	2.0 ± 2.5	23	23 ± 15	73FCa
K(T)	3.0 LiClO ₄	3.482	25	0.8	0.8 ± 2.5	11	11 ± 15	73FCa

¹Estimated by the present reviewer from graphical data in [73FCa] based on potentiometric measurements from 15–65 °C; uncertainties not given in original paper.

²Reported values with the present reviewer's assigned uncertainties.

 ${}^{3}\Delta_{r}S$ values are incorrectly labeled as negative in [73FCa].

APPENDIX 4

SIT plots and van't Hoff plots for Zn²⁺ + L systems



Fig. A4-1 Plot of $\log_{10} *K_1$ for reaction 4 (ZnOH⁺) against the inverse of thermodynamic temperature, using selected data for perchlorate media (Table A3-1). The slope of the regression line is $-(\Delta_r H^o/\ln(10)R)$ and the intercept ($\Delta_r S^o/\ln(10)R$).



Fig. A4-2 Extrapolation to $I_m = 0 \mod kg^{-1} \operatorname{of} \Delta(\log_{10} * K_1) + 2D - \log_{10} a(H_2O)$ for reaction 4 using selected data for perchlorate media, 25 °C (Table A3-1). $\Delta(\log_{10} * K_1) = \log_{10} * K_1 - \log_{10} * K_1^{\circ}$, with the value of $\log_{10} * K_1^{\circ}$ fixed in the regression at -8.96 ± 0.05 . The regression is therefore constrained to pass through the origin.

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Fig. A4-3 Plot of $\log_{10} *\beta_2$ for reaction 5 (Zn(OH)₂(aq)) against the inverse of thermodynamic temperature, using selected data for perchlorate media (Table A3-2).



Fig. A4-4 Plot of $\log_{10} *\beta_3$ for reaction 6 (Zn(OH)₃⁻) against the inverse of thermodynamic temperature, using selected data for perchlorate media (Table A3-3).



Fig. A4-5 Extrapolation to $I_m = 0 \text{ mol} \cdot \text{kg}^{-1}$ of $\Delta(\log_{10} *\beta_3) - 3\log_{10} a(\text{H}_2\text{O})$ for reaction 6 using selected data for perchlorate media, 25 °C (Table A3-3). $\Delta(\log_{10} *\beta_3) = \log_{10} *\beta_3 - \log_{10} *\beta_3^\circ$, with the value of $\log_{10} *\beta_3^\circ$ fixed in the regression at -28.05 ± 0.06 . The regression is therefore constrained to pass through the origin.



Fig. A4-6 Plot of $\log_{10} *\beta_4$ for reaction 7 (Zn(OH)₄²⁻) against the inverse of thermodynamic temperature, using selected data for perchlorate media (Table A3-4).



Fig. A4-7 Extrapolation to $I_m = 0 \text{ mol} \cdot \text{kg}^{-1}$ of $\Delta(\log_{10} *\beta_4) - 4\log_{10} a(\text{H}_2\text{O})$ for reaction 7 using selected data for perchlorate media, 25 °C (Table A3-4). $\Delta(\log_{10} *\beta_4) = \log_{10} *\beta_4 - 4D - \log_{10} *\beta_4^\circ$, with the value of $\log_{10} *\beta_4^\circ$ fixed in the regression at -40.41 ± 0.12 . The regression is therefore constrained to pass through the origin.



Fig. A4-8 Extrapolation to $I_m = 0 \text{ mol} \cdot \text{kg}^{-1}$ of $\log_{10} K_1 - \Delta(z^2)D$ for reaction 9 ($\Delta(z^2) = -4$) using selected data for perchlorate media, 25 °C (Table A3-6).



Fig. A4-9 Extrapolation to $I_m = 0 \text{ mol} \cdot \text{kg}^{-1}$ of $\log_{10} \beta_2 - \Delta(z^2)D$ for reaction 10 ($\Delta(z^2) = -6$) using selected data for perchlorate media, 25 °C (Table A3-7).



Fig. A4-10 Extrapolation to $I_m = 0 \text{ mol} \cdot \text{kg}^{-1}$ of $\log_{10} \beta_3 - \Delta(z^2)D$ for reaction 11 ($\Delta(z^2) = -6$) using selected data for perchlorate media, 25 °C (Table A3-8).



Fig. A4-11 Extrapolation to $I_m = 0 \text{ mol} \cdot \text{kg}^{-1}$ of $\log_{10} K - \Delta(z^2)D$ for reaction 15 ($\Delta(z^2) = -4$) using selected data for NaClO₄ and NaCl/NaHCO₃ media, 25 °C (Table A3-9).



Fig. A4-12 Extrapolation to $I_m = 0 \text{ mol} \cdot \text{kg}^{-1}$ of $\Delta(\log_{10} K_1) + 8D$ for reaction 20 using selected data for lithium perchlorate media, 25 °C (Table A3-10). $\Delta(\log_{10} K_1) = \log_{10} K_1 - \log_{10} K_1^\circ$, with the value of $\log_{10} K_1^\circ$ fixed in the regression at 2.304 ± 0.042. The regression is therefore constrained to pass through the origin.



Fig. A4-13 Extrapolation to $I_m = 0 \text{ mol} \cdot \text{kg}^{-1}$ of $\log_{10} \beta_2 + 8D$ for reaction 21 using selected data for lithium perchlorate media, 25 °C (Table A3-11).



Fig. A4-14 Plot of $\log_{10} *K_{s0}$ for reaction 24 against the inverse of thermodynamic temperature, using selected data for perchlorate media, $I_m = 1.0 \text{ mol} \cdot \text{kg}^{-1}$ (Table A3-13). The slope of the regression line is $-(\Delta_r H^o/\ln(10)R)$ and the intercept $(\Delta_r S^o/\ln(10)R)$.



Fig. A4-15 Plot of $\log_{10} *K_{s0}$ for reaction 25 (ε -Zn(OH)₂(s)) against the inverse of thermodynamic temperature, using selected data for perchlorate media (Table A3-13). The slope of the regression line is $-(\Delta_r H^{\circ}/\ln(10)R)$ and the intercept ($\Delta r S^{\circ}/\ln(10)R$).



Fig. A4-16 Extrapolation to $I_m = 0 \text{ mol} \cdot \text{kg}^{-1}$ of $\log_{10} * K_{\text{ps0}} - \Delta(z^2)D$ for reaction 26 using selected data for NaClO₄ media, 25 °C (Table A3-14).



Fig. A4-17 Extrapolation to $I_m = 0 \text{ mol} \cdot \text{kg}^{-1}$ of $\log_{10} * K_{\text{ps0}} - \Delta(z^2)D + 1.6\log_{10} a_W$ for reaction 28 using selected data for NaClO₄ media, 25 °C (Table A3-14).



Fig. A4-18 Plot of $\log_{10} * K_{ps0}$ for reaction 26 against the inverse of thermodynamic temperature, using selected data for perchlorate media (Table A3-14). The slope of the regression line is $-(\Delta_r H^o/\ln(10)R)$, and the intercept $(\Delta_r S^o/\ln(10)R)$.



Fig. A4-19 Extrapolation to $I_m = 0 \text{ mol} \cdot \text{kg}^{-1}$ of $\Delta_r H$ for reaction 20 in LiClO₄ solutions containing varying and significant proportions of Cl⁻.