

## Chemical speciation of environmentally significant metals with inorganic ligands. Part 4: The Cd<sup>2+</sup> + OH<sup>-</sup>, Cl<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, and PO<sub>4</sub><sup>3-</sup> systems (IUPAC Technical Report)\*

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**Abstract:** The numerical modeling of Cd<sup>II</sup> speciation amongst the environmental inorganic ligands Cl<sup>-</sup>, OH<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, and PO<sub>4</sub><sup>3-</sup> 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  $\log_{10} \beta_{p,q,r}^{\circ}$  valid at  $I_m = 0$  mol kg<sup>-1</sup> and 25 °C (298.15 K), along with the equations and empirical reaction ion interaction coefficients,  $\Delta\epsilon$ , required to calculate  $\log_{10} \beta_{p,q,r}$  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. Unfortunately, with the exception of the Cd<sup>II</sup>-chlorido system and (at low ionic strengths) the Cd<sup>II</sup>-sulfato system, the equilibrium reactions for the title systems are relatively poorly characterized.

In weakly acidic fresh water systems ( $-\log_{10} \{[\text{H}^+]/c^{\circ}\} < 6$ ), in the absence of organic ligands (e.g., humic substances), Cd<sup>II</sup> speciation is dominated by Cd<sup>2+</sup>(aq), with CdSO<sub>4</sub>(aq) as a minor species. In this respect, Cd<sup>II</sup> is similar to Cu<sup>II</sup> [2007PBa] and Pb<sup>II</sup> [2009PBa]. However, in weakly alkaline fresh water solutions,  $7.5 < -\log_{10} \{[\text{H}^+]/c^{\circ}\} < 8.6$ , the speciation of Cd<sup>II</sup> is still dominated by Cd<sup>2+</sup>(aq), whereas for Cu<sup>II</sup> [2007PBa] and Pb<sup>II</sup> [2009PBa] the carbonato- species MCO<sub>3</sub>(aq) dominates. In weakly acidic saline systems ( $-\log_{10} \{[\text{H}^+]/c^{\circ}\} < 6$ ;  $-\log_{10} \{[\text{Cl}^-]/c^{\circ}\} < 2.0$ ) the speciation is dominated by CdCl<sub>*n*</sub><sup>(2-*n*)+</sup> complexes, (*n* = 1–3), with Cd<sup>2+</sup>(aq) as a minor species. This is qualitatively similar to the situation for Cu<sup>II</sup> and Pb<sup>II</sup>. However, in weakly alkaline saline solutions, including seawater, the chlorido- complexes still dominate the speciation of Cd<sup>II</sup> because of the relatively low stability of CdCO<sub>3</sub>(aq). In contrast, the speciation of Cu<sup>II</sup> [2007PBa] and Pb<sup>II</sup> [2009PBa] in seawater is dominated by the respective species MCO<sub>3</sub>(aq).

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There is scope for additional high-quality measurements in the  $\text{Cd}^{2+} + \text{H}^+ + \text{CO}_3^{2-}$  system as the large uncertainties in the stability constants for the  $\text{Cd}^{2+}$ -carbonato complexes significantly affect the speciation calculations.

*Keywords:* chemical speciation; cadmium; environmental systems; IUPAC Analytical Chemistry Division; ligands; stability constants.

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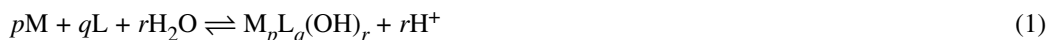
SIT plots for  $\text{Cd}^{2+} + \text{L}$  systems**1. INTRODUCTION**

This review is the fourth 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  $\text{Cd}^{2+}$  with the major inorganic ligands present in environmental systems:  $\text{Cl}^-$ ,  $\text{OH}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ , and  $\text{PO}_4^{3-}$ . The previous reviews in this series were on the  $\text{Hg}^{2+}$  [2005PBa],  $\text{Cu}^{2+}$  [2007PBa], and  $\text{Pb}^{2+}$  [2009PBa] complexation reactions with these ligands. The protonation\* reactions of  $\text{CO}_3^{2-}$  and  $\text{PO}_4^{3-}$  were also reviewed [2005PBa].

The final review will evaluate the equilibrium reactions of the same ligands with  $\text{Zn}^{2+}$ . 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 reader is referred to the earlier reviews in this series [2005PBa, 2007PBa, 2009PBa] 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.,  $\beta_{p,q,r}$ ,  $^*\beta_{p,q,r}^\circ$ ,  $K_n$ , and  $^*K_n$  (Appendix 1A in [2005PBa]), (ii) the principles of the Brønsted–Guggenheim–Scatchard specific ion interaction theory (SIT) [97GRE] and (iii) the application of SIT to the determination of standard equilibrium constants,  $\beta_{p,q,r}^\circ$ , valid at  $I_m = 0 \text{ mol kg}^{-1}$  (infinite dilution).

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



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

$$\log_{10} \beta_{p,q,r} - \Delta z^2 D - r \log_{10} a(\text{H}_2\text{O}) = \log_{10} \beta_{p,q,r}^\circ - \Delta \varepsilon I_m \quad (2)$$

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

In this equation,  $\Delta z^2$  is defined by

$$\Delta z^2 = (pz_M + qz_L - r)^2 + r - p(z_M)^2 - q(z_L)^2$$

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

$$\begin{aligned} \log_{10} \gamma_m(i) &= -z_i^2 A \sqrt{I_m} (1 + a_j B \sqrt{I_m})^{-1} + \sum_k \varepsilon(i,k) m_k \\ &= -z_i^2 D + \sum_k \varepsilon(i,k) m_k \end{aligned} \quad (3)$$

in which  $k$  represents the “swamping” electrolyte ions  $N^+$  or  $X^-$ ,  $\varepsilon(i,k)$  is the aqueous species interaction (SIT) coefficient for short-range interactions between ions  $i$  and  $k$ , and  $\Delta\varepsilon$  is the reaction-specific ion interaction coefficient, which is given by

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

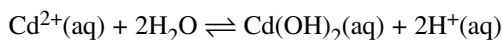
The term  $a_j B$  is set (with very occasional exceptions) at  $1.5 \text{ kg}^{1/2} \text{ mol}^{-1/2}$  [2005PBA]. For a 1:1 electrolyte the term  $\log_{10} a(\text{H}_2\text{O})$ , can be calculated from the solution osmotic coefficient [59ROB]. For  $\text{NaClO}_4$  media at  $25^\circ\text{C}$  the following approximation holds:  $\log_{10} a(\text{H}_2\text{O}) \approx -(0.01484 \pm 0.00018)$  ( $I_m/\text{mol kg}^{-1}$ ) at  $0 \leq I_m/\text{mol kg}^{-1} \leq 3.5$  [2009PBA].

The data that meet our selection criteria for use in the SIT regression analyses are listed in Tables A2-1 through A2-15 (Appendix 2). To assist the reader, 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 values for  $\log_{10} K_n$  (reported) are given on the molality ( $\text{mol kg}^{-1}$ ) or amount concentration ( $\text{mol dm}^{-3}$ ) 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. Some  $\log_{10} K_n$  (reported) values have much stronger experimental bases than others, being derived from a large amount of high-quality experimental data and/or from more than one experimental method. In determining the value of  $\log_{10} K_n$  (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, according to [97GRE, Appendix C]. The  $\log_{10} K_n$  (accepted) values are listed in the Tables on the molality scale (to facilitate SIT analysis).

The application of SIT to the accepted equilibrium constant values (Tables A2-1 to A2-12) involves extrapolation of  $\log_{10} \beta_{p,q,r} - \Delta z^2 D - r \log_{10} a(\text{H}_2\text{O})$  to  $m_k$  (or  $I_m$ ) =  $0 \text{ mol kg}^{-1}$  for a system with a large excess of a 1:1 electrolyte, using eq. 2. The regressions (shown in Appendix 3) yield  $\log_{10} \beta_{p,q,r}^\circ$  (or  $\log_{10} K_n^\circ$ ) as the intercept at  $I_m = 0 \text{ mol kg}^{-1}$  and the reaction specific ion interaction 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 A2-13 to A2-15), the SIT regressions to  $I_m = 0 \text{ mol kg}^{-1}$  [97GRE] involve the relationship  $\Delta_r H - 0.75\Delta(z^2)A_L \sqrt{I_m} (1 + 1.5\sqrt{I_m})^{-1} - rL_1 = \Delta_r H^\circ - RT^2 I_m \Delta\varepsilon_L$ ; 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 and definition of terms, see [2005PBA]. In Tables A2-1 to A2-15, 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. Where appropriate, an initial SIT analysis was used to identify (and reject) outliers based on their deviation from the calculated confidence limits.

In the data compilation tables (Appendix 2), abbreviations indicate the experimental methods used: **emf**: measurement of galvanic cell potentials; **Cd(Hg)**: emf using a Cd amalgam electrode; **sol**: solubility determination; **gl**: pH measurement by glass electrode; **con**: conductivity; **ise**: measurement of cell potentials using an ion selective electrode; **kin**: kinetic; **ix**: ion exchange; **cal**: calorimetry; **vlt**: voltammetry; **pol**: polarography; **sp**: (UV-vis) spectrophotometry; **dis**: distribution between immiscible solvents;  $K(T)$ : temperature dependence of equilibrium constant.

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



For simplicity, suffixes such as (aq) are not used unless a species has zero net charge, in which case the phase is specified, e.g.,  $\text{Cd}(\text{OH})_2(\text{aq})$ ,  $\text{CdCO}_3(\text{s})$ , and  $\text{CdO}(\text{s})$ . In this document, “amount concentration” is abbreviated to “concentration”, the units being  $\text{mol dm}^{-3}$  ( $= \text{mol L}^{-1}$ , or M).

For each  $\text{Cd}^{2+}$ -ligand combination, this review will, where possible

- identify the most reliable publications and stability constants;
- identify (and reject for specified reasons) unreliable stability constants;
- 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  $K_{s0}^\circ$  and related constants at 25 °C (298.15 K) and  $I_m = 0 \text{ mol kg}^{-1}$ , and of  $\Delta\epsilon$ ; and
- identify, where available, the most reliable reaction enthalpy values  $\Delta_r H$ .

Using the derived values of  $\beta_{p,q,r}^\circ$  and  $\Delta\epsilon$ , 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 ( $I_m = 0 \text{ mol kg}^{-1}$ ), SIT reaction coefficients ( $\Delta\epsilon$ ), and, where available, reaction enthalpies for the formation of  $\text{Cd}^{2+}$  complexes with the selected inorganic anions. These quantities were derived from a critical evaluation of the literature, followed by regression analyses of the accepted data using SIT functions. 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 experimental conditions and which therefore has an unknown uncertainty. The  $\log_{10} \beta_{p,q,r}^\circ$ ,  $\log_{10} K_n^\circ$ , and  $\log_{10} {}^*\beta_{p,q,r}^\circ$  values are for 298.15 K, 1 bar ( $10^5 \text{ Pa}$ ) and infinite dilution ( $I_m = 0 \text{ mol kg}^{-1}$ ).

**Table 1** Recommended (R), Provisional (P), and Indicative (I) values for the system  $\text{Cd}^{2+} + \text{OH}^-$  at 298.15 K, 1 bar, and  $I_m = 0 \text{ mol kg}^{-1}$ .  $\Delta\epsilon$  values for  $\text{Na}^+$  or  $\text{Li}^+ + \text{ClO}_4^-$  medium.

Reaction	Constant	Evaluation
$\text{Cd}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{CdOH}^+ + \text{H}^+$	$\log_{10} {}^*K_1^\circ = -9.80 \pm 0.10$	R
	$\Delta\epsilon = -(0.05 \pm 0.04) \text{ kg mol}^{-1}$	
	$\Delta_f H = 54.8 \pm 2.0 \text{ kJ mol}^{-1}$	P <sup>1</sup>
$\text{Cd}^{2+} + 2\text{OH}^- \rightleftharpoons \text{Cd}(\text{OH})_2(\text{aq})$	$\log_{10} \beta_2^\circ = 7.81 \pm 0.13$	R
	$\Delta\epsilon = -(0.32 \pm 0.02) \text{ kg mol}^{-1}$	
$\text{Cd}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Cd}(\text{OH})_2(\text{aq}) + 2\text{H}^+$	$\log_{10} {}^*\beta_2^\circ = -20.19 \pm 0.13$	R
$\text{Cd}^{2+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Cd}(\text{OH})_3^- + 3\text{H}^+$	$\log_{10} {}^*\beta_3^\circ = -33.5 \pm 0.5$	I
$\text{Cd}^{2+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Cd}(\text{OH})_4^{2-} + 4\text{H}^+$	$\log_{10} {}^*\beta_4^\circ = -47.28 \pm 0.15$	P
$2\text{Cd}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{Cd}_2\text{OH}^{3+} + \text{H}^+$	$\log_{10} {}^*\beta_{2,1}^\circ = -8.73 \pm 0.01$	R
	$\Delta\epsilon = (0.242 \pm 0.004) \text{ kg mol}^{-1}$	
	$\Delta_f H = 45.6 \pm 2.0 \text{ kJ mol}^{-1}$	P <sup>1</sup>
$\text{Cd}(\text{OH})_2(\text{s}) \rightleftharpoons \text{Cd}^{2+} + 2\text{OH}^-$	$\log_{10} K_{s0}^\circ = -14.28 \pm 0.12$	R
	$\Delta\epsilon = (0.31 \pm 0.04) \text{ kg mol}^{-1}$	
$\text{Cd}(\text{OH})_2(\text{s}) + 2\text{H}^+ \rightleftharpoons \text{Cd}^{2+} + 2\text{H}_2\text{O}$	$\log_{10} {}^*K_{s0}^\circ = 13.72 \pm 0.12$	P
	$\Delta_f H^\circ = -94.6 \pm 2.0 \text{ kJ mol}^{-1}$	P

<sup>1</sup>For  $I_m = 3.0 \text{ mol dm}^{-3} \text{ LiClO}_4$ .**Table 2** Recommended (R) and Provisional (P) values for the  $\text{Cd}^{2+} + \text{Cl}^-$  system at 298.15 K, 1 bar, and  $I_m = 0 \text{ mol kg}^{-1}$ .  $\Delta\epsilon$  values for  $\text{ClO}_4^-$  medium.

Reaction	Constant	Evaluation
$\text{Cd}^{2+} + \text{Cl}^- \rightleftharpoons \text{CdCl}^+$	$\log_{10} K_1^\circ = 1.98 \pm 0.06$	R
	$\Delta\epsilon = -(0.14 \pm 0.02) \text{ kg mol}^{-1}$	
	$\Delta_f H^\circ = 3.3 \pm 0.6 \text{ kJ mol}^{-1}$	R
$\text{Cd}^{2+} + 2\text{Cl}^- \rightleftharpoons \text{CdCl}_2(\text{aq})$	$\log_{10} \beta_2^\circ = 2.64 \pm 0.09$	R
	$\Delta\epsilon = -(0.27 \pm 0.03) \text{ kg mol}^{-1}$	
	$\Delta_f H^\circ = 7.8 \pm 1.4 \text{ kJ mol}^{-1}$	P
$\text{Cd}^{2+} + 3\text{Cl}^- \rightleftharpoons \text{CdCl}_3^-$	$\log_{10} \beta_3^\circ = 2.3 \pm 0.21$	R
	$\Delta\epsilon = -(0.40 \pm 0.07) \text{ kg mol}^{-1}$	

**Table 3** Recommended (R) and Provisional (P) values for the  $\text{Cd}^{2+} + \text{CO}_3^{2-}$  system at 293.15 K, 1 bar, and  $I_m = 0 \text{ mol kg}^{-1}$ .

Reaction	Constant	Evaluation
$\text{Cd}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{CdCO}_3(\text{aq})$	$\log_{10} K_1^\circ = 4.4 \pm 0.2^1$	P
$\text{CdCO}_3(\text{s}) + 2\text{H}^+ \rightleftharpoons \text{Cd}^{2+} + \text{H}_2\text{O} + \text{CO}_2(\text{g})$	$\log_{10} {}^*K_{ps0} = 6.08 \pm 0.03$	
	$\Delta\epsilon = (0.059 \pm 0.009) \text{ kg mol}^{-1}$	R
$\text{CdCO}_3(\text{s}) \rightleftharpoons \text{Cd}^{2+} + \text{CO}_3^{2-}$	$\log_{10} K_{s0}^\circ = -12.06 \pm 0.04$	R

<sup>1</sup>Based on the assumption that the term  $\Delta\epsilon(14)$  in the SIT analysis will be  $\approx 0 \text{ mol kg}^{-1}$  [2007PBA].

**Table 4** Recommended (R) and Indicative (I) values for the  $\text{Cd}^{2+} + \text{SO}_4^{2-}$  system at 298.15 K and  $I_m = 0 \text{ mol kg}^{-1}$ .  $\Delta\epsilon$  values for  $\text{ClO}_4^-$  medium.

Reaction	Constant <sup>1</sup>	Evaluation
$\text{Cd}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{CdSO}_4(\text{aq})$	$\log_{10} K_1^\circ = 2.36 \pm 0.04$ $\Delta\epsilon = -(0.09 \pm 0.0) \text{ kg mol}^{-1}$ $\Delta_r H^\circ = 8.3 \pm 0.5 \text{ kJ mol}^{-1}$	R  R
$\text{Cd}^{2+} + 2\text{SO}_4^{2-} \rightleftharpoons \text{Cd}(\text{SO}_4)_2^{2-}$	$\log_{10} \beta_2^\circ = 3.32 \pm 0.16$ $\Delta\epsilon = (0.11 \pm 0.05) \text{ kg mol}^{-1}$	I

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

**Table 5** Provisional (P) values for the  $\text{Cd}^{2+} + \text{PO}_4^{3-}$  system at 298.15 K in  $\text{NaClO}_4$  media.

Reaction	Constant <sup>1</sup>	Evaluation
$\text{Cd}^{2+} + \text{HPO}_4^{2-} \rightleftharpoons \text{CdHPO}_4(\text{aq})$	$\log_{10} K = 2.85 \pm 0.20$	P <sup>2</sup>
$\text{Cd}^{2+} + \text{H}_2\text{PO}_4^- \rightleftharpoons \text{CdH}_2\text{PO}_4^+$	$\log_{10} K = 0.76 \pm 0.20$	P <sup>3</sup>

<sup>1</sup>The uncertainties represent 95 % confidence limits of the regression intercept ( $\log_{10} K^\circ$ ) and of the slope ( $-\Delta\epsilon$ ).

<sup>2</sup>For  $I_m = 0.101 \text{ mol kg}^{-1} \text{ NaClO}_4$ .

<sup>3</sup>For  $I_c = 3.0 \text{ mol dm}^{-3} \text{ NaClO}_4$ .

### 3. Cd<sup>II</sup> SOLUTION CHEMISTRY

The aqueous chemistry of Cd<sup>II</sup> is dominated by its high affinity for sulfur and other “soft” donors. Thus, Cd<sup>II</sup> has a comparatively low affinity for the oxygen donor ligands involved in this review: OH<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, and PO<sub>4</sub><sup>3-</sup>, as reflected in its stability constants with these ligands. For example, the stability constants for the 1:1 Cd<sup>2+</sup>-hydroxido and Cd<sup>2+</sup>-carbonato complexes are both ca. 2 log units lower than the corresponding ones for the analogous complexes of Cu<sup>2+</sup> [2007PBA] and Pb<sup>2+</sup> [2009PBA]. In contrast, of these three elements, Cd<sup>II</sup> forms the most stable complexes with the more polarizable ligand Cl<sup>-</sup>.

Unlike Cu<sup>II</sup> and Pb<sup>II</sup>, Cd<sup>II</sup> has a rather weak tendency to form polymeric hydroxido-species in aqueous solution. The polymeric species Cd<sub>2</sub>OH<sup>3+</sup> makes a significant contribution only when  $[\text{Cd}^{\text{II}}]_{\text{T}} \geq 10^{-2} \text{ mol dm}^{-3}$ . In contrast, the formation of Pb<sub>3</sub>(OH)<sub>4</sub><sup>2-</sup>, Pb<sub>6</sub>(OH)<sub>8</sub><sup>4-</sup>, and Pb<sub>4</sub>(OH)<sub>4</sub><sup>4-</sup> is marked at  $[\text{Pb}^{\text{II}}]_{\text{T}} > 5 \times 10^{-4} \text{ mol dm}^{-3}$  [2009PBA], and the formation of Cu<sub>2</sub>(OH)<sub>2</sub><sup>2+</sup> becomes significant at  $[\text{Cu}^{\text{II}}]_{\text{T}} > 10^{-5} \text{ mol dm}^{-3}$  [2007PBA].

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

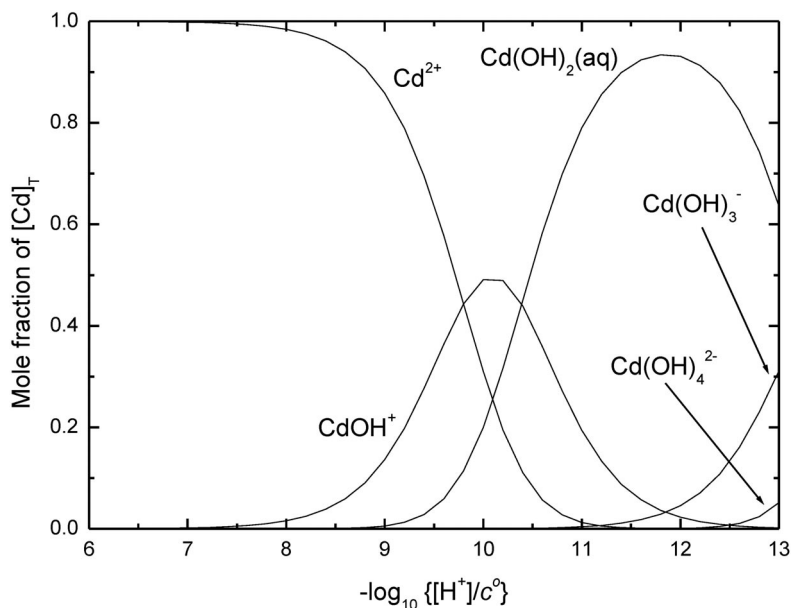
## 4. EVALUATION OF EQUILIBRIUM CONSTANTS (HOMOGENEOUS REACTIONS)

### 4.1 The Cd<sup>2+</sup> + OH<sup>-</sup> system

As will become apparent from the discussion below, further high-quality investigations of the stability constants for the hydrolysis reactions of Cd<sup>II</sup> are required. Thus, although the IUPAC *SC-Database* [2010PET] reports 44 studies on the hydrolysis reactions of Cd<sup>II</sup>, few provide reliable data. Consequently, the majority of the SIT analyses undertaken in this review for the Cd<sup>II</sup> + OH<sup>-</sup> complexes have been based on restricted data sets, some limited to just two ionic strengths. In the determination

of stability constant values for zero ionic strength, some reliance has therefore been placed on the similarity of the regression-derived reaction coefficients,  $\Delta\epsilon$ , with those for analogous equilibria involving  $\text{Pb}^{\text{II}}$  [2009PBA].

Speciation diagrams for the  $\text{Cd}^{2+} + \text{OH}^-$  system, based on our Recommended and Provisional values for stability constants at  $I_m = 0 \text{ mol kg}^{-1}$ , recorded in Table 1, are shown in Fig. 1 for  $[\text{Cd}^{\text{II}}]_{\text{T}} = 1 \times 10^{-6} \text{ mol dm}^{-3}$  ( $0.11 \text{ mg Cd (kg-H}_2\text{O)}^{-1}$ ). Results outside the range  $2 \leq -\log_{10}\{[\text{H}^+]/c^\circ\} \leq 12$  should be viewed with caution as activity coefficients may deviate significantly from unity. The speciation diagram is invariant in the range  $10^{-3} \geq [\text{Cd}^{\text{II}}]_{\text{T}} \geq 10^{-9} \text{ mol dm}^{-3}$ . At higher  $[\text{Cd}^{\text{II}}]_{\text{T}}$  (not shown) the species  $\text{Cd}_2\text{OH}^{3+}$  makes a significant contribution, with a maximum at  $-\log_{10}\{[\text{H}^+]/c^\circ\} = 9.6$ , at which it represents 4.6 % of  $[\text{Cd}^{\text{II}}]_{\text{T}}$  at  $10^{-2} \text{ mol dm}^{-3}$  and 60.5 % at  $1.0 \text{ mol dm}^{-3}$  (ignoring activity coefficient effects).



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

#### 4.1.1 Formation of $\text{CdOH}^+$

The formation of  $\text{CdOH}^+$  can be described by reaction 4



Data selected for the SIT analysis, to determine the stability constant at zero ionic strength and the reaction ion interaction coefficient,  $\Delta\epsilon(4)$ , are listed in Table A2-1, along with references and our assigned uncertainties. The weighted regression (Fig. A3-1) used the expression

$$\log_{10} {}^*K_1 + 2D - \log_{10} a(\text{H}_2\text{O}) = \log_{10} {}^*K_1^\circ - \Delta\epsilon I_m$$

derived from eqs. 2 and 4 ( $\Delta z^2 = -2$ ). The regression, using data for  $\text{NaClO}_4$  and  $\text{LiClO}_4$  media, yields the value

$$\log_{10} {}^*K_1^\circ(\text{eq. 4, } 298.15 \text{ K}) = -9.80 \pm 0.10$$



which is Recommended. The calculated value for  $\Delta\epsilon(4)$  in perchlorate media is  $-(0.05 \pm 0.04)$  kg mol<sup>-1</sup>. This value is similar to that found for PbOH<sup>+</sup>,  $\Delta\epsilon = -(0.06 \pm 0.04)$  kg mol<sup>-1</sup> [2009PBa] which is consistent with the similar ionic radii (0.97 Å (Cd<sup>2+</sup>) and 0.99 Å (Pb<sup>2+</sup>) [76SHA]) of the two metals [97GRE]. The derived stability constant at  $I_m = 0$  mol kg<sup>-1</sup> is slightly more positive than those preferred by Sadiq [89SAb] or Baes and Mesmer [76BMa], ( $\log_{10} {}^*K_1^\circ = -10.10$  and  $-10.08$ , respectively). This results from the inclusion of the more recent data for 0.10 mol dm<sup>-3</sup> NaClO<sub>4</sub> [2000KAa], which constrains the present SIT regression.

#### 4.1.2 Formation of Cd(OH)<sub>2</sub>(aq)

The formation of Cd(OH)<sub>2</sub>(aq) can be described by reaction 5



Data selected for the SIT analysis, to determine the stability constant at zero ionic strength and the reaction ion interaction coefficient,  $\Delta\epsilon(5)$ , are listed in Table A2-2, along with references and our assigned uncertainties. The weighted regression (Fig. A3-2) used the expression

$$\log_{10} \beta_2 + 6D = \log_{10} \beta_2^\circ - \Delta\epsilon I_m$$

derived from eqs. 2 and 5 ( $\Delta z^2 = -6$ ). The regression yields the Recommended value

$$\log_{10} \beta_2^\circ(\text{eq. 5, 298.15 K}) = 7.81 \pm 0.13$$

The value obtained for  $\Delta\epsilon(5)$  in NaClO<sub>4</sub> media is  $-(0.32 \pm 0.02)$  kg mol<sup>-1</sup>, which is similar to that derived for the formation of CdCl<sub>2</sub>(aq) (Section 4.2.2). Using the ion interaction coefficient  $\epsilon(\text{Na}^+, \text{OH}^-) = (0.04 \pm 0.01)$  kg mol<sup>-1</sup> [97GRE] and that derived in Section 5.1 for  $\epsilon(\text{Cd}^{2+}, \text{ClO}_4^-)$ , the calculated value for  $\epsilon(\text{Cd}(\text{OH})_2(\text{aq}), \text{Na}^+, \text{ClO}_4^-)$  is  $-(0.02 \pm 0.03)$  kg mol<sup>-1</sup>. This last value is near zero, as expected for a neutral species, which is consistent with values derived for analogous species in this review series [2005PBa, 2007PBa].

From  $\log_{10} \beta_2^\circ$ , and the ionization constant for water, we derive the value  $\log_{10} {}^*\beta_2^\circ = -20.19 \pm 0.13$  for reaction 6



This value is also Recommended. It is slightly more positive than the value selected by Baes and Mesmer [76BMa] ( $\log_{10} {}^*\beta_2^\circ = -20.35$ ) but is in excellent agreement with that derived in the review by Sadiq [89SAb] ( $\log_{10} {}^*\beta_2^\circ = -20.20$ ).

#### 4.1.3 Formation of Cd(OH)<sub>3</sub><sup>-</sup> and Cd(OH)<sub>4</sub><sup>2-</sup>

The formation of Cd(OH)<sub>4</sub><sup>2-</sup> can be described by reaction 7



Data selected for the SIT analysis, to determine the stability constant at zero ionic strength and the reaction ion interaction coefficient,  $\Delta\epsilon(7)$ , are listed in Table A2-3, along with references and our assigned uncertainties. The weighted regression (Fig. A3-3) used the expression

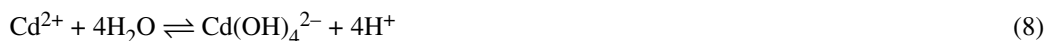
$$\log_{10} \beta_4 + 4D = \log_{10} \beta_4^\circ - \Delta\epsilon I_m$$

derived from eqs. 2 and 7 ( $\Delta z^2 = -4$ ). The regression yields the Provisional value

$$\log_{10} \beta_4^\circ(\text{eq. 7, 298.15 K}) = 8.72 \pm 0.15$$

The value obtained for  $\Delta\epsilon(7)$  in NaClO<sub>4</sub> medium is  $-(0.19 \pm 0.02)$  kg mol<sup>-1</sup>. No data for comparable species of Hg<sup>II</sup>, Cu<sup>II</sup>, and Pb<sup>II</sup> were derived in the earlier reviews in this series [2005PBa, 2007PBa, 2009PBa].

For reaction 8



we derive the value  $\log_{10} {}^*\beta_4^\circ$  (eq. 8, 298.15 K) =  $-47.28 \pm 0.15$ , which is also Provisional. This value is in excellent agreement with those selected by Sadiq [89SAb] ( $\log_{10} {}^*\beta_4^\circ = -47.29$ ) and Baes and Mesmer [76BMa] ( $\log_{10} {}^*\beta_4^\circ = -47.35$ ).

Data for the formation of  $\text{Cd}(\text{OH})_3^-$ , or the derivation thereof, have been reported in only two publications [57Gwa, 62DLa]. In both cases, the reported stability constant ( $\log_{10} {}^*\beta_3^\circ$ ) appears to be too positive (compared with the  $\log_{10} {}^*\beta_2^\circ$  and  $\log_{10} {}^*\beta_4^\circ$  values derived in the present review). Gayer and Woontner [57Gwa] studied the solubility of  $\text{Cd}(\text{OH})_2(\text{s})$  and derived values for  $K_{s1}$  to  $K_{s4}$  from which the values  ${}^*K_1$  to  ${}^*K_4$  can be derived utilising the  ${}^*K_{s0}$  value obtained in Section 5.1. In all cases, the hydrolysis constants derived are more positive than those selected in the present review. Gayer and Woontner [57Gwa] also did not report either the purity or the crystallinity of the  $\text{Cd}(\text{OH})_2(\text{s})$  they used and the enhanced solubility observed may have resulted from their use of a less crystalline phase. In the Dyrssen and Lumme study [62DLa], the value of  $\log_{10} \beta_4$  is much larger than values from other studies and the value of  $\log_{10} K_3$  also appears to be high, particularly when considering the indicative value for  $\log_{10} \beta_3$  selected in this review (see below). Accordingly, neither of the derived values for  $\text{Cd}(\text{OH})_3^-$  [57Gwa, 62DLa] has been accepted in this review.

On the basis of the hydrolysis constants selected for the other three monomeric  $\text{Cd}^{2+}$ -hydroxido species, it is suggested that for the formation of  $\text{Cd}(\text{OH})_3^-$  the  $\text{Cd}^{2+}$  hydrolysis constant lies in the range  $-33 > \log_{10} {}^*\beta_3 > -34$ . The value selected by Sadiq [89SAb] was  $-33.01$  whereas Baes and Mesmer [76BMa] suggested a value of  $< -33.3$ . Based on all the information currently available, a value of  $\log_{10} {}^*\beta_3 = -33.5 \pm 0.5$  is assigned as Indicative for the formation of  $\text{Cd}(\text{OH})_3^-$ .

#### 4.1.4 Formation of $\text{Cd}_2\text{OH}^{3+}$ and $\text{Cd}_4(\text{OH})_4^{4+}$

The formation of  $\text{Cd}_2\text{OH}^{3+}$  can be described by reaction 9



Data selected for the SIT analysis, to determine the stability constant at zero ionic strength and the reaction ion interaction coefficient,  $\Delta\epsilon(9)$ , are listed in Table A2-4, along with references and our assigned uncertainties. The weighted regression (Fig. A3-4) used the expression

$$\log_{10} {}^*\beta_{2,1} - 2D - \log_{10} a(\text{H}_2\text{O}) = \log_{10} {}^*\beta_{2,1}^\circ - \Delta\epsilon I_m$$

derived from eqs. 2 and 9 ( $\Delta z^2 = +2$ ). The regression yields the Recommended value

$$\log_{10} {}^*\beta_{2,1}^\circ (\text{eq. 9, 298.15 K}) = -8.73 \pm 0.01$$

The value obtained for  $\Delta\epsilon(9)$  in  $\text{NaClO}_4$  media is  $(0.242 \pm 0.004) \text{ kg mol}^{-1}$  (cf. for  $\text{Pb}_2\text{OH}^{3+}$ ,  $\Delta\epsilon = (0.11 \pm 0.10) \text{ kg mol}^{-1}$ ; [2009Pba]). The derived stability constant is significantly more positive than that selected by Baes and Mesmer [76BMa] ( $\log_{10} {}^*\beta_{2,1}^\circ = -9.39$ ). This difference can be ascribed to the inclusion in the present review of the more recent datum for  $0.10 \text{ mol dm}^{-3} \text{ NaClO}_4$  [2000Kaa]. The value selected by Sadiq [89SAb] was  $\log_{10} {}^*\beta_{2,1}^\circ = -6.4$ ; it is clearly incorrect and is rejected (it is possibly a misprint for  $-9.40$ ).

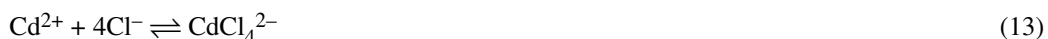
There is only one value reported for the formation of  $\text{Cd}_4(\text{OH})_4^{4+}$  [62BCb],  $\log_{10} {}^*\beta_{4,4} = -31.8$ . This species is only likely to form at elevated concentrations of cadmium, and therefore is unlikely to be important in the environment. Pending further studies, no data were selected for this species.

## 4.2 The $\text{Cd}^{2+} + \text{Cl}^-$ system

$\text{Cd}^{\text{II}}$  forms three consecutive chlorido- complexes in aqueous solution, reactions 10 to 12, each with a well-characterized stability constant

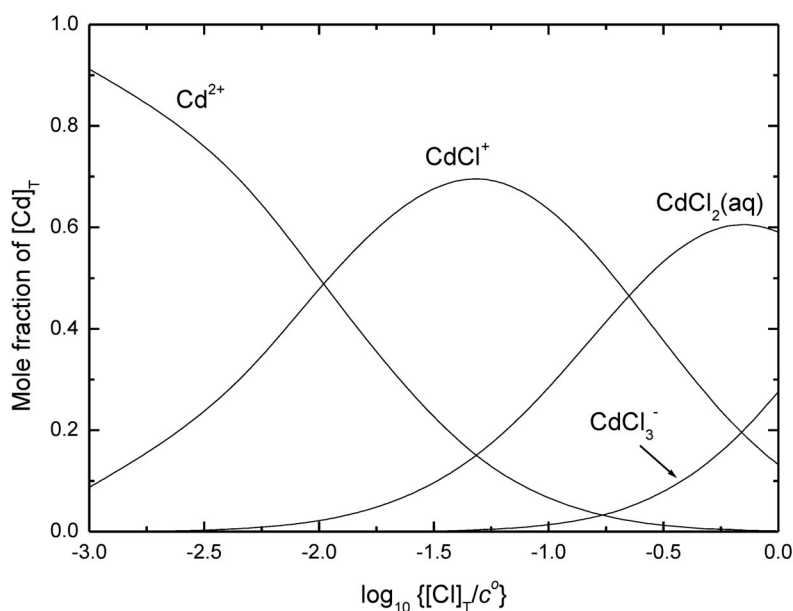


The stability constant for the tetrachlorido- complex, reaction 13, is less certain.



These reactions have been widely studied, there being 139 entries in the IUPAC Stability Constants Database [2010PET]. Analogous to the  $\text{Cu}^{2+} + \text{Cl}^-$  and  $\text{Pb}^{2+} + \text{Cl}^-$  systems, the complexes are all weak and are best studied in media of high  $[\text{Cl}^-]_{\text{T}}$ , high  $[\text{Cl}^-]_{\text{T}}:[\text{Cd}^{\text{II}}]_{\text{T}}$  ratios, and high ionic strength. The stability constants have been investigated mainly by potentiometry (emf), especially using the Cd/Hg electrode which allows direct measurement of  $[\text{Cd}(\text{aq})^{2+}]$ , but also by voltammetry (polarography) (vlt), ion selective electrode (ise) potentiometry, and calorimetric (cal) measurements. There is no convincing experimental evidence for the formation of the higher complexes,  $\text{CdCl}_5^{3-}$  or  $\text{CdCl}_6^{4-}$ , or of polynuclear complexes, in aqueous solution (see Section 4.2.4).

The speciation diagram for the  $\text{Cd}^{2+} + \text{Cl}^-$  system is shown in Fig. 2, based on the Recommended values for the stability constants at  $I_m = 0 \text{ mol kg}^{-1}$  (Table 2) and represents conditions in which hydrolysis is suppressed ( $-\log_{10} \{[\text{H}^+]/c^\circ\} < 7.5$ ). Results for values of  $\log_{10} \{[\text{Cl}^-]/c^\circ\} > -2$  should be viewed with caution as activity coefficients no longer remain constant. Figure 2 indicates that the predominance areas for the  $\text{Cd}^{2+}$ -chlorido complexes overlap significantly. Thus, experimental data evaluations that consider only the formation of an individual complex, e.g.,  $\text{CdCl}^+$ , without taking  $\text{CdCl}_2(\text{aq})$  into



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

account, will in general bear large systematic errors. As such they were rejected in the present analysis, unless the authors verified that the concentration of the 1:2 complex was small, e.g., [73HHb].

The following data analyses for the  $\text{Cd}^{2+}$ -chlorido complexes use only values reported for 25 °C and at constant ionic strength maintained with  $\text{NaClO}_4$  or  $\text{LiClO}_4$ . The SIT regression analyses were based on data from both of these media (using the appropriate density data to convert from molarity to molality units for each system). This was justified *a priori* on the basis of observations [63MKg] on the influence of electrolyte cations on the stability of the  $\text{Cd}^{2+}$ -chlorido complexes at  $I_c = 4.0 \text{ mol dm}^{-3}$  ( $\text{LiCl}$ ), but is also supported by the resultant regression plots A3-5 and A3-7. The effect of gradual replacement of  $\text{Li}^+$  ions by  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ , or  $\text{Cs}^+$  in  $\text{Cl}^-$  media was negligible on  $\beta_1$  and  $\beta_2$ , visible but not systematic on  $\beta_3$ , and fairly pronounced on  $\beta_4$ . We are inclined to support the explanation [63MKg] for the latter effect being due to the formation of ion pairs between  $\text{CdCl}_4^{2-}$  and the alkali metal ions, although other explanations (such as activity coefficient variations) are also plausible. In this review, appropriate larger uncertainties were assigned in the regression of  $\beta_3$  values. In contrast, Branica et al. [89BPb] reported significantly different constants for  $4.0 \text{ mol dm}^{-3} \text{ LiClO}_4$  and  $4.0 \text{ mol dm}^{-3} \text{ NaClO}_4$  media. However, the effect on the stepwise constants was not consistent and the authors did not report the temperature or whether it was held constant. They cited [63MKg] but did not comment on the contrasting results. Their data were therefore rejected.

Fedorov et al. published several investigations reporting formation constants for the  $\text{Cd}^{2+}$ -chlorido complexes at 25 °C and  $I_c = 0.1$  to  $4.0 \text{ mol dm}^{-3} \text{ LiClO}_4$  [71FCb, 72FKc, 74FRc, 75FCa, 75KLa]. They determined  $\beta_n$  values and  $\Delta_r H$  values for the binary chlorido- complexes [72FKc], and  $\beta_{p,q}$  values for mixed chlorido- complexes with iodide [75KLa], sulfate [71FCb, 75FCa], and nitrate [74FRc]. It appears that the formation constants for the binary chlorido- complexes were redetermined in each of the latter studies. Their  $\beta_n$  values show good agreement in general, although in some cases the constants differ by more than the reported uncertainties. These investigations provide a substantial amount of experimental data. To avoid overweighting, we selected for regression analysis the average of the values reported by Fedorov et al. for each ionic strength [as applicable: 72FKc, 74FRc, 75FCa, 75KLa]. The average values used are listed in Tables A2-5, A2-6, and A2-7 with the reference [FED].

#### 4.2.1 Formation of $\text{CdCl}^+$

Values selected for the SIT analysis, to determine the stability constant at zero ionic strength and the reaction ion interaction coefficient  $\Delta\epsilon(10)$ , are listed in Table A2-5, along with our assigned uncertainties according to the estimated overall precision of the data. For five ionic strengths in  $\text{LiClO}_4$ , this selection included the average of the values reported in [72FKc, 74FRc, 75FCa, 75KLa] which is referenced as [FED] in the Table. The assigned uncertainties (95 % confidence level) determine the weighting of each value in the SIT analysis. Ionic media other than  $\text{NaClO}_4$  or  $\text{LiClO}_4$  were not considered. Some studies were rejected (see footnotes in Table A2-5) because higher complexes had not been taken into account even though the (high) chloride concentrations used would promote their formation.

The SIT analysis shows excellent consistency amongst the 28 data for the two media. The weighted linear regression (Fig. A3-5) yields the Recommended standard constant

$$\log_{10} K_1^\circ(\text{eq. 10, 298.15 K}) = 1.98 \pm 0.06$$

This value is the same as that recommended by Martell and Smith [82MAR] for  $I_c = 0$ ,  $\log_{10} K_1^\circ = 1.98 \pm 0.03$ . The resulting reaction ion interaction coefficient is  $\Delta\epsilon(10) = -(0.14 \pm 0.02) \text{ kg mol}^{-1}$  for  $\text{NaClO}_4$  and  $\text{LiClO}_4$  media. Figure A3-5 indicates that the data are remarkably consistent and strongly correlated, hence confirming that the SIT equation can be applied reliably to this reaction over the ionic strength range  $0.1\text{--}5.0 \text{ mol kg}^{-1}$ , and that no systematic differences exist between the values for  $\text{LiClO}_4$  and  $\text{NaClO}_4$  media. It is inferred that the anion replacement (of perchlorate by chloride) during the experiments has a minimal effect on the reactant activity coefficients.

Heath and Hefter [77HHb] achieved excellent agreement between  $\log_{10} K_1$  values derived from independent methods, viz. differential pulse polarography and potentiometry. Masłowska and Chruścińska [85MCA] reported constants for  $\text{CdCl}^+$  and  $\text{CdCl}_2(\text{aq})$  measured in  $1.0 \text{ mol dm}^{-3}$   $\text{NaClO}_4/\text{NaCl}$  with  $[\text{Cl}^-]_{\text{T}}$  constant at  $0.6 \text{ mol dm}^{-3}$ . However, under these conditions the 1:3 complex,  $\text{CdCl}_3^-$ , should not have been neglected; further,  $\text{Cd}(\text{aq})^{2+}$  is present at negligible concentration, thus the reported constant for  $\text{CdCl}^+$  probably has a large error and the value was therefore rejected.

#### 4.2.2 Formation of $\text{CdCl}_2(\text{aq})$

Data selected for the SIT analysis, to determine the stability constant at zero ionic strength for reaction 11 and the reaction ion interaction coefficient  $\Delta\epsilon(11)$ , are listed in Table A2-6, along with our assigned uncertainties. For five ionic strengths this selection includes the average values taken from [72FKc, 74FRc, 75FCa, 75KLa], which are referenced as [FED]. The selected data all refer to  $\text{NaClO}_4$  and  $\text{LiClO}_4$  media and  $25^\circ\text{C}$ . The weighted linear regression for 25 data points (Fig. A3-6) indicates excellent consistency between the values and yields the Recommended standard constant

$$\log_{10} \beta_2^\circ(\text{eq. 11, } 298.15 \text{ K}) = 2.64 \pm 0.09$$

The reaction ion interaction coefficient is  $\Delta\epsilon(11) = -(0.27 \pm 0.03) \text{ kg mol}^{-1}$  for  $\text{NaClO}_4$  and  $\text{LiClO}_4$  media. The Recommended value of  $\log_{10} \beta_2^\circ$  agrees well with that of Martell and Smith [82MAR],  $\log_{10} \beta_2^\circ = 2.6 \pm 0.1$ .

#### 4.2.3 Formation of $\text{CdCl}_3^-$ and $\text{CdCl}_4^{2-}$

Most studies on the system  $\text{Cd}^{2+} + \text{Cl}^-$  report the formation of the 1:3 complex, reaction 12. However, high concentrations of chloride ion are necessary for  $\text{CdCl}_3^-$  to form in sufficient amounts for a reliable determination of its formation constant. Values determined at very high  $[\text{Cl}^-]_{\text{T}}$  in perchlorate media in reality refer to mixed media that may contain higher concentrations of chloride than perchlorate. However, we treat the data at these high  $[\text{Cl}^-]_{\text{T}}$  as referring to perchlorate media.

Data selected for the SIT analysis are recorded in Table A2-7 along with their assigned uncertainties; they refer to  $25^\circ\text{C}$  and  $\text{NaClO}_4$  or  $\text{LiClO}_4$  media and ionic strengths up to  $4.9 \text{ mol kg}^{-1}$ . For four ionic strengths these include the average values taken from [72FKc, 74FRc, 75FCa, 75KLa] which are referenced as [FED]. The weighted linear regression (Fig. A3-7) using 22 values shows that the data are strongly correlated and result in the Recommended value of

$$\log_{10} \beta_3^\circ(12, 298.15 \text{ K}) = 2.30 \pm 0.21$$

The reaction ion interaction coefficient derived from this regression is  $\Delta\epsilon(12) = -(0.40 \pm 0.07) \text{ kg mol}^{-1}$  for  $\text{NaClO}_4$  and  $\text{LiClO}_4$  media. The value of  $\log_{10} \beta_3^\circ$  is in good agreement with that of Martell and Smith [82MAR],  $\log_{10} \beta_3^\circ = 2.4 \pm 0.1$ , albeit with a greater (and probably more realistic) uncertainty.

On the basis of emf measurements [63MKg, 71FCb, 74FRc, 75FCa] and calorimetric measurements [67MFa], there is some evidence for the existence of  $\text{CdCl}_4^{2-}$  at ionic strengths  $\geq 3 \text{ mol dm}^{-3}$ , but the reported formation constants for its formation are limited in number and differ significantly in magnitude. These constants are not considered to be reliable and anyway are too few for a SIT analysis. If the 1:4 complex does exist then it is extremely weak. Martell and Smith [82MAR] proposed:  $\log_{10} \beta_4 = 2.2 \pm 0.3$  ( $I_c = 4.0 \text{ mol dm}^{-3}$ ),  $\log_{10} \beta_4 = 1.6$  ( $I_c = 3.0 \text{ mol dm}^{-3}$ ), and  $\log_{10} \beta_4^\circ = 1.7$  ( $I_c = 0 \text{ mol dm}^{-3}$ ), although it was not revealed on what basis these values were selected. It is noted that all of these quantities are less than the corresponding  $\log_{10} \beta_3$  values (Table A2.7), which emphasizes their uncertain nature.

#### 4.2.4 Formation of higher complexes

Using a  $\text{Cd}(\text{Hg})$  electrode, Mironov et al. [63MKg] investigated the effect of changing the inert electrolyte cation within a chloride medium at  $I_c = 4.0 \text{ mol dm}^{-3}$ . By gradually replacing  $\text{Li}^+$  by  $\text{Rb}^+$  or  $\text{Cs}^+$  they observed an effect that could be interpreted as indicating the formation of ion pairs between  $\text{Rb}^+$  or  $\text{Cs}^+$  and the complex ion  $\text{CdCl}_4^{2-}$ , or alternatively by the formation of  $\text{CdCl}_5^{3-}$  and  $\text{CdCl}_6^{4-}$ . Since

the formation of ion pairs and significant variation in activity coefficients is expected in such systems, and there is no independent (e.g., spectroscopic) evidence for  $\text{CdCl}_5^{3-}$  and  $\text{CdCl}_6^{4-}$ , the formation of these two complexes is considered to be very unlikely and the values reported are rejected.

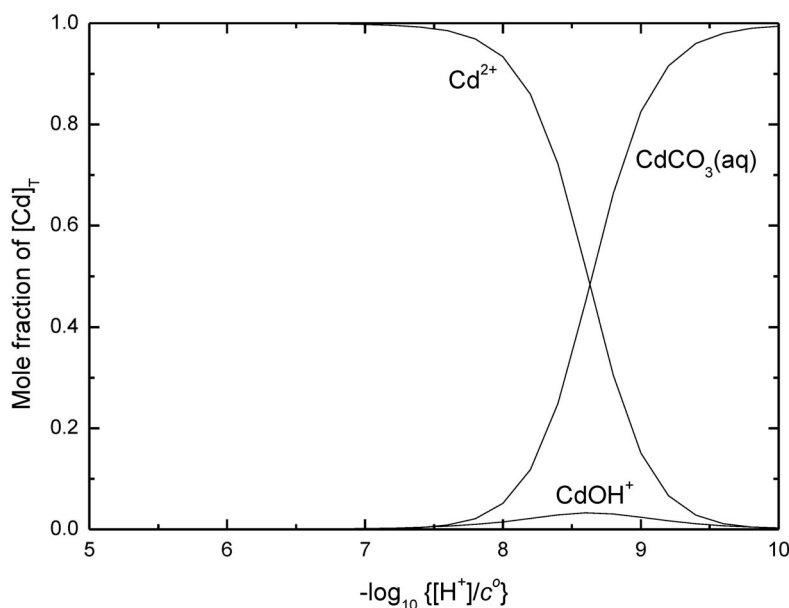
### 4.3 The $\text{Cd}^{2+} + \text{CO}_3^{2-}$ system

The equilibria reported for the homogeneous system  $\text{Cd}^{2+} + \text{H}^+ + \text{CO}_3^{2-}$  are



These equilibria have not been studied extensively. The *SC-Database* [2010PET] has only 14 references for the  $\text{Cd}^{2+} + \text{CO}_3^{2-}$  system. Of these, only seven report data for homogeneous equilibria, and only five investigations have produced useful stability constants. Two of these investigations were performed at 25 °C [76BHa, 92NEa], two at 20 °C [74GAa, 84STE], and one at an unspecified temperature [91RFa]. There are therefore insufficient data to justify preparation of a table in Appendix A2, or for SIT analyses.

Figure 3 shows a speciation diagram for the  $\text{Cd}^{2+} + \text{H}^+ + \text{CO}_3^{2-}$  system, based on the stability constants recorded for  $I_m = 0 \text{ mol kg}^{-1}$  and  $t = 25 \text{ °C}$  in Tables 1 and 3 and the protonation constants for the carbonate ion evaluated in a previous review [2005PBA]. The calculations assume  $f(\text{CO}_2) = 10^{-3.5} \text{ bar}$  (1 bar =  $10^5 \text{ Pa}$ ). Because the stabilities of the 1:1 and 1:2 carbonato- complexes and the 1:1 hydroxido- complexes of  $\text{Cd}^{2+}$  are significantly lower than those for the corresponding complexes



**Fig. 3** Speciation diagram for the ternary  $\text{Cd}^{2+} + \text{H}^+ + \text{CO}_3^{2-}$  system as obtained from the Recommended and Provisional stability constants at 25 °C and  $I_m = 0 \text{ mol kg}^{-1}$  (Tables 1 and 3), calculated for  $[\text{Cd}]_T = 10^{-8} \text{ mol dm}^{-3}$  and a  $\text{CO}_2$  fugacity of 370  $\mu\text{bar}$ .  $\text{Log } K_{10}(\text{CO}_2(\text{g}) = \text{CO}_2(\text{aq})) = -1.5$  [93MOR].

of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$ , the  $\text{Cd}^{\text{II}}$  speciation curve for each complex is displaced to higher values of  $-\log_{10}\{[\text{H}^+]/c^\circ\}$ . Thus, under the conditions applicable to the speciation calculations presented here: (a)  $\text{Cd}(\text{CO}_3)_2^{2-}$  is not present in measurable amount at  $-\log_{10}\{[\text{H}^+]/c^\circ\} < 10$ , whereas the bis-carbonato complex is the dominant species for  $\text{Cu}^{\text{II}}$  [2007PBa] and  $\text{Pb}^{\text{II}}$  [2009PBa] at  $-\log_{10}\{[\text{H}^+]/c^\circ\} = 10$ ; (b) the species  $\text{M}^{2+}$  and  $\text{MCO}_3(\text{aq})$  have equal concentrations at  $-\log_{10}\{[\text{H}^+]/c^\circ\} = 7.4, 7.6, \text{ and } 8.65$  for  $\text{M} = \text{Cu}, \text{Pb}, \text{ and } \text{Cd}$ , respectively. In contrast to  $\text{Hg}^{\text{II}}$ , the carbonato-species of  $\text{Cu}^{\text{II}}, \text{Pb}^{\text{II}}, \text{ and } \text{Cd}^{\text{II}}$  dominate over their hydroxido-species in the range  $2 \leq -\log_{10}\{[\text{H}^+]/c^\circ\} \leq 10$ , being most marked for  $\text{Cd}^{\text{II}}$ . It is emphasized, however, that the calculations for the  $\text{Cd}^{\text{II}}$ -carbonato system are based on rather poorly quantified stability constants (see below).

#### 4.3.1 Formation of $\text{CdCO}_3(\text{aq})$

Using ise potentiometry [74GAa] studied the formation of  $\text{CdCO}_3(\text{aq})$ , reaction 14, at 20 °C. Although results were obtained at several concentrations of  $\text{NaHCO}_3$  [2.5, 5.0, and 10 mmol  $\text{kg}^{-1}$ ] as the supporting electrolyte, due to the paucity of data at the lower concentrations only that obtained at the highest bicarbonate concentration ( $\log_{10} K_1 = 4.02 \pm 0.04$  at  $I_m = 0.01 \text{ mol kg}^{-1}$ ) appears to be reliable. Since the formation of  $\text{CdHCO}_3^+$  was not considered, this result can be regarded as a lower bound. Due to the low ionic strength used for the investigation, the result can be reasonably extrapolated to  $I_m = 0 \text{ mol kg}^{-1}$ . If the  $\Delta\epsilon I_m$  term in the SIT analysis is assumed to be negligible [2007PBa] then the following Provisional value is obtained:

$$\log_{10} K_1^\circ(\text{eq. 14, 293.15 K}) = 4.4 \pm 0.2$$

The data of [74GAa] indicate that the concentrations of  $\text{Cd}^{2+}$  and  $\text{CdCO}_3(\text{aq})$  are equal when  $[\text{HCO}_3^-]_{\text{T}} = 0.01 \text{ mol kg}^{-1}$  and  $-\log_{10}\{[\text{H}^+]/c^\circ\} = 8.24$ , from which it can be deduced that  $\log_{10} K(16) = -6.24$  at 20 °C and  $I_m = 0.01 \text{ mol kg}^{-1}$ .

The formation constant for reaction 14 has also been determined [84STE] at  $20 \pm 1$  °C in  $0.05 \text{ mol kg}^{-1} \text{ KNO}_3$ , using both  $\text{Cd}^{\text{II}}$ -ise potentiometry and anodic stripping voltammetry (ASV). However, the methodology and experimental conditions surrounding the ASV determination were rather poorly defined; therefore, the results are not considered reliable. The result obtained by ise was  $\log_{10} K_1(14) = 3.49 \pm 0.04$ . Due to the possible influence of ion-pairing between  $\text{Cd}^{2+}$  and  $\text{NO}_3^-$  this result is regarded as a lower bound. A SIT extrapolation to  $I_m = 0 \text{ mol kg}^{-1}$ , assuming  $\Delta\epsilon = 0$ , yields the Indicative value  $\log_{10} K_1^\circ(14) = 4.2 \pm 0.3$ .

Differential pulse polarography was used by [76BHa] to determine the formation constant  $\log_{10} K_1 \approx 3.5$  for reaction 14 at 25 °C in  $0.1 \text{ mol kg}^{-1} \text{ KNO}_3$ . The authors considered this result to be approximate only [76BHa] and, since ion-pairing of  $\text{Cd}^{2+}$  by  $\text{NO}_3^-$  and  $\text{HCO}_3^-$  was not considered, the result should represent a lower bound. A SIT extrapolation to  $I_m = 0 \text{ mol kg}^{-1}$ , assuming  $\Delta\epsilon = 0$ , but not considering the influence of nitrate ion pairing, yields  $\log_{10} K_1^\circ = 4.4 \pm 0.4$ , in reasonable agreement with the Indicative value derived above at 20 °C.

A value of  $\log_{10} K_1^\circ(14) = 4.7 \pm 0.1$  has been reported by [91RFa], based on measurements at an unspecified temperature and variable ionic strength. The reported constant was obtained from measurements at  $-\log_{10}\{[\text{H}^+]/c^\circ\} \approx 11$  and, although  $\text{Cd}(\text{OH})_2(\text{aq})$  formation appears to have been considered in the data interpretation, formation of  $\text{CdOH}^+$  was not. Due to ambiguities in experimental conditions and methods, the  $\log_{10} K_1$  result of [91RFa], although plausible, is not considered reliable.

#### 4.3.2 Formation of $\text{Cd}(\text{CO}_3)_2^{2-}$

From  $\text{Cd}^{\text{II}}$ -ise measurements at 20 °C, [84STE] obtained  $\log_{10} \beta_2 = 6.37 \pm 0.1$  ( $I_m = 0.05 \text{ mol kg}^{-1} \text{ KNO}_3$ ). In contrast to  $K_1$ , the equilibrium constant  $K_2$ , for formation of  $\text{Cd}(\text{CO}_3)_2^{2-}$  from  $\text{CdCO}_3(\text{aq})$



should not be influenced by nitrate ion-pairing. The formation constant obtained by [84STE] is  $\log_{10} K_2 = 2.88$ , while the value reported by [91RFa] at  $I_m = 0 \text{ mol kg}^{-1}$  is  $\log_{10} K_2^\circ = 1.78$ . Since reac-

tion 19 is isocoulombic, medium composition and ionic strength should have little effect on the magnitude of  $\log_{10} K_2$ , which indicates that these two results are in poor agreement. These  $\log_{10} K_2$  values [84STE, 91RFa] can also be compared with that for the corresponding  $\text{Pb}^{\text{II}}$  equilibrium,  $\log_{10} K_2^\circ = 3.7 \pm 0.7$  [2009PBa]. As the  $K_1^\circ$  results reported for  $\text{Pb}^{\text{II}}$  and  $\text{Cd}^{\text{II}}$  differ by two orders of magnitude, the difference of  $<1$  between the  $\log_{10} K_2$  value of [84STE] and the corresponding  $\text{Pb}^{\text{II}}$  result [2009PBa] suggests that the former is too high. Another insight comes from the comparison of  $\log_{10} K_2/K_1$  values for carbonato-complexes. These values are  $-2.9$  ( $\text{Pb}^{\text{II}}$ ) [2009PBa] and  $-3.3$  ( $\text{Cu}^{\text{II}}$ ) [2007PBa], while for  $\text{Cd}^{\text{II}}$  the calculated values are  $-2.6$  [91RFa] and  $-1.5$  [84STE], which also points to the [84STE] value of  $\log_{10} K_2$  being anomalously high.

Clearly, the formation constants for reactions 15 and 19 are very poorly defined by the available experimental data. Combining the  $\log_{10} K_2^\circ(19)$  result of [91RFa], at an unspecified temperature, with the Provisional value of  $\log_{10} K_1^\circ(14) = 4.4 \pm 0.2$  at  $20^\circ\text{C}$  gives  $\log_{10} \beta_2^\circ(15) = 6.2$ . The respective values for  $\text{Pb}^{\text{II}}$  and  $\text{Cu}^{\text{II}}$  are  $\log_{10} \beta_2^\circ = 10.13 \pm 0.24$  [2009PBa] and  $10.3 \pm 0.1$  [2007PBa].

#### 4.3.3 Formation of $\text{CdHCO}_3^+$

The  $\text{Cd}^{\text{II}}$ -carbonato formation constants, reactions 14 and 15, are much smaller (by 2 and 4 log units, respectively) than the corresponding values for  $\text{Cu}^{\text{II}}$  [2007PBa] and  $\text{Pb}^{\text{II}}$  [2009PBa]. It is reasonable to infer that the  $\text{Cd}^{\text{II}}$ -hydrogencarbonato complex will probably be less stable than those of  $\text{Cu}^{\text{II}}$  and  $\text{Pb}^{\text{II}}$ . However, there is considerable uncertainty in the equilibrium constant for the formation of  $\text{CdHCO}_3^+$ , reaction 17.

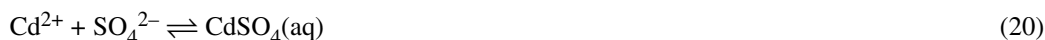
The value  $\log_{10} K(17) = 0.84 \pm 0.1$  ( $3.5 \text{ mol kg}^{-1} \text{ NaClO}_4$  and  $25^\circ\text{C}$ ) is derived when  $\log_{10} K(18) = -7.11$  ( $-7.04$  at  $I_c = 3.0 \text{ mol dm}^{-3}$  [92NEa]) is combined with  $\log_{10} K = 7.88$  for the reaction  $\text{H}^+ + \text{HCO}_3^- \rightleftharpoons \text{CO}_2(\text{g}) + \text{H}_2\text{O}$  obtained under the same conditions [58FNa]. Results for the analogous lead complex obtained by [92NEa] at the same temperature and ionic strength were used by [2009PBa] to calculate  $\log_{10} K(\text{PbHCO}_3^+) = 1.86 \pm 0.1$ . These values are consistent with the greater stability of the  $\text{Pb}^{\text{II}}$ -carbonato complex relative to its  $\text{Cd}^{\text{II}}$  analogue.

Reaction 17 was studied at  $20^\circ\text{C}$  and  $I_m = 0.05 \text{ mol kg}^{-1} \text{ KNO}_3$  [84STE]. Extrapolation of these results to zero ionic strength (assuming that the  $\Delta E I_m$  term in the SIT analysis is negligible) gave  $\log_{10} K^\circ(17) = 2.4 \pm 0.4$ . Comparison with values for the corresponding hydrogencarbonato-complexes of  $\text{Cu}^{\text{II}}$  ( $\log_{10} K^\circ = 1.8 \pm 0.1$  at  $25^\circ\text{C}$  [2007PBa]) and  $\text{Pb}^{\text{II}}$  ( $\log_{10} K = 1.86 \pm 0.1$  at  $25^\circ\text{C}$  and  $I_m = 3.5 \text{ mol kg}^{-1} \text{ NaClO}_4$  [2009PBa]), and with the results of [92NEa], suggests that the value of [84STE] is too large, and it is therefore rejected. The observations of [92NEa], if correct, suggest that  $\log_{10} K(17)$  for Cd should be smaller than the corresponding values for  $\text{Cu}^{\text{II}}$  and  $\text{Pb}^{\text{II}}$  by  $\sim 1$  log unit.

#### 4.4 The $\text{Cd}^{2+} + \text{SO}_4^{2-}$ system

Quantitative characterization of chemical speciation in relatively high-charge systems such as  $\text{Cd}^{2+} + \text{SO}_4^{2-}$  is complicated by a number of factors. Of particular importance is the activity coefficient variation in mixed  $\text{ClO}_4^- + \text{SO}_4^{2-}$  media at constant  $I$ , and the formation of solvent-separated (outer sphere) complexes. These problems have been discussed in detail in earlier parts of this series [2005PBa, 2007PBa] to which the reader is referred.

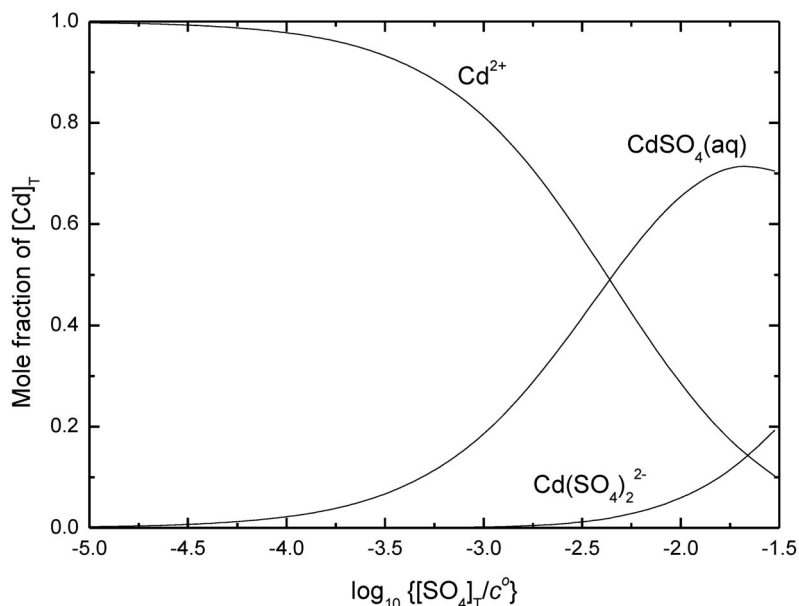
The stability constants for the formation of  $\text{Cd}^{2+}$ -sulfato complexes in homogenous solution, reactions 20 and 21



are relatively poorly characterized, except at very low ionic strengths (infinite dilution) [2010PET]. This is surprising because the required measurements should be relatively straightforward and the constants are of potential importance in natural water systems [89SAb].



The speciation diagram for the  $\text{Cd}^{2+} + \text{SO}_4^{2-}$  system, based on our Recommended and Indicative values given in Table 4 for  $K_1^\circ$  (reaction 20) and  $\beta_2^\circ$  (reaction 21) at  $I_m = 0 \text{ mol kg}^{-1}$  is shown in Fig. 4. Because of the marked decrease in each stability constant with increasing  $I_m$ , the calculations are truncated at  $[\text{SO}_4^{2-}]_T = 0.030 \text{ mol dm}^{-3}$ , which corresponds approximately to the standard seawater concentration. Note, however, that even at this low  $I_m$  the activity coefficients may deviate significantly from unity and the calculated results should be viewed with caution.



**Fig. 4** Speciation diagram for the ternary  $\text{Cd}^{2+} + \text{SO}_4^{2-}$  system as obtained from the Recommended and Provisional stability constants at  $25^\circ \text{C}$  and  $I_m = 0 \text{ mol kg}^{-1}$  (Table 4), calculated for  $[\text{Cd}]_T = 10^{-6} \text{ mol dm}^{-3}$ . No corrections were made for ionic strength-dependent changes in formation constants.

#### 4.4.1 Formation of $\text{CdSO}_4(\text{aq})$

Reaction 20 is the only significant equilibrium between  $\text{Cd}^{2+}$  and  $\text{SO}_4^{2-}$  relevant to typical natural water conditions. The accepted stability constants are summarized in Table A2-8. At low concentrations (ionic strengths) these values were determined mostly by conductivity measurements [38DAa, 76KAa, 81YYa, 84BAR, 85SGd]. Although these data are of high quality, well-recognized theoretical difficulties [2005BES, 2006MAR] make accurate derivation of  $\log_{10} K_1^\circ$  problematic. Similar considerations apply to the interpretation of activity coefficient data [38DAa, 72PIa, 2006MAR].

The seven accepted values of the formation constant for  $\text{CdSO}_4(\text{aq})$  at  $I_m = 0 \text{ mol kg}^{-1}$  (Table A2-8) give a weighted average of

$$\log_{10} K_1^\circ (\text{eq. 20, 298.15 K}) = 2.36 \pm 0.04$$

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

The value of  $\log_{10} K_1^\circ$  obtained via the normally reliable potentiometric method [73FCa] is rejected, because of the long extrapolation involved (the data were measured at  $I_c \geq 0.5 \text{ mol dm}^{-3}$ ) and because the value is inconsistent with those from the conductivity studies. Stability constants obtained by Raman spectroscopy [94RIa, 98RUD] are rejected because the technique is inappropriate if solvent-separated complexes (ion pairs) contribute to the speciation, as discussed in detail elsewhere

[2003RUD, 2004BCa, 2006HEF]. While no quantitative dielectric or ultrasonic relaxation study of solvent-separated species has been reported, qualitative investigations [65POa, 74BER, 84BAR] have clearly indicated their presence. It is relevant to note here that constants reported for “inner plus outer sphere” complexes, typically determined by UV–vis spectroscopy, have been rejected throughout this series as they represent an incomplete description of the equilibria involved. A full description using spectroscopic methods requires quantification of “outer-outer” sphere, outer sphere, and inner sphere complexes [2003RUD, 2006HEF].

At finite  $I$  there are comparatively few equilibrium data available for reaction 20 (Table A2-8). The majority of the accepted values have been determined by one group [71FCb, 71FCc, 73FCa, 75FCa], mostly using Cd(Hg) potentiometry in LiClO<sub>4</sub> media. The reported constants vary somewhat amongst these publications and do not constitute independent verification. To minimize overweighting, only the average values from these publications are given in Table A2-8. The few measurements reported by other researchers at finite ionic strengths were obtained in NaClO<sub>4</sub> media [41LEa, 52LEa, 69BGa, 89NWA]. These values are in fair agreement with those of [71FCb, 71FCc, 73FCa, 75FCa] although the differences are much greater than the claimed uncertainties (Table A2-8).

The SIT regression of the accepted results for both NaClO<sub>4</sub> and LiClO<sub>4</sub> media (Fig. A3-8) yields  $\log_{10} K_1^\circ(\text{eq. 20, 298.15 K}) = 2.41 \pm 0.07$ , which is consistent with (but less accurate than) the Recommended value discussed above. The derived value  $\Delta\epsilon(20) = -(0.09 \pm 0.02) \text{ kg mol}^{-1}$  can be regarded as Provisional.

#### 4.4.2 Formation of Cd(SO<sub>4</sub>)<sub>2</sub><sup>2-</sup>

While some M<sup>2+</sup> + SO<sub>4</sub><sup>2-</sup> systems form M(SO<sub>4</sub>)<sub>2</sub><sup>2-</sup> complexes [2005CHE, 2006ARa], others such as Cu<sup>2+</sup> + SO<sub>4</sub><sup>2-</sup> [2007PBA] and Pb<sup>2+</sup> + SO<sub>4</sub><sup>2-</sup> [2009PBA] appear not to. Data for equilibrium 21 are summarized in Table A2-9. At first sight, these results appear to provide conclusive evidence for the existence of Cd(SO<sub>4</sub>)<sub>2</sub><sup>2-</sup>. However, virtually all of these values were reported by one group [71FCb, 71FCc, 73FCa, 75FCa] as part of a very dubious speciation scheme (see Section 4.4.3). The only independently determined values for this complex are (a) an approximate value of  $\beta_2^\circ$  derived by Pitzer [72PIa] from an analysis of various thermodynamic data, and (b) an early experimental result reported by Leden [41LEa, 43LEa] that was subsequently queried by the author [52LEa] and others [54FRO]. Analogous to the Cu<sup>2+</sup> + SO<sub>4</sub><sup>2-</sup> and Pb<sup>2+</sup> + SO<sub>4</sub><sup>2-</sup> systems [2007PBA, 2009PBA], the apparent evidence for Cd(SO<sub>4</sub>)<sub>2</sub><sup>2-</sup> may simply reflect changes in activity coefficients when there is significant replacement of the medium anion (ClO<sub>4</sub><sup>-</sup>) by SO<sub>4</sub><sup>2-</sup>. Accordingly, pending further investigation, all the  $\log_{10} \beta_2$  values in Table A2-9 should be considered as indicative only.

The SIT regression of the combined data for NaClO<sub>4</sub> and LiClO<sub>4</sub> media (Fig. A3-9) yields the Indicative values  $\log_{10} \beta_2^\circ(\text{eq. 21, 298.15 K}) = 3.32 \pm 0.16$  and  $\Delta\epsilon(21) = (0.11 \pm 0.05) \text{ kg mol}^{-1}$ .

#### 4.4.3 Formation of higher-order and mixed complexes

The formation of higher-order complexes, Cd(SO<sub>4</sub>)<sub>*n*</sub><sup>(2*n*-2)-</sup> with  $3 \leq n \leq 5$  has been claimed in the extensive publications on the Cd<sup>2+</sup> + SO<sub>4</sub><sup>2-</sup> system by Fedorov et al. [71FCb, 71FCc, 73FCa, 75FCa]. Apart from the value of  $\beta_3$  reported by Leden [43LEa, 52LEa] but, as already noted, discounted by himself and others [52LEa, 54FRO], there are no independent data that support the existence of these complexes in aqueous solution. The formation of complexes with  $n > 2$  seems very unlikely on charge grounds alone, and also by analogy with better-studied analogous systems [2007PBA]. Thus, all reported stability constants for Cd(SO<sub>4</sub>)<sub>*n*</sub><sup>(2*n*-2)-</sup> with  $n > 2$  were rejected. Similar comments can be made regarding the plethora of mixed Cd<sup>2+</sup> + Cl<sup>-</sup> + SO<sub>4</sub><sup>2-</sup> complexes also reported by Fedorov et al. [71FCb].

### 4.5 The Cd<sup>2+</sup> + PO<sub>4</sub><sup>3-</sup> system

Difficulties in quantifying the speciation and stability constants in M<sup>2+</sup> + H<sup>+</sup> + PO<sub>4</sub><sup>3-</sup> systems have been discussed in the earlier parts of this series [2005PBA, 2007PBA, 2009PBA]. In the *SC-Database*

[2010PET] there are only nine references for the homogeneous system  $\text{Cd}^{2+} + \text{PO}_4^{3-}$ . The composition of the identified water-soluble phosphate complexes strongly depends on the pH range, the total concentrations and the concentration ratios,  $[\text{M}^{\text{II}}]_{\text{T}}:[\text{PO}_4^{3-}]_{\text{T}}$ , that are used. In the presence of  $\text{Cd}^{\text{II}}$  the formation of several protonated *mono*- and *bis*-complexes  $\text{CdH}_2\text{PO}_4^+$ ,  $\text{Cd}(\text{H}_2\text{PO}_4)_2(\text{aq})$ ,  $\text{CdHPO}_4(\text{aq})$ ,  $\text{Cd}(\text{HPO}_4)_2^{2-}$ , and  $\text{Cd}(\text{H}_2\text{PO}_4)(\text{HPO}_4)^-$  have been proposed (Table A2-10).

The available data at 25 °C allow the assignment of only two Provisional values. The constant reported by [74RMb] for reaction 22



( $\log_{10} K = 2.91 \pm 0.01$ ;  $I_m = 0.101 \text{ mol kg}^{-1} \text{ NaClO}_4$ ) is in acceptable agreement with that determined by Sigel et al. [96SSa] ( $\log_{10} K = 2.79 \pm 0.03$ ;  $I_m = 0.101 \text{ mol kg}^{-1} \text{ NaNO}_3$ ). The lower value reported by [96SSa] is consistent with the relatively strong complexing of  $\text{Cd}^{\text{II}}$  by  $\text{NO}_3^-$  [2010PET]. On the basis of these results, we assign the Provisional value at 25 °C and  $I_m = 0.10 \text{ mol kg}^{-1}$

$$\log_{10} K(\text{eq. 22}; 298.15 \text{ K}) = 2.85 \pm 0.20$$

From this value, and the protonation constant for  $\text{PO}_4^{3-}$  in  $I_m = 0.10 \text{ mol kg}^{-1} \text{ NaNO}_3$  ( $\log_{10} K_1 = 11.68 \pm 0.05$  [96SSa]), we derive  $\log_{10} \beta_{1,1,1}$  ( $I_m = 0.101 \text{ mol kg}^{-1}$ ) =  $14.53 \pm 0.20$  at 25 °C for reaction 23



The constants reported for the formation of  $\text{CdH}_2\text{PO}_4^+$  (reaction 24) in  $3.0 \text{ mol dm}^{-3} \text{ NaClO}_4$  medium



are in excellent agreement (Table A2-10). This allowed the assignment of the Provisional value ( $I_c = 3.0 \text{ mol dm}^{-3} \text{ NaClO}_4$ )

$$\log_{10} K(\text{eq. 24}; 298.15 \text{ K}) = 0.76 \pm 0.20.$$

A value of  $\log_{10} K = 7.04 \pm 0.1$  has been reported [73HSa] for reaction 25



in  $3.0 \text{ mol dm}^{-3} \text{ NaClO}_4$  at 25 °C. From the protonation constant for  $\text{HPO}_4^{2-}$  under these conditions ( $\log_{10} K = 6.27$  [2005PBA]) we calculate  $\log_{10} K(24) = 0.77 \pm 0.16$ , in excellent agreement with the assigned Provisional value.

Using the reported protonation constants for  $\text{PO}_4^{3-}$  in  $3.0 \text{ mol dm}^{-3} \text{ NaClO}_4$  ( $\log_{10} K_1 = 10.85$ ;  $\log_{10} K_2 = 6.2$ ; [69BSd]), the above values correspond to  $\log_{10} \beta_{1,2,1}$  ( $I_m = 3.0 \text{ mol dm}^{-3}$ ) =  $17.88 \pm 0.20$  at 25 °C for reaction 26



The stability constants reported in [74RMb] and [94IPa] for the formation of the other phosphate complexes can only be considered as indicative.

## 5. EVALUATION OF EQUILIBRIUM CONSTANTS (HETEROGENEOUS REACTIONS)

### 5.1 The $\text{Cd}^{2+} + \text{OH}^-$ system

There have been few reliable studies on the solubility of cadmium hydroxide,  $\text{Cd}(\text{OH})_2(\text{s})$ , reaction 27



The data are summarized in Table A2-11. Three of these values were determined in dilute solutions [28PIa, 51FRb, 91RFa]. The fourth was determined in 3.0 mol dm<sup>-3</sup> NaClO<sub>4</sub> [559SCa] but was extrapolated by the authors to  $I_m = 0$  mol kg<sup>-1</sup>. From the data at  $I_m = 0$  mol kg<sup>-1</sup> the equilibrium constant for reaction 27 at zero ionic strength is calculated as  $\log_{10} K_{s0}^\circ = -14.32 \pm 0.08$ . The equilibrium constant  $K_{s0}^\circ$  can also be calculated from the ionic strength dependent data (Table A2-11) by using the SIT relationship derived from equations 2 and 27

$$\log_{10} K_{s0} - 6D = \log_{10} K_{s0}^\circ - \Delta\epsilon I_m$$

The regression (Fig. A3-10) yields the value

$$\log_{10} K_{s0}^\circ(\text{eq. 27, 298.15 K}) = -14.28 \pm 0.12$$

which is in excellent agreement with the above average and is Recommended. The value for  $\Delta\epsilon(27)$  in NaClO<sub>4</sub> media is  $(0.31 \pm 0.04)$  kg mol<sup>-1</sup>. Generally, four values representing effectively only two ionic strengths, i.e., near zero and 3.0 mol dm<sup>-3</sup> NaClO<sub>4</sub> would be considered too few to conduct an analysis using the SIT model. However, the derived  $\Delta\epsilon$  value leads to the ion interaction parameter  $\epsilon(\text{Cd}^{2+}, \text{ClO}_4^-) = 0.23 \pm 0.04$  kg mol<sup>-1</sup> which is consistent with those reported for other divalent cations with the perchlorate ion [97GRE].

For reaction 28 the value calculated for  $\log_{10} {}^*K_{s0}^\circ$  is  $13.72 \pm 0.12$ .



This value is accepted as Provisional and is consistent with the value of 13.65 given in the reviews by Sadiq [89SAb] and Baes and Mesmer [76BMa].

The solubility data reported by Guebeli and Taillon [71GTa] for Cd(OH)<sub>2</sub>(s) at 25 °C and 1.0 mol dm<sup>-3</sup> NaClO<sub>4</sub> have not been used in the present evaluation. These data were acquired using an inappropriate value for the dissociation constant of water. More importantly, there also seems to be an offset in the pH ( $-\log_{10} \{[\text{H}^+]/c^\circ\}$ ) at which the formation of the hydrolysis species, CdOH<sup>+</sup> and Cd(OH)<sub>4</sub><sup>2-</sup>, increases the solubility of Cd(OH)<sub>2</sub>(s) at low and high pH respectively. However, this offset should not affect the constants  $K_{s1}$ ,  $K_{s2}$ , and  $K_{s4}$  derived in this work (defined in Section 8.1) and these constants have been used in the present study in conjunction with our solubility constant for Cd(OH)<sub>2</sub>(s) to determine the hydrolysis constants,  ${}^*K_1$ ,  ${}^*\beta_2$ , and  ${}^*\beta_4$ .

## 5.2 The Cd<sup>2+</sup> + CO<sub>3</sub><sup>2-</sup> system

### 5.2.1 Solubility of CdCO<sub>3</sub>(s) (otavite)

Solubility constants have been reported [65GSa, 91KHa] for the acid dissolution of CdCO<sub>3</sub>(s) (otavite) in 3.5 and 3.0 mol kg<sup>-1</sup> NaClO<sub>4</sub> at 25 °C. For reaction 29



the reported equilibrium quotients in the form  $\log_{10} \{[\text{Cd}^{2+}]p_{\text{CO}_2}[\text{H}^+]^{-2}(c^\circ/p^\circ)\}$  were  $\log_{10} {}^*K_{\text{ps}0} = 6.40 \pm 0.15$  and  $6.41 \pm 0.02$ , respectively.

Results for reaction 29 for ionic strengths 0.15 to 5.35 mol kg<sup>-1</sup> (NaClO<sub>4</sub>) at 25 °C have been reported by [99GPa] (Table A2-12). A SIT analysis using these data, along with the results of [65GSa] and [91KHa], Fig. A3-11, produced the Recommended value

$$\log_{10} {}^*K_{\text{ps}0}^\circ(\text{eq. 29, 298.15 K}) = 6.08 \pm 0.03$$

and  $\Delta\epsilon(29) = 0.058 \pm 0.009$  kg mol<sup>-1</sup>. This value of  $\log_{10} {}^*K_{\text{ps}0}$  is in excellent agreement with that selected on the basis of a critical evaluation of a much wider range of solubility and other data ( $\log_{10} {}^*K_{\text{ps}0} = 6.11 \pm 0.03$ ) as part of the IUPAC-NIST *Solubility Data Series* [H. Gamsjäger et al. *J. Phys. Chem. Ref. Data*, in preparation].

The solubility constant product for otavite has been reported [93SPa] for  $I_m = 0 \text{ mol kg}^{-1}$  and 25 °C, based on experiments at low ionic strength (0.0016 – 0.109 mol kg<sup>-1</sup> KClO<sub>4</sub>). For the solubility reaction written as



[93SPa] reported  $\log_{10} K_{s0}^\circ = [\text{Cd}^{2+}][\text{CO}_3^{2-}]/(c^\circ)^2 = -12.1 \pm 0.10$ . This value can be compared with our Recommended value,  $\log_{10} {}^*K_{ps0}^\circ = 6.08 \pm 0.03$  ( $I_m = 0 \text{ mol kg}^{-1}$  and 25 °C), via the CODATA value for the equilibrium  $\text{CO}_2(\text{g}) + \text{H}_2\text{O} \rightleftharpoons 2\text{H}^+ + \text{CO}_3^{2-}$  ( $\log_{10} K^\circ = -18.143$ ; [82WAG]), viz.  $\log_{10} K_{s0}^\circ = \log_{10} K^\circ + \log_{10} {}^*K_{ps0}^\circ = -12.06 \pm 0.04$  ( $I_m = 0 \text{ mol kg}^{-1}$ , 25 °C). Thus, the reported results of [93SPa] and [99GPa] are in good agreement within the stated uncertainties. The value

$$\log_{10} K_{s0}^\circ(\text{eq. 30, 298.15 K}) = -12.06 \pm 0.04$$

is Recommended.

The  $\log_{10} K_{s0}^\circ$  result of [91RFa] is smaller than that of [93SPa] by 0.14. Due to uncertainties in experimental conditions and methods, the result of [91RFa] is rejected.

### 5.3 The Cd<sup>2+</sup> + SO<sub>4</sub><sup>2-</sup> system

Under conditions typically encountered in the natural environment, the equilibrium form of solid cadmium(II) sulfate is the monohydrate, CdSO<sub>4</sub>·H<sub>2</sub>O(s). The solubility of this salt is high (>3 mol kg<sup>-1</sup> in water at 25 °C) and increases rapidly with temperature [65LIN]. Therefore, it will not influence Cd<sup>II</sup> speciation in natural waters. A number of “basic cadmium sulfates” have also been reported [45FEa, 89SAb, 2010PET] but their solubility and stoichiometry in contact with saturated aqueous solutions have not been well characterized nor confirmed by independent studies. By comparison with the analogous Hg<sup>II</sup>, Cu<sup>II</sup>, and Pb<sup>II</sup> systems [2005Pba, 2007Pba, 2009Pba], the solubilities of such mixed salts are probably not sufficiently low to influence the speciation in typical natural water systems. Therefore, they have not been considered further in this review.

### 5.4 The Cd<sup>2+</sup>+ PO<sub>4</sub><sup>3-</sup> system

The formation of insoluble phosphates is one of the most effective methods for cadmium immobilization in soils [2008MAT]. The effectiveness is strongly dependent on pH, with the largest reduction in cadmium concentrations achieved at pH = 6.75 to 9.00, where a mixture of Cd(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>(s), Cd<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>(s) and Cd<sub>5</sub>H<sub>2</sub>(PO<sub>4</sub>)<sub>4</sub>·4H<sub>2</sub>O(s) is formed [2008MAT]. At pH <5 and pH >9 the formation of Cd<sub>5</sub>H<sub>2</sub>(PO<sub>4</sub>)<sub>4</sub>·4H<sub>2</sub>O(s) and amorphous cadmium phosphates, respectively, was observed [2008MAT]. The few available quantitative data for the solubility of cadmium phosphates support this picture.

The solubility constants reported for Cd<sub>5</sub>H<sub>2</sub>(PO<sub>4</sub>)<sub>4</sub>·4H<sub>2</sub>O(s), reaction 31,



are in poor agreement:  $\log_{10} {}^*K_s(31) = -30.9 \pm 0.3$  ( $I_m = 0.0 \text{ mol kg}^{-1}$ , 37 °C; [2001AMa]) and  $\log_{10} {}^*K_s(31) = -25.4 \pm 0.3$  ( $I_c = 3.0 \text{ mol dm}^{-3}$  NaClO<sub>4</sub>, 25 °C; [73Hsa]) even after considering the contribution of the term  $\Delta z^2 D$  (eq. 2) in which  $\Delta z^2 = 34$  for reaction 31. The only value reported for reaction 32



indicates a considerably lower solubility for this species. From the solubility at 20 °C in media of low but varying ionic strength [61CAa] derived  $\log_{10} K_{s0}(32) = -36.9 \pm 0.4$ ; however, complex formation between Cd<sup>2+</sup> and PO<sub>4</sub><sup>3-</sup> was not taken into account, and therefore the reported constant can be considered only as a rough estimate.

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

### 6.1 The $\text{Cd}^{2+} + \text{OH}^-$ system

There are few reliable data for reaction enthalpies in the system  $\text{Cd}^{2+} + \text{OH}^-$ . Arnek [67AKc, 70ARb] reported enthalpy values based on the stability constants of Biedermann and Ciavatta [62BCb] that were obtained at 25 °C in 3 mol dm<sup>-3</sup> LiClO<sub>4</sub>. Arnek's values (expressed as the average of the two values presented in the two studies, which agree within the uncertainties of the measurements) are 54.8, 45.6, and 169 kJ mol<sup>-1</sup> for formation of CdOH<sup>+</sup> (reaction 4), Cd<sub>2</sub>OH<sup>3+</sup> (reaction 9), and Cd<sub>4</sub>(OH)<sub>4</sub><sup>4+</sup> respectively. The reaction enthalpy values for formation of CdOH<sup>+</sup> and Cd<sub>2</sub>OH<sup>3+</sup> [67AKc, 70ARb] are selected in this review and assigned Provisional status. The reaction enthalpy for Cd<sub>4</sub>(OH)<sub>4</sub><sup>4+</sup> is not accepted as further evidence for the formation of this species is required (see Section 4.1.1).

Latysheva and Goryanina [62LGa] determined  $\Delta_r H = -88.7$  kJ mol<sup>-1</sup> for the reaction  $\text{Cd}(\text{OH})_2(\text{s}) + 2\text{H}^+ \rightleftharpoons \text{Cd}^{2+} + 2\text{H}_2\text{O}$  at 25 °C and in 8.76 mol dm<sup>-3</sup> NaClO<sub>4</sub>. For the same reaction, Shchukarev et al. [59SLc] determined a value of  $\Delta_r H = -94.6$  kJ mol<sup>-1</sup> also at 25 °C but at zero ionic strength. These values are in reasonable agreement, given the large difference in ionic strength; the latter value is accepted, with a Provisional status, as the standard (infinite dilution) value. The accepted enthalpies are assigned uncertainties of  $\pm 2$  kJ mol<sup>-1</sup>.

The stability constants determined by Burkov et al. [77BGa, 77BGb] at 60 °C in 3 mol dm<sup>-3</sup> NaClO<sub>4</sub> for the species CdOH<sup>+</sup> and Cd<sub>2</sub>OH<sup>3+</sup> can be compared with those selected in the present work at 25 °C. This is achieved by application of the van't Hoff equation (assuming  $\Delta_r C_p = 0$ ) using the enthalpy data of Arnek [67AKc, 70ARb] and the stability constants at 25 °C and 3 mol dm<sup>-3</sup> NaClO<sub>4</sub> calculated from the SIT values determined in this review. This leads to the respective values  $\log_{10} {}^*K_1(4) = -9.2$  and  $\log_{10} {}^*\beta_{2,1}(9) = -8.3$  for 60 °C and 3 mol dm<sup>-3</sup> NaClO<sub>4</sub>. While the latter value agrees well with that reported by Burkov et al. [77BGa, 77BGb] ( $\log_{10} {}^*\beta_{2,1}(9) = -8.1$ ), the former is significantly more positive ( $\log_{10} {}^*K_1(4) = -10$ ; [77BGa, 77BGb]). Further studies will be required to resolve these differences.

### 6.2 The $\text{Cd}^{2+} + \text{Cl}^-$ system

Reaction enthalpies for the formation of CdCl<sup>+</sup> have been published by many authors, using direct calorimetry [66GEb, 67MFa, 68GJc, 72FKc] and the temperature variation of the stability constants [49KIa, 53Vda, 62Bdc, 69SPa, 81MBa]. As the former technique generally gives more reliable results [58SIL], and as the reaction enthalpies are very small and therefore have large uncertainties, the latter have been rejected. The accepted values are presented in Table A2-13.

Direct calorimetric determinations have been reported by Swedish [66GEb, 68GJc] and Russian [67MFa, 72FKc] groups. The data from these groups are broadly consistent, although the ionic strength dependence reported by the latter group is larger. Due to the very detailed description of the experimental procedures by [66GEb, 68GJc], we give their values a higher weighting in the regression analysis (an assigned uncertainty of  $\pm 1.0$  kJ mol<sup>-1</sup>, compared with  $\pm 1.5$  kJ mol<sup>-1</sup> for the results from [67MFa, 72FKc]). The uncertainties assigned to the accepted values include our estimates of possible systematic errors.

Figure A3-12 shows the weighted linear regression SIT analysis for reaction 10 enthalpies. The resulting standard reaction enthalpy is Recommended

$$\Delta_r H^\circ(10, 298.15 \text{ K}) = 3.3 \pm 0.6 \text{ kJ mol}^{-1}$$

and the reaction ion interaction coefficient for the enthalpy, derived from the slope of the regression line, is  $\Delta \epsilon_L(10) = (0.6 \pm 0.3) \times 10^{-3} \text{ kg K}^{-1} \text{ mol}^{-1}$ .

Calorimetric data for the formation of CdCl<sub>2</sub>(aq), reaction 11, have been published by the same authors. Again, the values from the Swedish group [66GEb, 68GJc] show an ionic strength dependence

distinctly smaller than that of the Russian group [67MFa, 72FKc]. We assign uncertainties accordingly as:  $\pm 2.0$  and  $\pm 3.0$  kJ mol<sup>-1</sup>, respectively. The weighted linear regression, Fig. A3-13, leads to the following Provisional value:

$$\Delta_r H^\circ(11, 298.15 \text{ K}) = 7.9 \pm 1.4 \text{ kJ mol}^{-1}$$

and a reaction ion interaction coefficient of  $\Delta \epsilon_L(11) = (2.1 \pm 0.6) \times 10^{-3} \text{ kg K}^{-1} \text{ mol}^{-1}$ .

It may be argued that the data plotted in Fig. A3-13 according to the SIT relationship tend towards a nonlinear ionic strength dependence (which would result in a slightly lower value at  $I_m = 0$ ). However, the estimated uncertainties and the scatter of these data are too large for a reliable evaluation of any possible curvature. Hence, we accept the above linear regression but qualify the resultant reaction enthalpy obtained from the intercept as Provisional.

Many determinations of the reaction enthalpies for the formation of  $\text{CdCl}_3^-$ , reaction 12, have been published [49KIa, 53VDA, 66GEB, 67MFa, 68GJc, 72FKc] and  $\text{CdCl}_4^{2-}$  [67FMA, 72FKc]. However, the data show considerable scatter, which may relate to the minor contribution of these weak complexes to solution composition (Section 4.2.3 and Fig. 2), and none has been selected for this review.

### 6.3 The $\text{Cd}^{2+} + \text{CO}_3^{2-}$ system

Investigation of the temperature dependence of  $\text{CdCO}_3(\text{s})$  (otavite) solubility, reaction 29, in 1 mol kg<sup>-1</sup>  $\text{NaClO}_4$ , over a temperature range between 25 and 75 °C [99GPa], indicated that  $*K_{\text{ps0}}$  is constant within experimental error. Similarly, although otavite solubility from 5 to 50 °C showed a slight maximum at 25 °C [93SPa], the observed differences were only marginally larger than experimental uncertainty. Since this marginal difference was not seen in the data of [93SPa], it is reasonable to conclude that the reaction enthalpy for equilibrium 29 is approximately zero between 5 and 75 °C. A similar conclusion was reached in the critical evaluation of H. Gamsjäger et al. [*J. Phys. Chem. Ref. Data*, in preparation.]

### 6.4 The $\text{Cd}^{2+} + \text{SO}_4^{2-}$ system

#### 6.4.1 Formation of $\text{CdSO}_4(\text{aq})$

The enthalpy change for the formation of  $\text{CdSO}_4(\text{aq})$  has been extensively studied using a range of approaches (Table A2-14). The techniques employed include (a) titration calorimetry, both with [73POa, 78ARa] and without [69BGa, 69IEe] independent determination of  $K_1$ , (b) heats of dilution [70LAe, 72PIa], and (c) the variation of  $K_1$  with temperature (using potentiometric [73FCa] or conductometric [76KAA, 81YYa, 84BAR] data). The problems associated with the quantification of  $\Delta_r H(\text{CdSO}_4(\text{aq}))$  are essentially the same as those discussed previously for  $\text{CuSO}_4(\text{aq})$  [2007PBA] and therefore will not be considered in detail here. However, it is important to note that, because of strong correlations between  $K_1$ ,  $\Delta_r H$  and the activity coefficient model adopted [73POa], the independent determination of  $K_1$  is more reliable than the popular “entropy titration” technique [69IEe].

At infinite dilution ( $I_m = 0$ ), the six accepted reaction enthalpy values (Table A2-14) give unweighted average values  $\Delta_r H^\circ = 8.3 \pm 0.5$  kJ mol<sup>-1</sup> and  $\Delta_r S^\circ = 72 \pm 2$  J K<sup>-1</sup> mol<sup>-1</sup>. These values are Recommended. Note that the values of [69IEe] and [73POa] are rejected as they are respectively too high and too low (by  $>3\sigma$ ) with respect to this average. From the thermodynamic relationship  $\Delta_r G^\circ = -RT \ln K^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$  we derive  $\Delta_r G^\circ = -13.15 \pm 1.1$  kJ mol<sup>-1</sup> and thus  $\log_{10} K_1^\circ = 2.30 \pm 0.20$  at 25 °C, which is consistent with the Recommended value of  $\log_{10} K_1^\circ = 2.36 \pm 0.04$  (Section 4.4.1).

At finite  $I$ , most of the available reaction enthalpy values (Table A2-14) have been derived from potentiometric  $K(T)$  data [73FCa]. While the real uncertainties in these results are probably quite high, the values are in fair agreement with independent calorimetric data where comparison is possible

[69BGa]. The calorimetric value for  $\Delta_r H$  at  $I = 0.5 \text{ mol dm}^{-3}$  [78ARa] is probably low but there are insufficient alternative data to justify its rejection.

The SIT regression of the combined reaction enthalpy data for  $\text{NaClO}_4$  and  $\text{LiClO}_4$  media (Fig. A3-14) yields  $\Delta_r H^\circ(\text{eq. 20}, 298.15 \text{ K}) = (9.2 \pm 1.9) \text{ kJ mol}^{-1}$  and  $\Delta \varepsilon_L(20) = (1.8 \pm 1.2) \times 10^{-3} \text{ kg K}^{-1} \text{ mol}^{-1}$ , with the former being consistent with (but less precise than) the above Recommended value.

#### 6.4.2 Formation of $\text{Cd}(\text{SO}_4)_2^{2-}$

The only enthalpy and entropy data available for the formation of  $\text{Cd}(\text{SO}_4)_2^{2-}$  are those derived via the less reliable  $K(T)$  method [73FCa]. Because of doubts about the quality of the stability constant data for this complex (Section 4.4.2) and the speciation model adopted (Section 4.4.3), the enthalpy and entropy values listed in Table A2-15 have been assigned rather large uncertainties and should be regarded as indicative only.

### 7. SPECIATION IN MULTICOMPONENT SYSTEMS: $\text{Cd}^{2+} + \text{Cl}^- + \text{CO}_3^{2-} + \text{PO}_4^{3-} + \text{SO}_4^{2-}$

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,  $a(\text{H}_2\text{O})$ , 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 (<[http://www.winsgw.se/WinSGW\\_eng.htm](http://www.winsgw.se/WinSGW_eng.htm)>), 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 minimal within the prescribed pH ranges.

#### 7.1 Fresh water in equilibrium with $\text{CO}_2(\text{g})$

To illustrate the speciation of  $\text{Cd}^{\text{II}}$  in representative fresh water in equilibrium with  $\text{CO}_2(\text{g})$ , the total concentration of  $\text{Cd}^{\text{II}}$  was set to  $1 \text{ nmol dm}^{-3}$  and it was assumed that the system was in equilibrium with air having a  $\text{CO}_2$  fugacity of  $10^{-3.5} \text{ bar}$ . Total concentrations of inorganic anions were those typically found in fresh water [93MOR]:  $[\text{Cl}^-]_{\text{T}} = 0.23 \text{ mmol dm}^{-3}$ ,  $[\text{SO}_4^{2-}]_{\text{T}} = 0.42 \text{ mmol dm}^{-3}$ , and  $[\text{HPO}_4^{2-}]_{\text{T}} = 0.7 \text{ } \mu\text{mol dm}^{-3}$ . Furthermore,  $-\log_{10} \{[\text{H}^+]/c^\circ\}$  was allowed to vary between 4.98 and 8.96 (ca. pH 5.0–9.0); in this range the ionic strength is approximately constant, ca.  $I_c = 0.0015 \text{ mol dm}^{-3}$  up to  $-\log_{10} \{[\text{H}^+]/c^\circ\} = 7$ , and  $0.008 \text{ mol dm}^{-3}$  at  $-\log_{10} \{[\text{H}^+]/c^\circ\} = 9$ , an increase due to the increase in  $[\text{HCO}_3^-]$  and  $[\text{CO}_3^{2-}]$  at constant  $f(\text{CO}_2)$ .

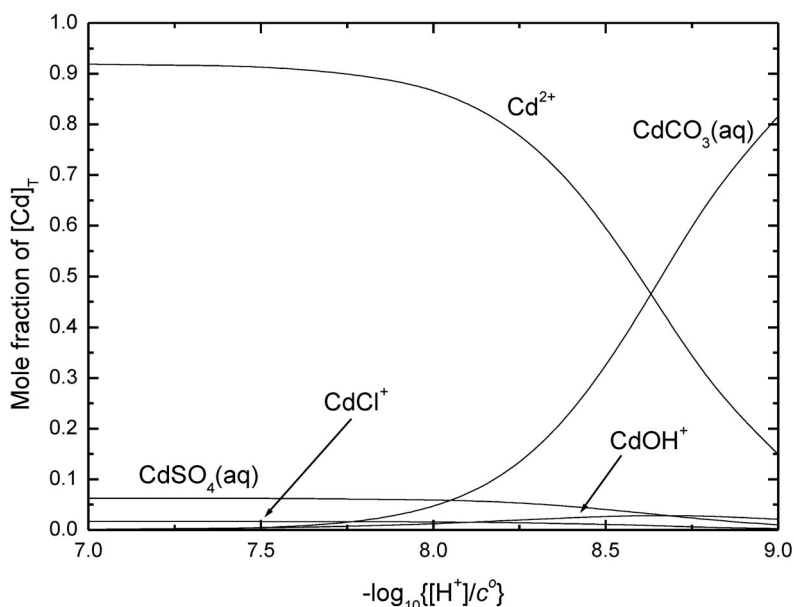
The stability constants applicable at  $I_c = 0.0015 \text{ mol dm}^{-3}$  for the major species are shown in Table 6. Note that although the calculations included all of the species critically evaluated in this review, Table 6 includes only those species that make a significant contribution to the speciation of  $\text{Cd}^{\text{II}}$  in the two media considered. The constants are shown for the equilibrium reactions as defined in this review and also in the format used in the speciation calculations, i.e., in terms of the component species  $\text{H}_2\text{CO}_3(\text{aq})$  with  $[\text{H}_2\text{CO}_3(\text{aq})]_{\text{T}} = [\text{CO}_2(\text{aq})] + [\text{H}_2\text{CO}_3(\text{aq})]$ . The reported  $\Delta \varepsilon$  values apply to  $\text{NaClO}_4$  media. For calculations in fresh water media of low ionic strength, (i) the use of  $\Delta \varepsilon(\text{NaClO}_4)$  values has minimal effect, and (ii) the activity of water can be set equal to one.



**Table 6** Stability constants for species critical to the speciation of Cd<sup>II</sup> in fresh water and seawater at 25 °C. Refer to [2009PBA] for the data for Mg<sup>2+</sup> and Ca<sup>2+</sup> complexes.

Reaction	Medium ionic strength $I_c/\text{mol dm}^{-3}$		
	$\log_{10} K^\circ$ ( $I_c = 0$ )	$\log_{10} K$ ( $I_c = 0.0015$ )	$\log_{10} K$ ( $I_c = 0.67$ )
$\text{Cd}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{CdOH}^+ + \text{H}^+$	-9.81	-9.85	-10.14
$\text{Cd}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Cd}(\text{OH})_2(\text{aq}) + 2\text{H}^+$	-20.19	-20.23	-20.59
$\text{Cd}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{CdCO}_3(\text{aq})$	4.4	4.25	2.72
$\text{Cd}^{2+} + \text{H}_2\text{CO}_3 \rightleftharpoons \text{CdCO}_3(\text{aq}) + 2\text{H}^+$	-12.29	-12.33	-12.80
$\text{Cd}^{2+} + 2\text{CO}_3^{2-} \rightleftharpoons \text{Cd}(\text{CO}_3)_2^{2-}$	6.2	6.06	4.34
$\text{Cd}^{2+} + 2\text{H}_2\text{CO}_3 \rightleftharpoons \text{Cd}(\text{CO}_3)_2^{2-} + 4\text{H}^+$	-27.18	-27.10	-26.70
$\text{H}_2\text{CO}_3 \rightleftharpoons \text{HCO}_3^- + \text{H}^+$	-6.355	-6.317	-5.983
$\text{H}_2\text{CO}_3 \rightleftharpoons \text{CO}_3^{2-} + 2\text{H}^+$	-16.691	-16.58	-15.52
$\text{Cd}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{CdSO}_4(\text{aq})$	2.36	2.21	0.93
$\text{Cd}^{2+} + \text{Cl}^- \rightleftharpoons \text{CdCl}^+$	1.98	1.90	1.33
$\text{Cd}^{2+} + 2\text{Cl}^- \rightleftharpoons \text{CdCl}_2(\text{aq})$	2.63	2.52	1.68
$\text{Cd}^{2+} + 3\text{Cl}^- \rightleftharpoons \text{CdCl}_3^-$	2.3	2.19	1.45

The results from this calculation are presented in a distribution diagram in Fig. 5. The speciation is very similar to that for the ternary  $\text{Cd}^{2+} + \text{H}^+ + \text{CO}_3^{2-}$  system. The figure indicates that the predominant species are  $\text{Cd}^{2+}$  ( $-\log_{10} \{[\text{H}^+]/c^\circ\} \leq 8.65$ ) and  $\text{CdCO}_3(\text{aq})$  ( $-\log_{10} \{[\text{H}^+]/c^\circ\} \geq 8.65$ ). Besides these two species  $\text{CdSO}_4(\text{aq})$  (ca. 6 % at  $-\log_{10} \{[\text{H}^+]/c^\circ\} \leq 8.0$ ) and  $\text{CdOH}^+$  (ca. 4 % at  $-\log_{10} \{[\text{H}^+]/c^\circ\} = 8.7$ ) are the only species formed to more than 2 % of  $[\text{Cd}^{2+}]_T$ . The chlorido- and phosphato-



**Fig. 5** Speciation diagram for the  $\text{Cd}^{2+} + \text{H}^+ + \text{Cl}^- + \text{CO}_2 + \text{HPO}_4^{2-} + \text{SO}_4^{2-}$  system with total concentrations  $[\text{Cl}^-]_T = 0.23 \text{ mmol dm}^{-3}$ ,  $[\text{SO}_4^{2-}]_T = 0.42 \text{ mmol dm}^{-3}$ ,  $[\text{HPO}_4^{2-}]_T = 0.7 \text{ } \mu\text{mol dm}^{-3}$  (fresh water medium) and  $[\text{Cd}^{\text{II}}]_T = 1 \text{ nmol dm}^{-3}$ . It was assumed that the system is in equilibrium with air having a  $\text{CO}_2$  fugacity of 370  $\mu\text{bar}$ .  $\text{Log } K_{10}(\text{CO}_2(\text{g}) = \text{CO}_2(\text{aq})) = -1.5$  [93MOR]. All other formation constants are according to Table 6 ( $I_c = 0.0015 \text{ mol dm}^{-3}$ ).

complexes do not contribute significantly to the speciation of  $\text{Cd}^{\text{II}}$  in fresh waters. The speciation diagram is much simpler than those for  $\text{Cu}^{\text{II}}$  [2007PBa] and  $\text{Pb}^{\text{II}}$  [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 ternary species  $\text{M}(\text{CO}_3)\text{OH}^-$  is also indicated.

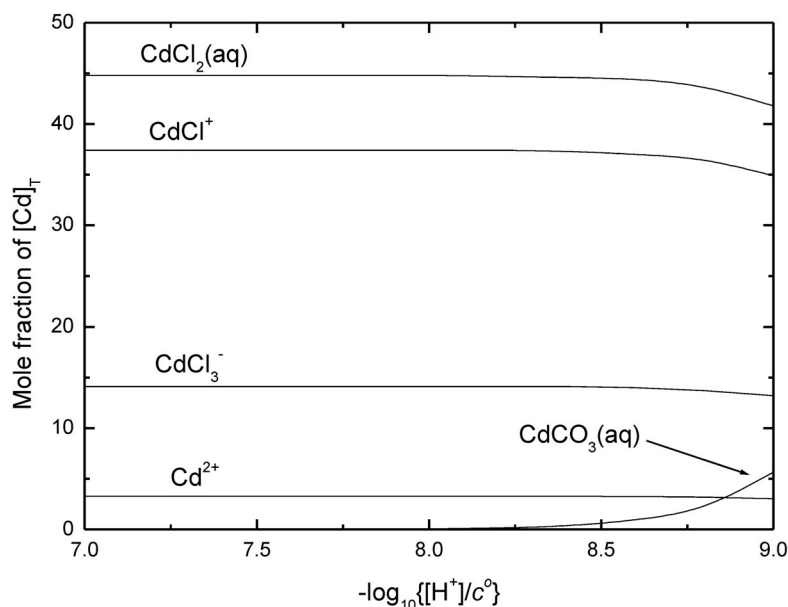
## 7.2 Seawater and saline systems

Distinctive features of natural saline systems are: the higher pH (seawater), the much higher concentrations of  $\text{Cl}^-$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ , and  $\text{SO}_4^{2-}$ , and the significant concentrations of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  both of which form moderately stable complexes with  $\text{CO}_3^{2-}$  and  $\text{SO}_4^{2-}$  [2009 PET]. Although the pH of surface seawater is in a narrow band,  $-\log_{10} \{[\text{H}^+]/c^\circ\}$  ca.  $8.2 \pm 0.2$ , it is informative to effect a calculation for a more generic saline system over a range of pH but approximating to seawater composition. The calculations presented here 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  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  with the inorganic anions (see [2009PBa] for the relevant stability constants for  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  species). Weaker interactions, such as those between  $\text{Na}^+$  and  $\text{CO}_3^{2-}$  and  $\text{SO}_4^{2-}$ , are considered as an implicit aspect of the SIT theory when applied to measurements in  $\text{NaClO}_4$  media and so do not require inclusion as ion-pairing interactions in the speciation calculations. For saline media a larger approximation arises in using SIT parameters,  $\Delta\epsilon$ , that were derived for  $\text{NaClO}_4$  media rather than  $\text{NaCl}$ , although the overall uncertainty may be small (because of the relative importance of the terms  $\Delta z^2 D$  and  $\Delta \epsilon I_m$  in eq. 2).

The increase in ionic strength in the range  $-\log_{10} \{[\text{H}^+]/c^\circ\} = 7$  to 9 due to increasing  $[\text{HCO}_3^-]$  and  $[\text{CO}_3^{2-}]$  at constant  $f(\text{CO}_2)$  was negligible in this medium and therefore had minimal effect on the stability constants. The stability constants calculated by WinSGW applicable at  $I_c = 0.67 \text{ mol dm}^{-3}$  for the critical species are shown in Table 6.

The speciation diagram (Fig. 6) indicates that at  $-\log_{10} \{[\text{H}^+]/c^\circ\} < 8.5$  (a range that includes seawater) the composition (mole fraction) is invariant with pH and is ca. 37.4 %  $\text{CdCl}^+$ , 44.8 %  $\text{CdCl}_2(\text{aq})$ , 14.1 %  $\text{CdCl}_3^-$ , and 3.3 %  $\text{Cd}^{2+}$ . In the presence of a high  $[\text{Cl}^-]_T$  the formation of  $\text{CdCO}_3(\text{aq})$  is suppressed significantly relative to fresh water (a displacement of the species curve to a much higher pH, with significant formation of  $\text{CdCO}_3(\text{aq})$  and  $\text{Cd}(\text{CO}_3)_2^{2-}$  only at  $-\log_{10} \{[\text{H}^+]/c^\circ\} > 8.8$  and 9.2 (not shown), respectively).

The speciation diagram for  $\text{Cd}^{\text{II}}$  contrasts with that for  $\text{Cu}^{\text{II}}$  [2007PBa] and  $\text{Pb}^{\text{II}}$  [2009PBa] for which at the pH of seawater the  $\text{MCO}_3(\text{aq})$  species dominates over the  $\text{MCl}_n^{(2-n)+}$  species. This is a result of the relatively low stability of the  $\text{Cd}^{2+}$ -carbonato- complexes and the relatively high stability of the  $\text{Cd}^{2+}$ -chlorido- complexes, a reflection of the greater “softness” of  $\text{Cd}^{\text{II}}$  compared with  $\text{Cu}^{\text{II}}$ .



**Fig. 6** Speciation diagram for the  $\text{Cd}^{2+} + \text{H}^+ + \text{Cl}^- + \text{CO}_2 + \text{HPO}_4^{2-} + \text{SO}_4^{2-}$  system in a simulated seawater medium,  $I_c = 0.67 \text{ mol dm}^{-3}$  including carbonato- and sulfato- complexes of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ . It was assumed that  $[\text{Cd}^{\text{II}}]_{\text{T}} = 1 \text{ nmol dm}^{-3}$  and that the system is in equilibrium with air having a  $\text{CO}_2$  fugacity of  $10^{-3.5}$  bar.  $\text{Log } K_{10}(\text{CO}_2(\text{g}) = \text{CO}_2(\text{aq})) = -1.5$  [93MOR]. All other formation constants are according to Table 6 ( $I_c = 0.67 \text{ mol dm}^{-3}$ ).

### 7.3 Summary

The speciation calculations indicate that, in neutral/weakly acidic fresh water systems in equilibrium with atmospheric  $\text{CO}_2$ ,  $\text{Cd}^{2+}(\text{aq})$  is the dominant  $\text{Cd}^{\text{II}}$  species and  $\text{CdSO}_4(\text{aq})$  is a minor species in the absence of organic ligands such as humates. In weakly alkaline solutions,  $8.65 < -\log_{10} \{[\text{H}^+]/c^\circ\}$ , the speciation is dominated by the carbonato-species  $\text{CdCO}_3(\text{aq})$ . In contrast, in saline systems the  $\text{CdCl}_n^{(2-n)+}$  species ( $n = 1-3$ ) prevail. When  $-\log_{10} \{[\text{H}^+]/c^\circ\} > 9$  the formation of  $\text{CdCO}_3(\text{aq})$  becomes significant whereas only small amounts of  $\text{Cd}(\text{OH})_n^{(2-n)+}$  species are formed.

Table 6 provides the user with values for the critical constants in media at  $I_c = 0.0015 \text{ mol dm}^{-3}$  (simulating fresh water) and  $I_c = 0.67 \text{ mol dm}^{-3}$  (simulating seawater), calculated from those reported here for  $I_m = 0 \text{ mol kg}^{-1}$ . For reliable speciation calculations of  $\text{Cd}^{\text{II}}$  in environmental systems the accuracy of the equilibrium data ( $I_m = 0 \text{ mol kg}^{-1}$ ) for formation of the complexes  $\text{Cd}(\text{CO}_3)_n^{(2-2n)+}$ ,  $\text{CdOH}^+$ ,  $\text{CdSO}_4(\text{aq})$ , and  $\text{CdCl}_n^{(2-n)+}$  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  $\text{Cd}^{2+}-\text{CO}_3^{2-}$  subsystem a lack of reliable equilibrium data is evident; this made it impossible to apply a rigorous SIT approach for the evaluation of  $\text{Cd}^{2+}$ -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	$n$	(SI base unit)	mol
molar mass	$M$	$M_A = m_A/n_A$ (= mass/amount)	kg mol <sup>-1</sup>
molality	$m, b$	$m_B = n_B/M_A(n - \sum_B n_B)$	mol kg <sup>-1</sup>
amount concentration	$c, [species]$	$c_B = [species B] = n_B/V$	mol m <sup>-3</sup> a(mol dm <sup>-3</sup> )
ionic strength, molality basis	$I_m$	$I_m = \frac{1}{2} \sum m_i z_i^2$	mol kg <sup>-1</sup>
ionic strength, amount concentration basis	$I_c$	$I_c = \frac{1}{2} \sum c_i z_i^2$	mol m <sup>-3</sup> (mol dm <sup>-3</sup> ) <sup>1</sup>
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	$\beta_n$	$\beta_n = [ML_n](c^\circ)^n/[M][L]^n$ for the reaction: $M + nL \rightleftharpoons ML_n$	1
stepwise (metal ion) hydrolysis constant	$*K_n$	$*K_n = [M(H_2O)_{6-n}(OH)_n][H^+]/[M(H_2O)_{6-n+1}(OH)_{n-1}](c^\circ)$ for the reaction: $M(H_2O)_{6-n+1}(OH)_{n-1} + H_2O \rightleftharpoons M(H_2O)_{6-n}(OH)_n + H^+$ or: $M(OH)_{n-1} + H_2O \rightleftharpoons M(OH)_n + H^+$	1
cumulative (metal ion) hydrolysis constant	$*\beta_n$ $*\beta_{m,n}$	$*\beta_n = [M(H_2O)_{6-n}(OH)_n][H^+]^n/[M(H_2O)_6](c^\circ)^n$ for: $M(H_2O)_6 + nH_2O \rightleftharpoons M(H_2O)_{6-n}(OH)_n + nH^+$ $*\beta_{m,n} = [M_m(OH)_n][H^+]^n/[M(H_2O)_6]^m(c^\circ)^{n-m+1}$ for: $mM(H_2O)_6 + nH_2O \rightleftharpoons M_m(OH)_n + nH^+$	1 1
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	$K_{sn}$	$K_{sn} = [MX_{p+q}](c^\circ)^{q-1}/[X]^q$ (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

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(Continued).

Name	Symbol	Definition	SI Unit
cumulative (overall) equilibrium concentration product	$\beta_{p,q,r}$	$\beta_{p,q,r} = [M_p L_q(OH)_r][H^+]^r/[M]^p[L]^q(c^\circ)^{r-p-q+1}$ for the reaction: $pM + qL + rH_2O \rightleftharpoons M_p L_q(OH)_r + rH^+$	1
(molar) enthalpy	$H$	$H/n$	J mol <sup>-1</sup>
(molar) reaction enthalpy	$\Delta_r H$	$\Delta_r H = \Sigma H(\text{products}) - \Sigma H(\text{reactants})$	J mol <sup>-1</sup>
activity coefficient, molality basis	$\gamma_m$	$RT \ln(\gamma_{m,B} m_B / m^\ominus) = \mu_B - \mu_B^\ominus = \lim_{m_B \rightarrow 0} [\mu_B - RT \ln(m_B / m^\ominus)]$	1
osmotic coefficient, molality basis	$\phi_m$	$\phi_m = (\mu_A^* - \mu_A) / RT M_A \Sigma m_B$	1
temperature (Celsius)	$\theta, t$	$\theta / ^\circ\text{C} = T / \text{K} - 273.15$	°C
temperature, thermodynamic	$T$	(SI base unit)	K

<sup>1</sup>Common 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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## APPENDIX 1

### 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,
- 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 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;
- (o) predicted values.

## APPENDIX 2

## Selected equilibrium constants

**Table A2-1** Selected equilibrium constants for the reaction  $\text{Cd}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{CdOH}^+ + \text{H}^+$  in perchlorate media at 25 °C.

Method	Ionic medium		<i>t</i> /°C (reported)	$\log_{10} {}^*K_1$ (accepted) <sup>1</sup>	$\log_{10} {}^*K_1$	Ref. <sup>2</sup>
	Amount concn./mol dm <sup>-3</sup>	Molality/ mol kg <sup>-1</sup>				
gl	0.1 NaClO <sub>4</sub>	0.101	25	-10.01 ± 0.01	-10.01 ± 0.10	2000KAa
gl	1.0 NaClO <sub>4</sub>	1.051	25		-10.24 ± 0.20	71GTa <sup>3</sup>
gl	3.0 LiClO <sub>4</sub>	3.482	25	-10.3 ± 0.1	-10.24 ± 0.10	77MOa
gl	3.0 LiClO <sub>4</sub>	3.482	25	-10.2 ± 0.1	-10.14 ± 0.10	62BCb

<sup>1</sup>Constant converted from molar to molal units and including our assigned errors.

<sup>2</sup>References for rejected data: [95STa]<sup>a,j</sup>, [89TRb]<sup>b</sup>, [74GAa]<sup>a,b</sup>, [64SMd]<sup>e,j</sup>, [64STb]<sup>j</sup>, [62DLa]<sup>j</sup>, [54GOa]<sup>b,j</sup>, [52CCa]<sup>a,j</sup>, [33JEa]<sup>a,j</sup>.

<sup>3</sup>Calculated using  $\log_{10} K_{s0} = -13.39$  (eq. 27), a reported  $\log_{10} K_{s1} = -9.9$  and  $\log_{10} K_w = -13.75$ .

<sup>4</sup>Calculated from  $\log_{10} K_1 = 4.30$  using  $\log_{10} K_w = -14.05$ .

**Table A2-2** Selected equilibrium constants for the reaction  $\text{Cd}^{2+} + 2\text{OH}^- \rightleftharpoons \text{Cd}(\text{OH})_2(\text{aq})$  in NaClO<sub>4</sub> media at 25 °C.

Method	Ionic medium		<i>t</i> /°C	$\log_{10} \beta_2$ (reported)	$\log_{10} \beta_2$ (accepted) <sup>1</sup>	Ref. <sup>2</sup>
	Amount concn./mol dm <sup>-3</sup>	Molality/ mol kg <sup>-1</sup>				
sol	0.01 NaClO <sub>4</sub>	0.01	25	7.10 ± 0.30	7.10 ± 0.30	91RFa
gl	1.0 NaClO <sub>4</sub>	1.051	25		6.55 ± 0.20	71GTa <sup>3</sup>
sol	1.0 NaClO <sub>4</sub>	1.051	25		7.35 ± 0.20	65RDa <sup>4</sup>
dis	3.0 NaClO <sub>4</sub>	3.503	25	7.74 ± 0.20	7.61 ± 0.20	62DLa
sol	7.0 NaClO <sub>4</sub>	10.56	25		9.43 ± 0.20	65RDa <sup>5</sup>

<sup>1</sup>Constant converted from molar to molal units and including our assigned errors.

<sup>2</sup>References for rejected data: [98ALa]<sup>a,b</sup>, [64SMd]<sup>e,j</sup>, [59KBa]<sup>a,j</sup>, [54GOa]<sup>b,j</sup>.

<sup>3</sup>Calculated using  $\log_{10} K_{s0} = -13.39$  (eq. 27) and a reported  $\log_{10} K_{s2} = -6.8$ .

<sup>4</sup>Calculated using  $\log_{10} K_{s0} = -13.39$  (eq. 27) and a reported  $\log_{10} K_{s2} = -6.0$ .

<sup>5</sup>Calculated using  $\log_{10} K_{s0} = -15.79$  (eq. 27) and a reported  $\log_{10} K_{s2} = -6.0$ .

**Table A2-3** Selected equilibrium constants for the reaction  $\text{Cd}^{2+} + 4\text{OH}^- \rightleftharpoons \text{Cd}(\text{OH})_4^{2-}$  in  $\text{NaClO}_4$  media at 25 °C.

Method	Ionic medium		<i>t</i> /°C	$\log_{10} \beta_4$ (reported)	$\log_{10} \beta_4$ (accepted) <sup>1</sup>	Ref. <sup>2</sup>
	Amount concn./mol dm <sup>-3</sup>	Molality/ mol kg <sup>-1</sup>				
gl	0.01 NaClO <sub>4</sub>	0.01	25	8.52 ± 0.38	8.52 ± 0.38	91RFa
gl	1.0 NaClO <sub>4</sub>	1.051	25		8.40 ± 0.20	71GTa <sup>3</sup>
sol	1.0 NaClO <sub>4</sub>	1.051	25		7.80 ± 0.20	65RDa <sup>4</sup>
sol	7.0 NaClO <sub>4</sub>	10.56	25		9.58 ± 0.20	65RDa <sup>5</sup>

<sup>1</sup>Constant converted from molar to molal units and including our assigned errors.<sup>2</sup>References for rejected data: [58LGa]<sup>i</sup>, [64SMd]<sup>e,j</sup>.<sup>3</sup>Calculated using  $\log_{10} K_{s0} = -13.39$  (eq. 27) and a reported  $\log_{10} K_{s4} = -4.9$ .<sup>4</sup>Calculated using  $\log_{10} K_{s0} = -13.39$  (eq. 27) and a reported  $\log_{10} K_{s4} = -5.51$ .<sup>5</sup>Calculated using  $\log_{10} K_{s0} = -15.79$  (eq. 27) and a reported  $\log_{10} K_{s4} = -5.51$ .**Table A2-4** Selected equilibrium constants for the reaction  $2\text{Cd}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{Cd}_2\text{OH}^{3+} + \text{H}^+$  in perchlorate media at 25 °C.

Method	Ionic medium		<i>t</i> /°C	$\log_{10} \beta_{2,1}$ (reported)	$\log_{10} \beta_{2,1}$ (accepted) <sup>1</sup>	Ref.
	Amount concn./mol dm <sup>-3</sup>	Molality/ mol kg <sup>-1</sup>				
gl	0.1 NaClO <sub>4</sub>	0.101	25	-8.54 ± 0.01	-8.54 ± 0.01	2000KAa
gl	3.0 LiClO <sub>4</sub>	3.482	25	-9.13 ± 0.01	-9.13 ± 0.01	77MOa
gl	3.0 LiClO <sub>4</sub>	3.482	25	-9.10 ± 0.05	-9.10 ± 0.05	62BCb

<sup>1</sup>Constant converted from molar to molal units and including our assigned errors.**Table A2-5** Selected equilibrium constants for the reaction  $\text{Cd}^{2+} + \text{Cl}^- \rightleftharpoons \text{CdCl}^+$  at 25 °C.

Method	Ionic medium		<i>t</i> /°C	$\text{Log}_{10} K_1$ (reported)	$\text{Log}_{10} K_1$ (accepted) <sup>1</sup>	Ref. <sup>2</sup>
	Amount concn./mol dm <sup>-3</sup>	Molality/ mol kg <sup>-1</sup>				
kin/sp	0.10 NaClO <sub>4</sub>	0.101	25	1.59 ± 0.04	1.59 ± 0.30	73HHb
emf	0.10 LiClO <sub>4</sub>	0.101	25	1.45 ± 0.09	1.45 ± 0.20	75KLa
emf	0.50 NaClO <sub>4</sub>	0.513	25	1.37 ± 0.004	1.36 ± 0.20	53BDa
emf	0.50 LiClO <sub>4</sub>	0.513	25	1.33	1.32 ± 0.10	FED <sup>3</sup>
emf	1.0 NaClO <sub>4</sub>	1.051	25	1.35 ± 0.004	1.33 ± 0.20	53BDa
kin/sp	1.0 NaClO <sub>4</sub>	1.051	25	1.34 ± 0.04	1.32 ± 0.30	73HHb
ise-Cl	1.0 NaClO <sub>4</sub>	1.051	25	1.38 ± 0.01	1.36 ± 0.30	74BLb
pol	1.0 NaClO <sub>4</sub>	1.051	25	1.34 ± 0.02	1.32 ± 0.20	77HHb
emf	1.0 NaClO <sub>4</sub>	1.051	25	1.33 ± 0.03	1.31 ± 0.20	77HHb
emf	1.0 NaClO <sub>4</sub>	1.051	25	1.36	1.34 ± 0.20	93VJa
emf	1.0 NaClO <sub>4</sub>	1.051	25	1.39 <sup>4</sup>	1.37 ± 0.20	2001TVa
emf	1.0 LiClO <sub>4</sub>	1.050	25	1.34	1.32 ± 0.10	FED <sup>5</sup>
emf	2.0 NaClO <sub>4</sub>	2.212	25	1.42 ± 0.004	1.38 ± 0.20	53BDa
pol	2.0 NaClO <sub>4</sub>	2.212	25	1.41 ± 0.04	1.37 ± 0.20	57KLa
pol	2.0 NaClO <sub>4</sub>	2.212	25	1.36	1.32 ± 0.20	66SGa
emf	2.0 NaClO <sub>4</sub>	2.212	25	1.44	1.40 ± 0.20	93VJa
emf	2.0 LiClO <sub>4</sub>	2.204	25	1.46	1.42 ± 0.10	FED <sup>6</sup>
emf	3.0 NaClO <sub>4</sub>	3.503	25	1.54 ± 0.004	1.47 ± 0.20	53BDa

*(continues on next page)*

Table A2-5 (Continued).

Method	Ionic medium		<i>t</i> /°C	Log <sub>10</sub> <i>K</i> <sub>1</sub> (reported)	Log <sub>10</sub> <i>K</i> <sub>1</sub> (accepted) <sup>1</sup>	Ref. <sup>2</sup>
	Amount concn./mol dm <sup>-3</sup>	Molality/ mol kg <sup>-1</sup>				
emf	3.0 NaClO <sub>4</sub>	3.503	25	1.50 ± 0.05	1.43 ± 0.20	74BIa
ise	3.0 NaClO <sub>4</sub>	3.503	25	1.59 ± 0.007	1.52 ± 0.20	74EMa
emf	3.0 NaClO <sub>4</sub>	3.503	25	1.59	1.52 ± 0.20	41LEa
sol	3.0 NaClO <sub>4</sub>	3.503	25	1.40 ± 0.05	1.33 ± 0.20	49KIa
pol	3.0 NaClO <sub>4</sub>	3.503	25	1.54 ± 0.004	1.47 ± 0.20	53ERa
emf	3.0 NaClO <sub>4</sub>	3.503	25	1.54	1.47 ± 0.20	93VJa
emf	3.0 LiClO <sub>4</sub>	3.482	25	1.51	1.45 ± 0.10	FED <sup>7</sup>
emf	4.0 LiClO <sub>4</sub>	4.906	25	1.72	1.63 ± 0.20	FED <sup>8</sup>
emf	4.0 LiClO <sub>4</sub>	4.906	25	1.77 ± 0.02	1.68 ± 0.20	63MKg
cal	4.0 LiClO <sub>4</sub>	4.906	25	1.77	1.68 ± 0.20	67MFa

<sup>1</sup>Constant converted from molar (amount concentration) to molal units and including our assigned errors representing a 95 % confidence interval.

<sup>2</sup>References for rejected data: [30RDa]<sup>e</sup>, [36HFa]<sup>c</sup>, [58TFa]<sup>e</sup>, [62BSc]<sup>e</sup>, [65MAd]<sup>a,c</sup>, [85MCa]<sup>e</sup>, [89BPb]<sup>a</sup>. (Superscripts indicate reasons for rejection of the references; see Appendix 1).

<sup>3</sup>The average of values from [72FKc] (1.37), [74FRc] (1.26 ± 0.07), [75FCa] (1.37 ± 0.01), [75KL<sub>a</sub>] (1.33 ± 0.06). The uncertainties on the accepted values (95 % confidence interval) are estimated based on the data scattering and assumed systematic errors.

<sup>4</sup>Average of values calculated from the same experimental data by four different methods.

<sup>5</sup>The average of values from [72FKc] (1.33), [74FRc] (1.26 ± 0.07), [75FCa] (1.33 ± 0.02), [75KL<sub>a</sub>] (1.36 ± 0.05). Uncertainties on the accepted values as above.

<sup>6</sup>The average of values from [72FKc] (1.46), [74FRc] (1.46 ± 0.06), [75FCa] (1.46 ± 0.01), [75KL<sub>a</sub>] (1.46 ± 0.07). Uncertainties on the accepted values as above.

<sup>7</sup>The average of values from [72FKc] (1.51), [74FRc] (1.58 ± 0.06), [75FCa] (1.48 ± 0.03), [75KL<sub>a</sub>] (1.51 ± 0.08). Uncertainties on the accepted values as above.

<sup>8</sup>The average of values from [74FRc] (1.66 ± 0.06), [75FCa] (1.77 ± 0.02). Uncertainties on the accepted values as above.

**Table A2-6** Selected stability constants for the reaction  $\text{Cd}^{2+} + 2 \text{Cl}^- \rightleftharpoons \text{CdCl}_2(\text{aq})$  at 25 °C.

Method	Ionic medium		<i>t</i> /°C	$\text{Log}_{10} \beta_2$ (reported)	$\text{Log}_{10} \beta_2$ (accepted) <sup>1</sup>	Ref. <sup>2</sup>
	Amount concn./mol dm <sup>-3</sup>	Molality/ mol kg <sup>-1</sup>				
emf	0.10 LiClO <sub>4</sub>	0.101	25	1.86 ± 0.10	1.85 ± 0.30	75KLa
emf	0.50 LiClO <sub>4</sub>	0.513	25	1.67	1.65 ± 0.20	FED <sup>3</sup>
emf	0.50 NaClO <sub>4</sub>	0.513	25	1.80 ± 0.01	1.78 ± 0.20	53BDa
emf	1.0 LiClO <sub>4</sub>	1.050	25	1.68	1.64 ± 0.30	FED <sup>4</sup>
emf	1.0 NaClO <sub>4</sub>	1.051	25	1.78 ± 0.01	1.74 ± 0.20	53BDa
pol	1.0 NaClO <sub>4</sub>	1.051	25	1.75 ± 0.03	1.71 ± 0.20	77HHb
emf	1.0 NaClO <sub>4</sub>	1.051	25	1.69 ± 0.03	1.65 ± 0.20	77HHb
emf	1.0 NaClO <sub>4</sub>	1.051	25	1.71	1.67 ± 0.20	93VJa
emf	1.0 NaClO <sub>4</sub>	1.051	25	1.82 <sup>8</sup>	1.78 ± 0.20	2001TVa
emf	2.0 NaClO <sub>4</sub>	2.212	25	1.95 ± 0.01	1.86 ± 0.20	53BDa
pol	2.0 NaClO <sub>4</sub>	2.212	25	1.92 ± 0.04	1.83 ± 0.20	57KLa
pol	2.0 NaClO <sub>4</sub>	2.212	25	1.64	1.55 ± 0.30	66SGa
emf	2.0 NaClO <sub>4</sub>	2.212	25	1.92	1.83 ± 0.20	93VJa
emf	2.0 LiClO <sub>4</sub>	2.204	25	1.92	1.84 ± 0.20	FED <sup>5</sup>
emf	3.0 NaClO <sub>4</sub>	3.503	25	2.23	2.10 ± 0.20	41LEa
sol	3.0 NaClO <sub>4</sub>	3.503	25	2.19 ± 0.05	2.06 ± 0.20	49KIa
pol	3.0 NaClO <sub>4</sub>	3.503	25	2.06 ± 0.02	1.93 ± 0.20	53ERa
emf	3.0 NaClO <sub>4</sub>	3.503	25	2.20 ± 0.01	2.07 ± 0.20	53BDa
emf	3.0 NaClO <sub>4</sub>	3.503	25	2.30 ± 0.05	2.17 ± 0.20	74BIa
ise	3.0 NaClO <sub>4</sub>	3.503	25	2.25 ± 0.10	2.12 ± 0.30	74EMa
emf	3.0 LiClO <sub>4</sub>	3.482	25	2.29	2.16 ± 0.20	FED <sup>6</sup>
emf	3.0 NaClO <sub>4</sub>	3.503	25	2.21	2.08 ± 0.20	93VJa
emf	4.0 LiClO <sub>4</sub>	4.906	25	2.56 ± 0.05	2.38 ± 0.20	63MKg
cal	4.0 LiClO <sub>4</sub>	4.906	25	2.57	2.39 ± 0.20	67MFa
emf	4.0 LiClO <sub>4</sub>	4.906	25	2.49	2.31 ± 0.30	FED <sup>7</sup>

<sup>1</sup>Constant corrected from molar to molal units and including our assigned errors representing a 95 % confidence interval.

<sup>2</sup>References for rejected data: [65MAd]<sup>a,c</sup>, [85MCa]<sup>e</sup>, [89BPb]<sup>a</sup>.

<sup>3</sup>The average of values from [72FKc] (1.77), [74FRc] (1.52 ± 0.08), [75FCa] (1.77 ± 0.02), [75KLa] (1.60 ± 0.08). The uncertainties on the accepted values (95 % confidence interval) are estimated based on the data scattering and assumed systematic errors.

<sup>4</sup>The average of values from [72FKc] (1.60), [74FRc] (1.85 ± 0.06), [75FCa] (1.60 ± 0.03), [75KLa] (1.65 ± 0.10).

Uncertainties on the accepted values as above.

<sup>5</sup>The average of values from [72FKc] (1.95), [74FRc] (1.83 ± 0.06), [75FCa] (1.95 ± 0.01), [75KLa] (1.95 ± 0.05).

Uncertainties on the accepted values as above.

<sup>6</sup>The average of values from [71FCb] (2.2 ± 0.01), [72FKc] (2.33), [74FRc] (2.35 ± 0.08), [75FCa] (2.20 ± 0.02), [75KLa] (2.33 ± 0.04). Uncertainties on the accepted values as above.

<sup>7</sup>The average of values from [74FRc] (2.41 ± 0.07), [75FCa] (2.56 ± 0.02). Uncertainties on the accepted values as above.

<sup>8</sup>Average value from stability constants calculated from the same experimental data using four different methods.

**Table A2-7** Selected stability constants for the reaction  $\text{Cd}^{2+} + 3 \text{Cl}^- \rightleftharpoons \text{CdCl}_3^-$  at 25 °C.

Method	Ionic medium		<i>t</i> /°C	Log <sub>10</sub> β <sub>3</sub> (reported)	Log <sub>10</sub> β <sub>3</sub> (accepted) <sup>1</sup>	Ref. <sup>2</sup>
	Amount concn./mol dm <sup>-3</sup>	Molality/ mol kg <sup>-1</sup>				
emf	1.0 NaClO <sub>4</sub>	1.051	25	1.41 ± 0.03	1.35 ± 0.40	53BDa
emf	1.0 LiClO <sub>4</sub>	1.050	25	1.62	1.56 ± 0.50	FED <sup>3</sup>
pol	1.0 NaClO <sub>4</sub>	1.051	25	1.49 ± 0.07	1.42 ± 0.40	77HHb
emf	1.0 NaClO <sub>4</sub>	1.051	25	1.53 ± 0.12	1.46 ± 0.40	77HHb
emf	1.0 NaClO <sub>4</sub>	1.051	25	1.70	1.63 ± 0.40	93VJa
emf	1.0 NaClO <sub>4</sub>	1.051	25	1.86 <sup>4</sup>	1.79 ± 0.50	2001TVa
emf	2.0 NaClO <sub>4</sub>	2.212	25	1.79 ± 0.03	1.66 ± 0.40	53BDa
pol	2.0 NaClO <sub>4</sub>	2.212	25	1.76 ± 0.04	1.63 ± 0.40	57KL <sub>a</sub>
pol	2.0 NaClO <sub>4</sub>	2.212	25	1.76	1.63 ± 0.40	66SG <sub>a</sub>
emf	2.0 LiClO <sub>4</sub>	2.204	25	2.14	2.01 ± 0.50	FED <sup>5</sup>
emf	2.0 NaClO <sub>4</sub>	2.212	25	1.96	1.83 ± 0.40	93VJa
emf	3.0 NaClO <sub>4</sub>	3.503	25	2.41	2.21 ± 0.40	41LE <sub>a</sub>
sol	3.0 NaClO <sub>4</sub>	3.503	25	2.40 ± 0.10	2.20 ± 0.40	49KI <sub>a</sub>
pol	3.0 NaClO <sub>4</sub>	3.503	25	2.46 ± 0.04	2.26 ± 0.40	53ER <sub>a</sub>
emf	3.0 NaClO <sub>4</sub>	3.503	25	2.29 ± 0.03	2.09 ± 0.40	53BD <sub>a</sub>
emf	3.0 NaClO <sub>4</sub>	3.503	25	2.3 ± 0.1	2.10 ± 0.40	74BI <sub>a</sub>
ise	3.0 NaClO <sub>4</sub>	3.503	25	2.40 ± 0.09	2.20 ± 0.40	74EM <sub>a</sub>
emf	3.0 NaClO <sub>4</sub>	3.503	25	2.35	2.15 ± 0.40	93VJa
emf	3.0 LiClO <sub>4</sub>	3.482	25	2.48	2.29 ± 0.50	FED <sup>6</sup>
emf	4.0 LiClO <sub>4</sub>	4.906	25	3.19 ± 0.07	2.92 ± 0.40	63MK <sub>g</sub>
cal	4.0 LiClO <sub>4</sub>	4.906	25	3.21	2.94 ± 0.40	67MF <sub>a</sub>
emf	4.0 LiClO <sub>4</sub>	4.906	25	2.33	2.06 ± 0.50	FED <sup>7</sup>

<sup>1</sup>Constant corrected from molar to molal units and including our assigned errors.

<sup>2</sup>References for rejected data: [65MAd]<sup>a,c</sup>, [85MCa]<sup>e</sup>, [89BPb]<sup>a</sup>.

<sup>3</sup>The average of values from [72FKc] (1.70), [75FCa] (1.70 ± 0.03), [75KL<sub>a</sub>] (1.45 ± 0.08). The uncertainties on the accepted values (95 % confidence interval) are estimated based on the data scattering and assumed systematic errors.

<sup>4</sup>Average value from stability constants calculated from the same experimental data with four different methods.

<sup>5</sup>The average of values from [72FKc] (2.10), [74FRc] (2.13 ± 0.10), [75FCa] (2.17 ± 0.02), [75KL<sub>a</sub>] (2.08 ± 0.06). The uncertainties on the accepted values as above.

<sup>6</sup>The average of values from [71FCb] (2.43 ± 0.02), [72FKc] (2.63), [74FRc] (2.41 ± 0.07), [75FCa] (2.44 ± 0.03), [75KL<sub>a</sub>] (2.51 ± 0.05). The uncertainties on the accepted values as above.

<sup>7</sup>The average of values from [74FRc] (2.47 ± 0.07), [75FCa] (2.19 ± 0.04). The uncertainties on the accepted values as above.

**Table A2-8** Selected equilibrium constants for the reaction:  $\text{Cd}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{CdSO}_4(\text{aq})$  at 25 °C.

Method	Ionic medium		<i>t</i> /°C	Log <sub>10</sub> <i>K</i> <sub>1</sub> (reported) <sup>1</sup>	Log <sub>10</sub> <i>K</i> <sub>1</sub> (accepted) <sup>2</sup>	Ref. <sup>3</sup>
	Amount concn./mol dm <sup>-3</sup>	Molality/ mol kg <sup>-1</sup>				
recalc(act)	0 corr	0 corr	25	2.29 ± 0.05	2.29 ± 0.10	31LAM, 38DAa
recalc(con)	0 corr	0 corr	25	2.34 ± 0.05 <sup>4</sup>	2.34 ± 0.10	27DAb, 38DAa
recalc(act, Δ <sub>dil</sub> <i>H</i> )	0 corr	0 corr	25	2.40	2.40 ± 0.10	72PIa
con	0 corr	0 corr	25	2.326 ± 0.006	2.33 ± 0.03	76KAa
recalc(con)	0 corr	0 corr	25	2.305 ± 0.009	2.31 ± 0.05	81YYa
con	0 corr	0 corr	25	2.389 ± 0.002	2.39 ± 0.01	84BAR
con	0 corr	0 corr	25	2.34 ± 0.01	2.34 ± 0.05	85SGd
ise	0.01 KNO <sub>3</sub>	0.01	25	2.36 ± 0.04 <sup>4</sup>	2.36 ± 0.10	74GAa
Cd(Hg)	0.5 LiClO <sub>4</sub>	0.513	25	1.08 ± 0.02 <sup>5</sup>	1.07 ± 0.10	73FCa, 75FCa
Cd(Hg)	1.0 LiClO <sub>4</sub>	1.050	25	0.95 ± 0.01 <sup>5</sup>	0.93 ± 0.10	73FCa, 75FCa
vlt	1.0 NaClO <sub>4</sub>	1.051	25	0.85 ± 0.06	0.83 ± 0.15	89NWA
Cd(Hg)	2.0 LiClO <sub>4</sub>	2.204	25	0.86 ± 0.01 <sup>5</sup>	0.82 ± 0.10	73FCa, 75FCa
cal	2.0 NaClO <sub>4</sub>	2.212	25	0.63 ± 0.02	0.59 ± 0.10	69BGa
Cd(Hg), vlt, sol, ix	3.0 LiClO <sub>4</sub>	3.482	25	0.67 ± 0.05 <sup>6</sup>	0.60 ± 0.10	71FCc
Cd(Hg)	3.0 LiClO <sub>4</sub>	3.482	25	0.72 ± 0.02 <sup>5</sup>	0.65 ± 0.10	71FCb, 73FCa, 75FCa
emf (Ag)	3.0 NaClO <sub>4</sub>	3.503	25	0.85 ± 0.15	0.77 ± 0.10	52LEa
Cd(Hg)	3.0 NaClO <sub>4</sub>	3.503	25	0.90 ± 0.05	0.83 ± 0.10	41LEa, 52LEa
Cd(Hg)	4.0 LiClO <sub>4</sub>	4.906	25	0.95 ± 0.02	0.85 ± 0.10	75FCa

<sup>1</sup>Uncertainties as given by the original authors or calculated by the present reviewer from the spread of values given by the original authors.

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

<sup>3</sup>References containing rejected data: [27DAb]<sup>l</sup>, [62JPa]<sup>h,j</sup>, [65HSc]<sup>e,j</sup>, [65POa]<sup>l</sup>, [68PRd]<sup>h,j</sup>, [69IEa]<sup>d,j</sup>, [72CAc]<sup>j</sup>, [73FCa, *I*→0 value]<sup>j</sup>, [74BLN]<sup>j</sup>, [80SRa]<sup>h</sup>, [89AGa]<sup>j,k</sup>, [89SAb]<sup>g</sup>, [90CHA]<sup>j</sup>, [94RIa]<sup>d,e,h</sup>, [98RUD]<sup>d,e,h</sup>, [2000TMa]<sup>j,k</sup>, [2001MTa]<sup>j,k</sup>. (Superscripts indicate reasons for rejection of the references; see Appendix 1).

<sup>4</sup>Constant converted to 25 °C by present reviewer assuming Δ<sub>*d*</sub>*H* = 8.3 kJ mol<sup>-1</sup> (Table 4).

<sup>5</sup>Listed values and uncertainties differ slightly between [71FCb], [73FCa] and [75FCa]; data at other temperatures given in [73FCa].

<sup>6</sup>Average value from all techniques calculated by present reviewer.



**Table A2-9** Selected equilibrium constants for the reaction:  $\text{Cd}^{2+} + 2\text{SO}_4^{2-} \rightleftharpoons \text{Cd}(\text{SO}_4)_2^{2-}$ .

Method	Ionic medium		<i>t</i> /°C	Log <sub>10</sub> β <sub>2</sub> (reported) <sup>1</sup>	Log <sub>10</sub> β <sub>2</sub> (accepted) <sup>2</sup>	Ref. <sup>3</sup>
	Amount concn./mol dm <sup>-3</sup>	Molality/ mol kg <sup>-1</sup>				
recalc(act, Δ <sub>dil</sub> H)	0 corr	0 corr	25	3.1	3.1 ± 0.5	72PIa
Cd(Hg)	→ 0	→ 0	25	2.95 ± 0.08 <sup>4</sup>	3.0 ± 0.4	73Fca
Cd(Hg)	0.5 LiClO <sub>4</sub>	0.513	25	1.96 ± 0.014 <sup>4,5,6</sup>	1.95 ± 0.20	73FCa, 75FCa
Cd(Hg)	1.0 LiClO <sub>4</sub>	1.050	25	1.55 ± 0.02 <sup>4,5,6</sup>	1.53 ± 0.20	73FCa, 75FCa
Cd(Hg)	2.0 LiClO <sub>4</sub>	2.204	25	1.31 ± 0.01 <sup>4,6</sup>	1.27 ± 0.20	73FCa, 75FCa
Cd(Hg), vlt, sol	3.0 LiClO <sub>4</sub>	3.482	25	0.89 ± 0.07 <sup>6,7</sup>	0.82 ± 0.20	71FCc
Cd(Hg)	3.0 LiClO <sub>4</sub>	3.482	25	0.84 ± 0.01 <sup>4,5,6</sup>	0.77 ± 0.20	71FCb, 73FCa, 75FCa
Cd(Hg)	3.0 NaClO <sub>4</sub>	3.503	25	1.0 ± 0.3 <sup>8</sup>	0.9 ± 0.3	52Lea
Cd(Hg)	4.0 LiClO <sub>4</sub>	4.906	25	0.99 ± 0.04 <sup>6</sup>	0.90 ± 0.20	75FCa

<sup>1</sup>Uncertainties as given by the original authors or calculated by the present reviewer from the spread of values given by the original authors.

<sup>2</sup>Constant corrected from molar to molal units; errors assigned by present reviewer (see text).

<sup>3</sup>References containing rejected data: [62JPa]<sup>h,j</sup>, [65HSc]<sup>e,j</sup>, [68PRd]<sup>h,j</sup>, [89AGa]<sup>j,k</sup>.

<sup>4</sup>Data at other temperatures given in [73FCa].

<sup>5</sup>Listed values and uncertainties differ slightly between [71FCb], [73FCa] and [75FCa]; higher order complexes (up to β<sub>5</sub>) also reported.

<sup>6</sup>Slightly different values for β<sub>2</sub> are also given in [71FCc].

<sup>7</sup>Average value from all techniques calculated by present reviewer.

<sup>8</sup>Higher-order complex (β<sub>3</sub>) also reported but criticised by [54FRO].

**Table A2-10** Selected stability constants for the system  $\text{Cd}^{2+} + \text{H}^+ + \text{PO}_4^{3-}$  at 25 °C.

Method	Ionic medium		<i>t</i> /°C	Log <sub>10</sub> K (reported)	Log <sub>10</sub> K (accepted) <sup>1</sup>	Ref.
	Amount conc./ mol dm <sup>-3</sup>	Molality/ mol kg <sup>-1</sup>				
<b>Cd<sup>2+</sup> + HPO<sub>4</sub><sup>2-</sup> ⇌ CdHPO<sub>4</sub>(aq)</b>						
gl, ise	3.0 NaClO <sub>4</sub>	3.503	25	2.68 ± 0.09	2.6 ± 0.2	73HSa
vlt	0.50 NaClO <sub>4</sub>	0.513	25	3.0	3.0 ± 0.5	73NMB
gl	0.10 NaClO <sub>4</sub>	0.101	25	2.91 ± 0.01	2.9 ± 0.2	74RMb
gl	0.10 NaNO <sub>3</sub>	0.101	25	2.79 ± 0.03	2.8 ± 0.2	96SSa
<b>Cd<sup>2+</sup> + H<sub>2</sub>PO<sub>4</sub><sup>-</sup> ⇌ CdH<sub>2</sub>PO<sub>4</sub><sup>+</sup></b>						
gl, ise	3.0 NaClO <sub>4</sub>	3.503	25	0.77 ± 0.10 <sup>2</sup>	0.7 ± 0.2	73HSa
gl, ise	3.0 NaClO <sub>4</sub>	3.503	25	0.75 ± 0.02	0.7 ± 0.2	94IPa
		→ 0		1.2 ± 0.2 <sup>3</sup>		
<b>Cd<sup>2+</sup> + 2HPO<sub>4</sub><sup>2-</sup> ⇌ Cd(HPO<sub>4</sub>)<sub>2</sub><sup>2-</sup></b>						
gl, ise	3.0 NaClO <sub>4</sub>	3.503	25	3.85 ± 0.02 <sup>2</sup>	3.7 ± 0.2	94IPa
		→ 0		5.4 ± 0.2 <sup>3</sup>		
vlt	0.50 NaClO <sub>4</sub>	0.513	25	3.9	3.9 ± 0.5	73NMB
gl	0.10 NaClO <sub>4</sub>	0.101	25	5.15 ± 0.01	5.1 ± 0.3	74RMb
<b>Cd<sup>2+</sup> + 2H<sub>2</sub>PO<sub>4</sub><sup>-</sup> ⇌ Cd(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>(aq)</b>						
gl, ise	3.0 NaClO <sub>4</sub>	3.503	25	1.01 ± 0.02	0.9 ± 0.2	94IPa
		→ 0		1.9 ± 0.2 <sup>3</sup>		

(continues on next page)

**TableA2-10** (Continued).

Method	Ionic medium		<i>t</i> /°C	Log <sub>10</sub> <i>K</i> (reported)	Log <sub>10</sub> <i>K</i> (accepted) <sup>1</sup>	Ref.
	Amount conc./ mol dm <sup>-3</sup>	Molality/ mol kg <sup>-1</sup>				
<b>Cd<sup>2+</sup> + H<sub>2</sub>PO<sub>4</sub><sup>-</sup> + HPO<sub>4</sub><sup>2-</sup> ⇌ Cd(H<sub>2</sub>PO<sub>4</sub>)(HPO<sub>4</sub>)<sup>-</sup></b> gl, ise	3.0 NaClO <sub>4</sub>	3.503 → 0	25	3.25 ± 0.02 <sup>2</sup> 4.8 ± 0.2 <sup>3</sup>	3.1 ± 0.2	94IPa
<b>Cd<sup>2+</sup> + 3HPO<sub>4</sub><sup>2-</sup> ⇌ Cd(HPO<sub>4</sub>)<sub>3</sub><sup>4-</sup></b> vlt	0.513 NaClO <sub>4</sub>		25	5.1		73NMB
<b>Cd<sup>2+</sup> + H<sub>3</sub>PO<sub>4</sub> ⇌ CdH<sub>2</sub>PO<sub>4</sub><sup>+</sup> + H<sup>+</sup></b> dis	0.2 HClO <sub>4</sub> + 0.2–2 H <sub>3</sub> PO <sub>4</sub>		RT	-1.1		90EBa
<b>Cd<sup>2+</sup> + 2H<sub>3</sub>PO<sub>4</sub> ⇌ Cd(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>(aq) + 2H<sup>+</sup></b> dis	0.2 HClO <sub>4</sub> + 0.2–2 H <sub>3</sub> PO <sub>4</sub>		RT	-2.9		90EBa
<b>Cd<sup>2+</sup> + 2H<sub>3</sub>PO<sub>4</sub> ⇌ Cd(HPO<sub>4</sub>)<sub>2</sub>(aq) + 4H<sup>+</sup></b> dis	0.2 HClO <sub>4</sub> + 0.2–2 H <sub>3</sub> PO <sub>4</sub>		RT	-6.9		90EBa

<sup>1</sup>Constant corrected from molar to molal units and including our assigned errors.

<sup>2</sup>Extrapolated to *I<sub>m</sub>* = 0 by the authors using SIT and estimated ion interaction coefficients.

<sup>3</sup>Recalculated by the reviewers using the protonation constants for phosphate ion reported for 3 mol dm<sup>-3</sup> NaClO<sub>4</sub> in [69BSd] (log<sub>10</sub> *K*<sub>2</sub> = 6.27, log<sub>10</sub> *K*<sub>3</sub> = 1.89).

**Table A2-11** Selected solubility constants for the reaction Cd(OH)<sub>2</sub>(s) ⇌ Cd<sup>2+</sup> + 2OH<sup>-</sup> in NaClO<sub>4</sub> media at 25 °C.

Method	Ionic medium		<i>t</i> /°C	log <sub>10</sub> <i>K</i> <sub>s0</sub> (reported)	log <sub>10</sub> <i>K</i> <sub>s0</sub> (accepted) <sup>1</sup>	Ref. <sup>2</sup>
	Amount concn./mol dm <sup>-3</sup>	Molality/ mol kg <sup>-1</sup>				
sol	0	0	25	-14.22	-14.22 ± 0.20	28PIa
gl	var.	0 corr	25	-14.23	-14.23 ± 0.20	51FRb
gl	var.	0 corr	25	-14.41 ± 0.10	-14.41 ± 0.10	59SCa
sol	0.01 NaClO <sub>4</sub>	0.01	25	-14.14 ± 0.21	-14.14 ± 0.21	91RFa
gl	3.0 NaClO <sub>4</sub>	3.503	25	-14.07 ± 0.04 <sup>3</sup>	-13.87 ± 0.04	59SCa

<sup>1</sup>Constant converted from molar to molal units and including our assigned errors.

<sup>2</sup>References for rejected data: [71GTa]<sup>h</sup>, [54NRa]<sup>i</sup>, [51Vla]<sup>a,j</sup>, [50Afa]<sup>a</sup>, [42MRa]<sup>j</sup>, [38OKa]<sup>j</sup>, [32Isa]<sup>d</sup>, [25Wla]<sup>j</sup>.

<sup>3</sup>Converted from log<sub>10</sub> \**K*<sub>s0</sub> = 14.03 using log<sub>10</sub> *K*<sub>w</sub> = -14.05.

**Table A2-12** Selected solubility constant data for the reaction<sup>1</sup>  $\text{CdCO}_3(\text{s}) + 2\text{H}^+ \rightleftharpoons \text{Cd}^{2+} + \text{CO}_2(\text{aq}) + \text{H}_2\text{O}$  in  $\text{NaClO}_4$  media at 25 °C.

Method	Ionic medium		<i>t</i> /°C	$\log_{10} {}^*K_{\text{ps0}}$ (reported)	$\log_{10} {}^*K_{\text{ps0}}$ (accepted) <sup>2</sup>	Ref. <sup>3</sup>
	Amount concn./mol dm <sup>-3</sup>	Molality/ mol kg <sup>-1</sup>				
sol	0.150 NaClO <sub>4</sub> <sup>4</sup>	0.150	25	6.269	6.27 ± 0.10	99GPa
sol	0.150 NaClO <sub>4</sub> <sup>4</sup>	0.150	25	6.272	6.27 ± 0.10	99GPa
sol	0.150 NaClO <sub>4</sub> <sup>4</sup>	0.150	25	6.243	6.24 ± 0.10	99GPa
sol	0.165 NaClO <sub>4</sub> <sup>4</sup>	0.165	25	6.364	6.36 ± 0.10	99GPa
sol	0.166 NaClO <sub>4</sub> <sup>4</sup>	0.166	25	6.366	6.37 ± 0.10	99GPa
sol	0.166 NaClO <sub>4</sub> <sup>4</sup>	0.166	25	6.466	6.47 ± 0.10	99GPa
sol	0.166 NaClO <sub>4</sub> <sup>4</sup>	0.166	25	6.585	6.59 ± 0.10	99GPa
sol	0.167 NaClO <sub>4</sub> <sup>4</sup>	0.167	25	6.524	6.52 ± 0.10	99GPa
sol	0.506 NaClO <sub>4</sub> <sup>4</sup>	0.506	25	6.418	6.42 ± 0.10	99GPa
sol	0.506 NaClO <sub>4</sub> <sup>4</sup>	0.506	25	6.348	6.35 ± 0.10	99GPa
sol	0.550 NaClO <sub>4</sub> <sup>4</sup>	0.550	25	6.414	6.41 ± 0.10	99GPa
sol	0.550 NaClO <sub>4</sub> <sup>4</sup>	0.550	25	6.478	6.48 ± 0.10	99GPa
sol	0.982 NaClO <sub>4</sub> <sup>4</sup>	0.982	25	6.300	6.30 ± 0.10	99GPa
sol	0.982 NaClO <sub>4</sub> <sup>4</sup>	0.982	25	6.371	6.37 ± 0.10	99GPa
sol	1.000 NaClO <sub>4</sub> <sup>4</sup>	1.000	25	6.356	6.36 ± 0.10	99GPa
sol	1.002 NaClO <sub>4</sub> <sup>4</sup>	1.002	25	6.343	6.34 ± 0.10	99GPa
sol	1.000 NaClO <sub>4</sub> <sup>4</sup>	1.000	25	6.366	6.37 ± 0.10	99GPa
sol	1.000 NaClO <sub>4</sub> <sup>4</sup>	1.000	25	6.252	6.25 ± 0.10	99GPa
sol	1.051 NaClO <sub>4</sub> <sup>4</sup>	1.051	25	6.390	6.39 ± 0.10	99GPa
sol	2.149 NaClO <sub>4</sub> <sup>4</sup>	2.149	25	6.328	6.33 ± 0.10	99GPa
sol	2.150 NaClO <sub>4</sub> <sup>4</sup>	2.150	25	6.413	6.41 ± 0.10	99GPa
sol	3.000 NaClO <sub>4</sub> <sup>4</sup>	3.000	25		6.41 ± 0.02	91KHa
sol	3.000 NaClO <sub>4</sub> <sup>4</sup>	3.503	25		6.40 ± 0.15	65GSa
sol	4.329 NaClO <sub>4</sub> <sup>4</sup>	4.329	25	6.334	6.33 ± 0.10	99GPa
sol	4.331 NaClO <sub>4</sub> <sup>4</sup>	4.331	25	6.361	6.36 ± 0.10	99GPa
sol	4.331 NaClO <sub>4</sub> <sup>4</sup>	4.331	25	6.303	6.30 ± 0.10	99GPa
sol	5.349 NaClO <sub>4</sub> <sup>4</sup>	5.349	25	6.400	6.40 ± 0.10	99GPa
sol	5.350 NaClO <sub>4</sub> <sup>4</sup>	5.350	25	6.396	6.40 ± 0.10	99GPa
sol	5.350 NaClO <sub>4</sub> <sup>4</sup>	5.350	25	6.277	6.28 ± 0.10	99GPa
sol	5.350 NaClO <sub>4</sub> <sup>4</sup>	5.350	25	6.237	6.24 ± 0.10	99GPa
sol	5.350 NaClO <sub>4</sub> <sup>4</sup>	5.350	25	6.286	6.29 ± 0.10	99GPa

<sup>1</sup>CdCO<sub>3</sub>(s) is otavite.<sup>2</sup>Constant corrected from molar to molal units and including our assigned errors.<sup>3</sup>References for rejected data: [91RFa]<sup>a,d,f,i</sup>, [93SPa]<sup>d</sup>.<sup>4</sup>Reported on the molality scale.

**Table A2-13** Selected reaction enthalpy values for the formation of  $\text{CdCl}^+$  and  $\text{CdCl}_2(\text{aq})$  at 25 °C.

Method	Ionic medium		<i>t</i> /°C	$\Delta_r H^\circ / \text{kJ mol}^{-1}$ (reported)	$\Delta_r H^\circ / \text{kJ mol}^{-1}$ (accepted) <sup>1</sup>	Ref. <sup>2,3</sup>
	Amount concn./mol dm <sup>-3</sup>	Molality/ mol kg <sup>-1</sup>				
<b><math>\text{Cd}^{2+} + \text{Cl}^- \rightleftharpoons \text{CdCl}^+</math></b>						
cal	0.25 NaClO <sub>4</sub>	0.254	25	0.88 ± 0.08	0.88 ± 1.0	68GJc
cal	0.50 NaClO <sub>4</sub>	0.513	25	1.05 ± 0.04	1.05 ± 1.0	68GJc
cal	0.50 LiClO <sub>4</sub>	0.513	25	1.15 ± 0.08	1.15 ± 1.5	72FKc
cal	1.0 NaClO <sub>4</sub>	1.051	25	0.54 ± 0.04	0.54 ± 1.0	68GJc
cal	1.0 LiClO <sub>4</sub>	1.050	25	0.57 ± 0.06	0.57 ± 1.5	72FKc
cal	2.0 NaClO <sub>4</sub>	2.212	25	0.00 ± 0.04	0.00 ± 1.0	68GJc
cal	2.0 LiClO <sub>4</sub>	2.204	25	-0.46 ± 0.06	-0.46 ± 1.5	72FKc
cal	3.0 NaClO <sub>4</sub>	3.503	25	-0.42 ± 0.04	-0.42 ± 1.0	66GEb
cal	3.0 LiClO <sub>4</sub>	3.482	25	-1.42 ± 0.10	-1.42 ± 1.5	72FKc
cal	4.0 LiClO <sub>4</sub>	4.906	25	-2.5 ± 0.4	-2.5 ± 1.5	67MFa
cal	4.0 LiClO <sub>4</sub>	4.906	25	-2.85 ± 0.04	-2.85 ± 1.5	72FKc
<b><math>\text{Cd}^{2+} + 2\text{Cl}^- = \text{CdCl}_2(\text{aq})</math></b>						
cal	0.50 NaClO <sub>4</sub>	0.513	25	2.8 ± 0.5	2.8 ± 2.0	68GJc
cal	0.50 LiClO <sub>4</sub>	0.513	25	4.31 ± 0.33	4.31 ± 3.0	72FKc
cal	1.0 NaClO <sub>4</sub>	1.051	25	2.05 ± 0.17	2.05 ± 2.0	68GJc
cal	1.0 LiClO <sub>4</sub>	1.050	25	3.53 ± 0.13	3.53 ± 3.0	72FKc
cal	2.0 NaClO <sub>4</sub>	2.212	25	1.42 ± 0.13	1.42 ± 2.0	68GJc
cal	2.0 LiClO <sub>4</sub>	2.204	25	0.90 ± 0.13	0.90 ± 3.0	72FKc
cal	3.0 NaClO <sub>4</sub>	3.503	25	0.08 ± 0.08	0.08 ± 2.0	66GEb
cal	3.0 LiClO <sub>4</sub>	3.482	25	-2.85 ± 0.21	-2.85 ± 3.0	72FKc
cal	4.0 LiClO <sub>4</sub>	4.906	25	-5.4 ± 0.9	-5.4 ± 3.0	67MFa
cal	4.0 LiClO <sub>4</sub>	4.906	25	-5.52 ± 0.13	-5.52 ± 3.0	72FKc

<sup>1</sup>Reported values with the present reviewer's assigned uncertainties.

<sup>2</sup>Enthalpy values from the references [49KIa, 53VDa, 62BDc, 69SPa, 81MBa] were not used for the SIT analysis, since these data were derived from temperature variations of stability constants. Only the more reliable data from direct calorimetric measurements were used.

<sup>3</sup>Enthalpy values were determined for a different ionic medium [69SPa, 81MBa].

**Table A2-14** Selected reaction enthalpies and entropies for the formation of CdSO<sub>4</sub>(aq) at 25 °C.

Method	Ionic medium		<i>t</i> /°C	$\Delta_r H/$ kJ mol <sup>-1</sup> (reported)	$\Delta_r H/$ kJ mol <sup>-1</sup> (accepted) <sup>1</sup>	$\Delta_r S/$ J K <sup>-1</sup> mol <sup>-1</sup> (reported)	$\Delta_r S/$ J K <sup>-1</sup> mol <sup>-1</sup> (accepted) <sup>1</sup>	Ref. <sup>2</sup>
	Amount concn./ mol dm <sup>-3</sup>	Molality/ mol kg <sup>-1</sup>						
cal <sup>3</sup>	0 corr	0 corr	25	9.0 ± 0.7	9.0 ± 1.0	74 ± 2 <sup>4</sup>	74 ± 5	70LAe
cal	0 corr	0 corr	25	7.7 <sup>6,7</sup>	7.7 ± 1.0	72 <sup>5,6</sup>	72 ± 5	72PIa
<i>K</i> ( <i>T</i> ) <sup>7</sup>	→ 0	→ 0	25	8.8 <sup>6,8</sup>	8.8 ± 1.0	70 <sup>6,8,9</sup>	70 ± 10	73FCa
<i>K</i> ( <i>T</i> ) <sup>10</sup>	0 corr	0 corr	25	8.4 ± 0.7	8.4 ± 1.0	73 ± 2	73 ± 5	76KAa
<i>K</i> ( <i>T</i> ) <sup>12</sup>	0 corr	0 corr	25	8.1 ± 0.1 <sup>11</sup>	8.1 ± 1.0	71 ± 1 <sup>11</sup>	71 ± 5	81YYa
<i>K</i> ( <i>T</i> ) <sup>12</sup>	0 corr	0 corr	25	7.9 <sup>6,11</sup>	7.9 ± 1.0	72 <sup>6</sup>	72 ± 5	84BAR
<i>K</i> ( <i>T</i> ) <sup>7</sup>	0.5 LiClO <sub>4</sub>	0.513	25	4.6 <sup>6,8</sup>	4.6 ± 2.0	37 <sup>6,8,9</sup>	37 ± 10	73FCa
<i>K</i> ( <i>T</i> ) <sup>7</sup>	1 LiClO <sub>4</sub>	1.050	25	5.3 <sup>6,8</sup>	5.3 ± 2.0	35 <sup>6,8,9</sup>	35 ± 10	73FCa
<i>K</i> ( <i>T</i> ) <sup>7</sup>	2 LiClO <sub>4</sub>	2.204	25	5.7 <sup>6,8</sup>	5.7 ± 2.0	35 <sup>6,8,9</sup>	35 ± 10	73FCa
cal	2 NaClO <sub>4</sub>	2.212	25	7.9 ± 0.4	7.9 ± 1.0	38 ± 2	38 ± 5	69BGa
<i>K</i> ( <i>T</i> ) <sup>7</sup>	3 LiClO <sub>4</sub>	3.482	25	6.0 <sup>6,8</sup>	6.0 ± 2.0	35 <sup>6,8,9</sup>	35 ± 10	73FCa

<sup>1</sup>Reported values with the present reviewer's assigned uncertainties.

<sup>2</sup>Rejected data: [69IEa]<sup>h,j</sup>, [73POa]<sup>i</sup>, [78ARa]<sup>b</sup>, [89AGa]<sup>j,k</sup>, [94RIA]<sup>d,j,k</sup>, [98RUD]<sup>d,j,k</sup>. For [78ARa] (titration calorimetry) the medium is not clearly specified but probably 0.5 mol dm<sup>-3</sup> Et<sub>4</sub>NNO<sub>3</sub>.

<sup>3</sup>Recalculation using  $\Delta_{\text{dil}}H$  data from various literature sources.

<sup>4</sup>Uncertainty estimated by present reviewer.

<sup>5</sup>Estimated by present reviewer from  $\Delta_{\text{dil}}H$  and activity information in [72PIa].

<sup>6</sup>Uncertainty not given in original paper

<sup>7</sup>Using potentiometric data from 15–65 °C.

<sup>8</sup>Estimated by present reviewer from graphical data in [73FCa].

<sup>9</sup> $\Delta_r S$  values in [73FCa] incorrectly labeled as negative.

<sup>10</sup>Using conductometric data from 0–45 °C.

<sup>11</sup>Reported value and uncertainty rounded up by present reviewer.

<sup>12</sup>Using conductometric data from 0–35 °C.

**Table A2-15** Selected reaction enthalpies and entropies for the formation of Cd(SO<sub>4</sub>)<sub>2</sub><sup>2-</sup> at 25 °C.

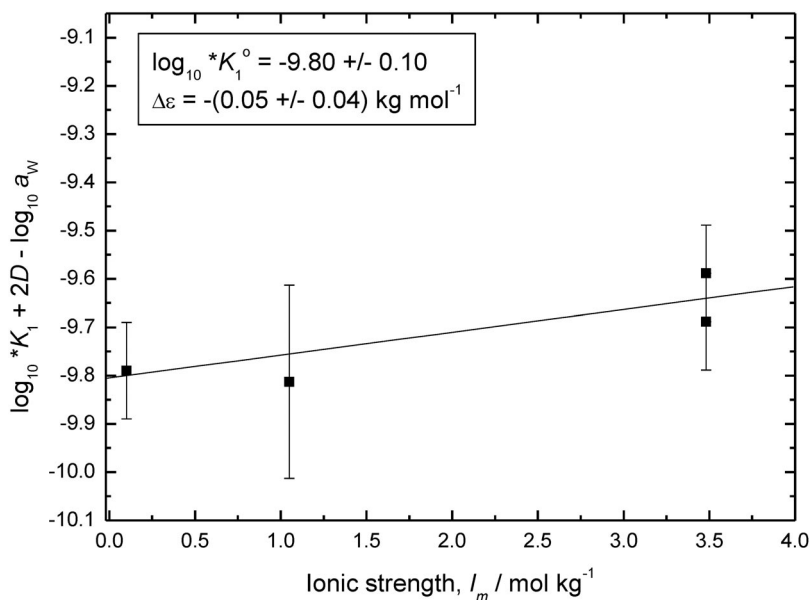
Method	Ionic medium		<i>t</i> /°C	$\Delta_r H/$ kJ mol <sup>-1</sup> (reported) <sup>1</sup>	$\Delta_r H/$ kJ mol <sup>-1</sup> (accepted) <sup>2</sup>	$\Delta_r S/$ J K <sup>-1</sup> mol <sup>-1</sup> (reported) <sup>1</sup>	$\Delta_r S/$ J K <sup>-1</sup> mol <sup>-1</sup> (accepted) <sup>2</sup>	Ref. <sup>3</sup>
	Amount concn./ mol dm <sup>-3</sup>	Molality/ mol kg <sup>-1</sup>						
<i>K</i> ( <i>T</i> )	→ 0	→ 0	25	5.7	5.7 ± 2.5	73	70 ± 15	73FCa
<i>K</i> ( <i>T</i> )	0.5 LiClO <sub>4</sub>	0.513	25	6.1	6.1 ± 2.5	58	37 ± 15	73FCa
<i>K</i> ( <i>T</i> )	1.0 LiClO <sub>4</sub>	1.050	25	2.4	2.4 ± 2.5	40	35 ± 15	73FCa
<i>K</i> ( <i>T</i> )	2.0 LiClO <sub>4</sub>	2.204	25	3.1	3.1 ± 2.5	26	35 ± 15	73FCa
<i>K</i> ( <i>T</i> )	3.0 LiClO <sub>4</sub>	3.482	25	6.0	11.0 ± 2.5	37	35 ± 15	73FCa

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

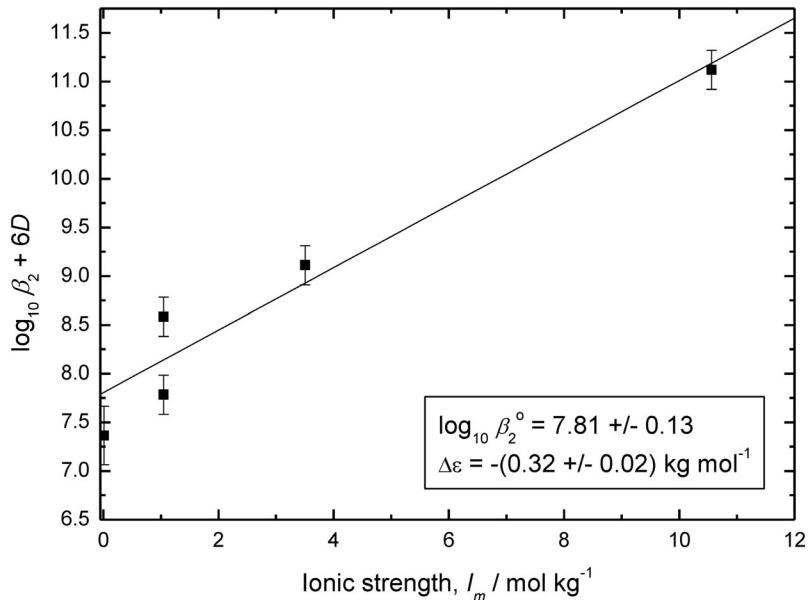
<sup>2</sup>Reported values with the present reviewer's assigned uncertainties.

<sup>3</sup> $\Delta_r S$  values are incorrectly labelled as negative in [73FCa].

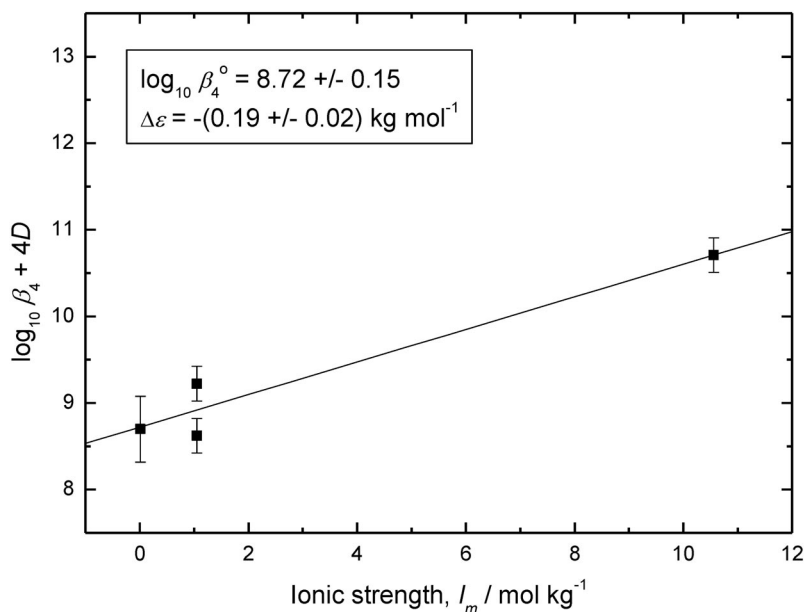
## APPENDIX A3



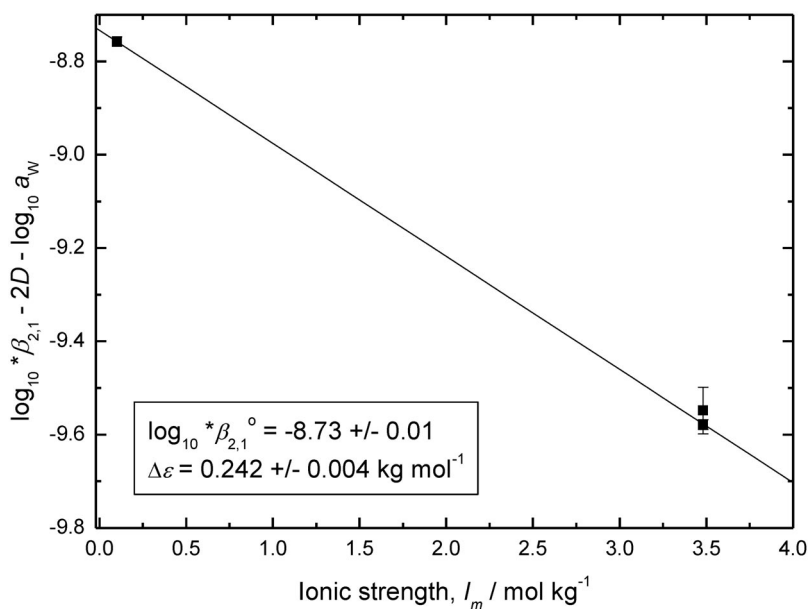
**Fig. A3-1** Extrapolation to  $I_m = 0 \text{ mol kg}^{-1}$  of  $\log_{10} {}^*K_1 - \Delta(z^2)D - \log_{10} a(\text{H}_2\text{O})$  (eq. 2, Section 1) for reaction 4 ( $\Delta z^2 = -2$ ) using selected data for perchlorate media, 25 °C (Table A2-1).



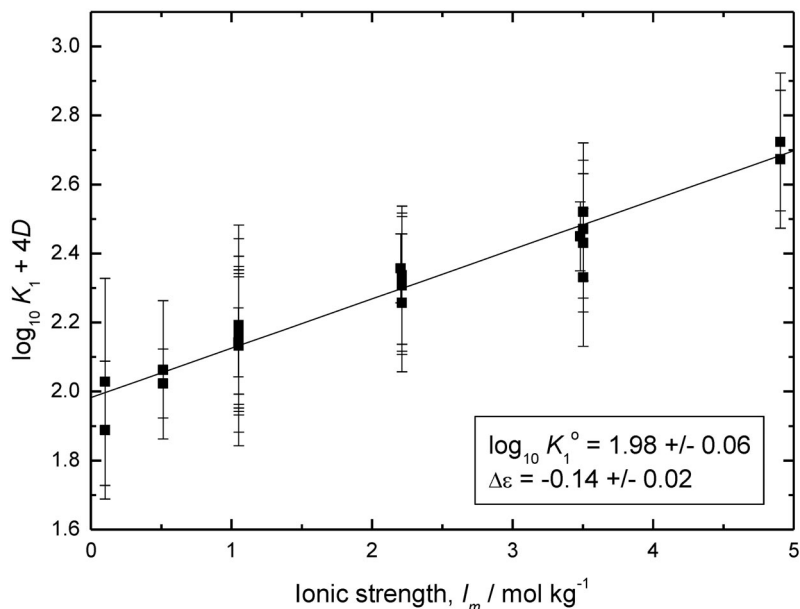
**Fig. A3-2** Extrapolation to  $I_m = 0 \text{ mol kg}^{-1}$  of  $\log_{10} \beta_2 - \Delta(z^2)D$  for reaction 5 ( $\Delta z^2 = -6$ ) using selected data for perchlorate media, 25 °C (Table A2-2).



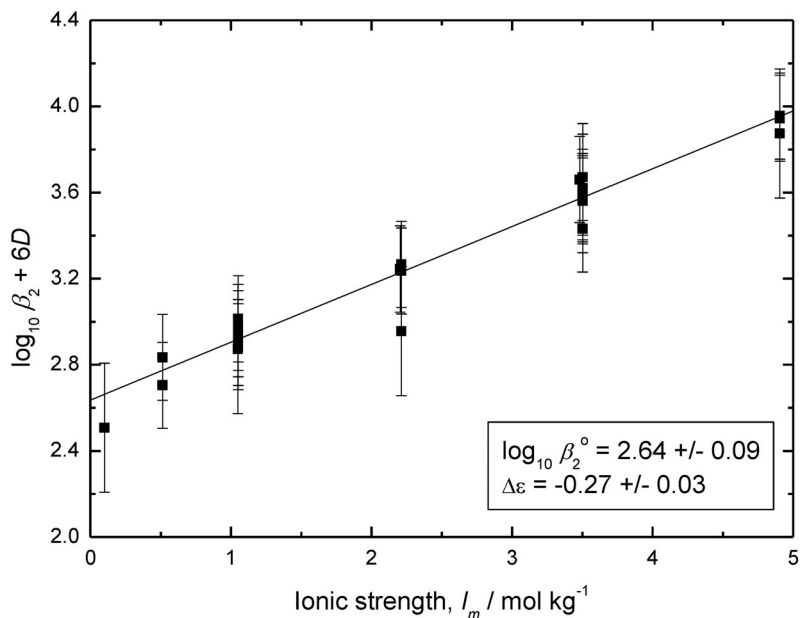
**Fig. A3-3** Extrapolation to  $I_m = 0 \text{ mol kg}^{-1}$  of  $\log_{10} \beta_3 - \Delta(z^2)D$  for reaction 7 ( $\Delta z^2 = -4$ ) using selected data for perchlorate media, 25 °C (Table A2-3).



**Fig. A3-4** Extrapolation to  $I_m = 0 \text{ mol kg}^{-1}$  of  $\log_{10} \beta_{2,1}^* - \Delta(z^2)D - \log_{10} a(\text{H}_2\text{O})$  for reaction 9 ( $\Delta z^2 = 2$ ) using selected data for perchlorate media, 25 °C (Table A2-4).

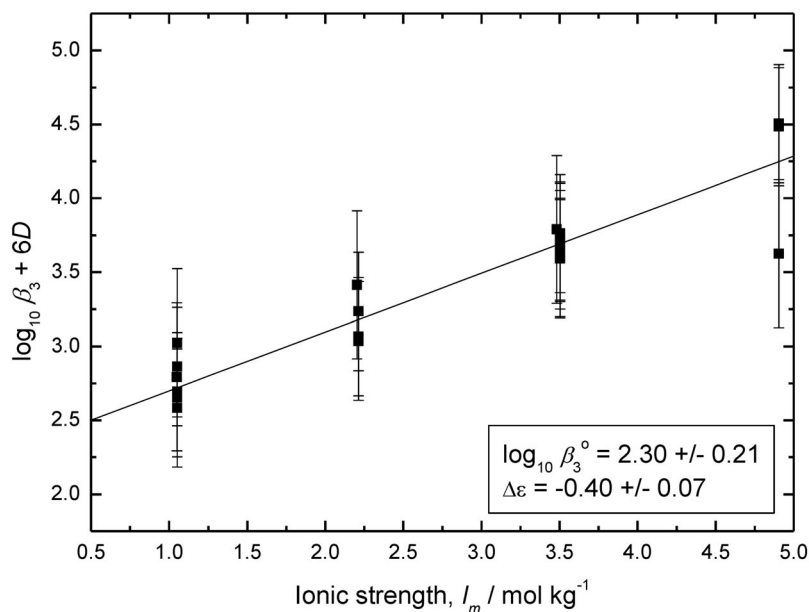


**Fig. A3-5** Extrapolation to  $I_m = 0 \text{ mol kg}^{-1}$  of  $\log_{10} K_1 - \Delta(z^2)D$  for reaction 10 ( $\Delta z^2 = -4$ ) using selected data for perchlorate media, 25 °C (Table A2-5).

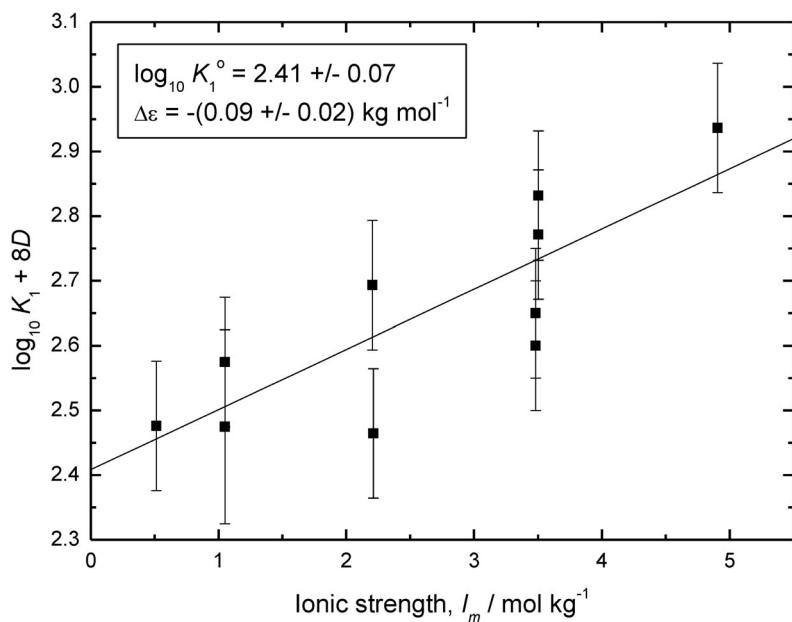


**Fig. A3-6** Extrapolation to  $I_m = 0 \text{ mol kg}^{-1}$  of  $\log_{10} \beta_2 - \Delta(z^2)D$  for reaction 11 ( $\Delta z^2 = -6$ ) using selected data for perchlorate media, 25 °C (Table A2-6).

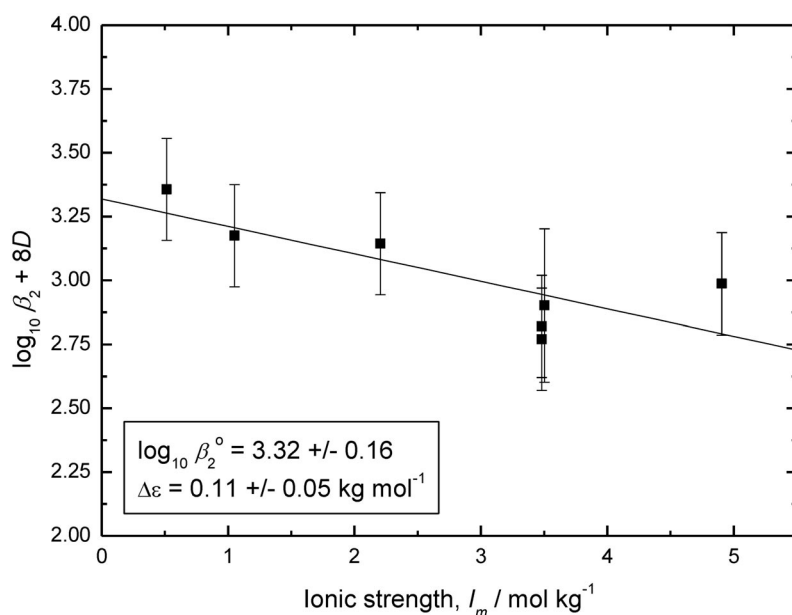




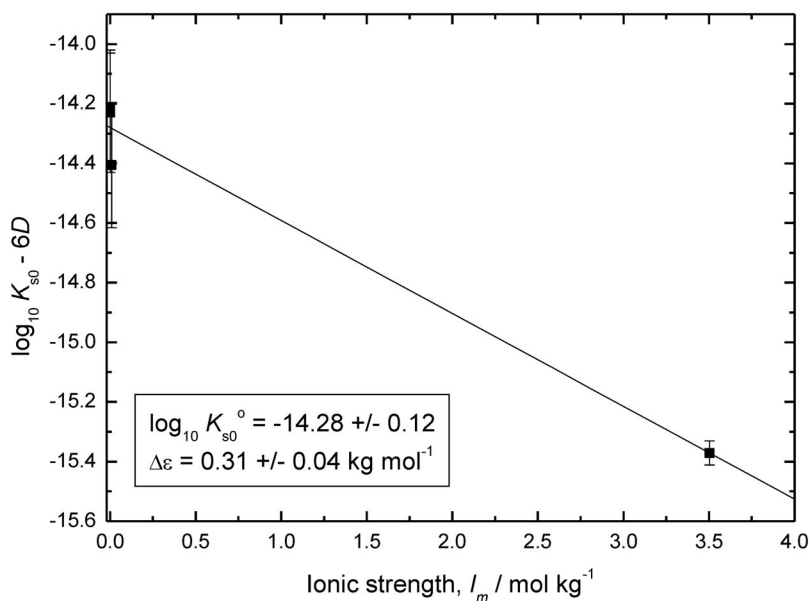
**Fig. A3-7** Extrapolation to  $I_m = 0 \text{ mol kg}^{-1}$  of  $\log_{10} \beta_3 - \Delta(z^2)D$  for reaction 12 ( $\Delta z^2 = -6$ ) using selected data for perchlorate media, 25 °C (Table A2-7).



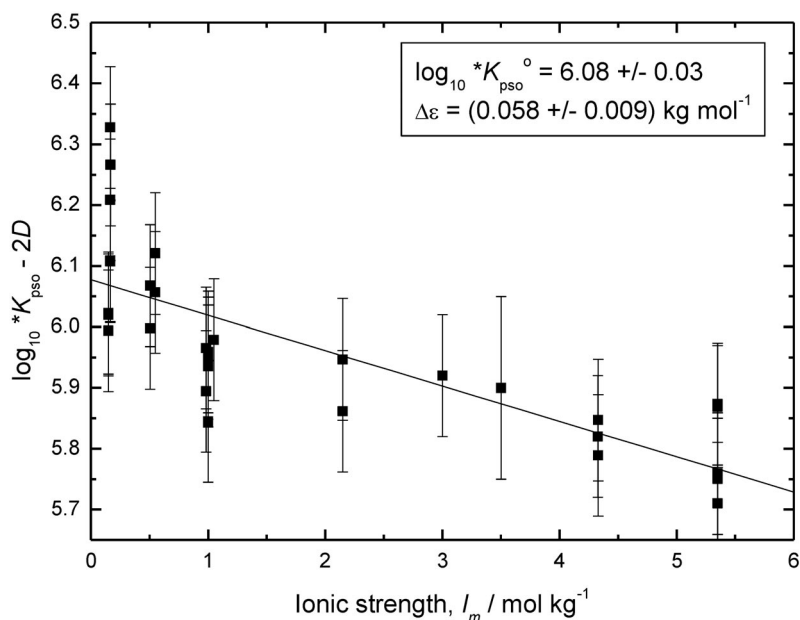
**Fig. A3-8** Extrapolation to  $I_m = 0 \text{ mol kg}^{-1}$  of  $\log_{10} K_1 - \Delta(z^2)D$  for reaction 20 ( $\Delta z^2 = -8$ ) using selected data for perchlorate media, 25 °C (Table A2-8).



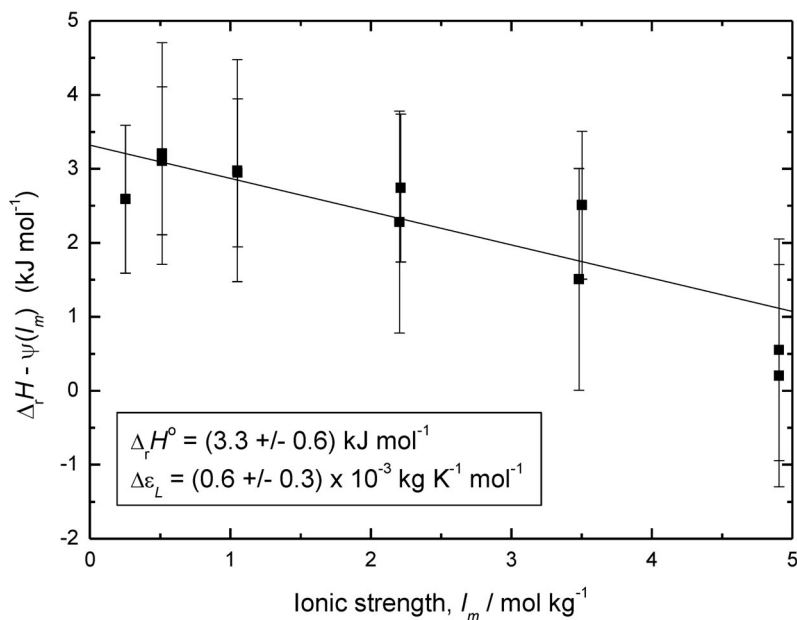
**Fig. A3-9** Extrapolation to  $I_m = 0 \text{ mol kg}^{-1}$  of  $\log_{10} \beta_2 - \Delta(z^2)D$  for reaction 21 ( $\Delta z^2 = -8$ ) using selected data for perchlorate media, 25 °C (Table A2-9).



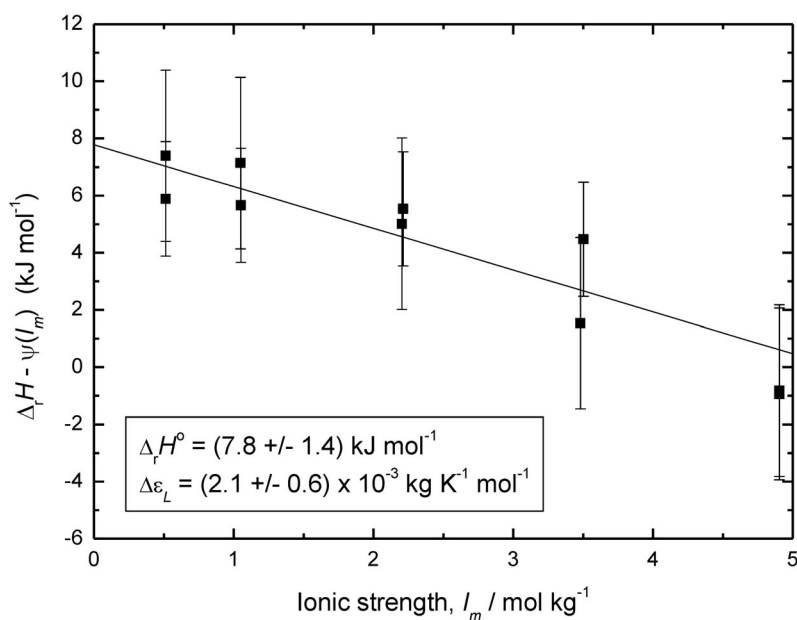
**Fig. A3-10** Extrapolation to  $I_m = 0 \text{ mol kg}^{-1}$  of  $\log_{10} K_{s0} - \Delta(z^2)D$  for reaction 27 ( $\Delta z^2 = 6$ ) using selected data for perchlorate media, 25 °C (Table A2-11).



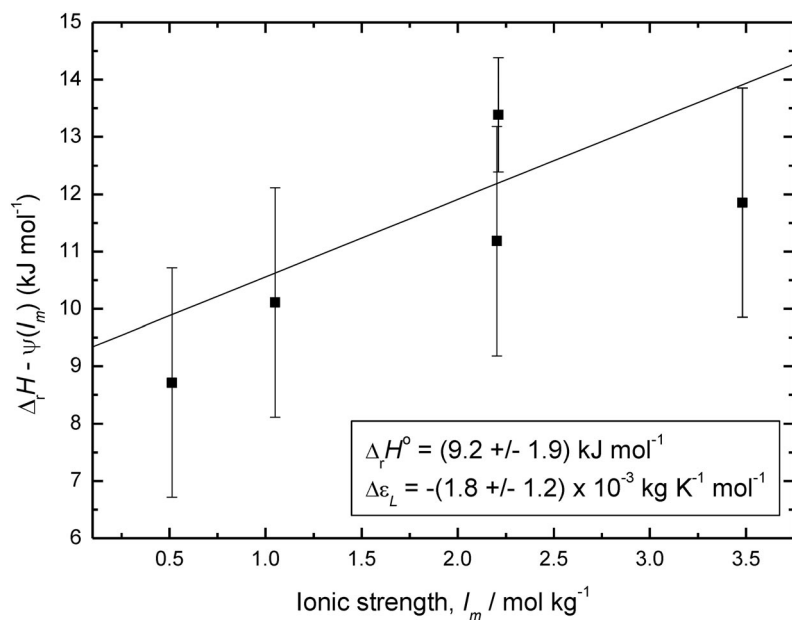
**Fig. A3-11** Extrapolation to  $I_m = 0 \text{ mol kg}^{-1}$  of  $\log_{10} *K_{\text{ps0}}^0 - \Delta(z^2)D$  for reaction 29 ( $\Delta z^2 = 2$ ) using selected data for perchlorate media, 25 °C (Table A2-12).



**Fig. A3-12** Extrapolation to  $I_m = 0 \text{ mol kg}^{-1}$  of  $\Delta_r H$  for reaction 10 in  $\text{NaClO}_4$  and  $\text{LiClO}_4$  solutions containing varying and significant proportions of  $\text{Cl}^-$ .



**Fig. A3-13** Extrapolation to  $I_m = 0 \text{ mol kg}^{-1}$  of  $\Delta_r H$  for reaction 11 in  $\text{NaClO}_4$  and  $\text{LiClO}_4$  solutions containing varying and significant proportions of  $\text{Cl}^-$ .



**Fig. A3-14** Extrapolation to  $I_m = 0 \text{ mol kg}^{-1}$  of  $\Delta_r H$  for reaction 20 in  $\text{LiClO}_4$  solutions containing varying and significant proportions of  $\text{Cl}^-$ .