INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

ANALYTICAL CHEMISTRY DIVISION*

CHEMICAL SPECIATION OF ENVIRONMENTALLY SIGNIFICANT HEAVY METALS WITH INORGANIC LIGANDS

PART 1: THE Hg^{2+}– Cl^-, OH^-, CO_3^{2-}, SO_4^{2-}, AND PO_4^{3-} AQUEOUS SYSTEMS

(IUPAC Technical Report)

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Chemical speciation of environmentally significant heavy metals with inorganic ligands. Part 1: The Hg^{2+}– Cl^-, OH^-, CO_3^{2-}, SO_4^{2-}, and PO_4^{3-} aqueous systems

(IUPAC Technical Report)

Abstract: This document presents a critical evaluation of the equilibrium constants and reaction enthalpies for the complex formation reactions between aqueous Hg(II) and the common environmental inorganic ligands Cl^-, OH^-, CO_3^{2-}, SO_4^{2-}, and PO_4^{3-}. The analysis used data from the IUPAC Stability Constants database, *SC-Database*, focusing particularly on values for 25 °C and perchlorate media. Specific ion interaction theory (SIT) was applied to reliable data available for the ionic strength range $I_c \leq 3.0$ mol dm^{-3}.

Recommended values of $\log_{10} \beta_{p,q,r}°$ and the associated reaction enthalpies, $\Delta_r H_m°$, valid at $I_m = 0$ mol kg^{-1} and 25 °C, were obtained by weighted linear regression using the SIT equations. Also reported are the equations and specific ion interaction coefficients required to calculate $\log_{10} \beta_{p,q,r}$ values at higher ionic strengths and other temperatures. A similar analysis is reported for the reactions of H^+ with CO_3^{2-} and PO_4^{3-}.

Diagrams are presented to show the calculated distribution of Hg(II) amongst these inorganic ligands in model natural waters. Under typical environmental conditions, Hg(II) speciation is dominated by the formation of $HgCl_2$(aq), Hg(OH)Cl(aq), and Hg(OH)$_2$(aq).

Keywords: chemical speciation; heavy metals; environmental; ligands; stability constants; Division V.

CONTENTS

1. INTRODUCTION

This review is the first in a series relevant to speciation of heavy metal ions in environmental systems of low ionic strength. The series will provide access to the best possible equilibrium data for chemical speciation modeling of reactions of heavy metal ions with the major inorganic ligands. The metal ions and ligands selected for review are: Hg^{2+}, Cd^{2+}, Cu^{2+}, Pb^{2+}, Zn^{2+} and Cl^-, OH^-, CO_3^{2-}, SO_4^{2-} and PO_4^{3-}, respectively. To enable speciation calculations on these systems, recommended values for the $H^+- CO_3^{2-}$ and $-PO_4^{3-}$ systems are also reported.

    Chemical speciation modeling for labile systems is based on the assumption that all component and derived species are in equilibrium and that reliable stability constants are available at the applicable ionic strength and temperature. The validity of these assumptions is often uncertain. Further, full details of component (stoichiometric) concentrations are required. Despite these factors, modeling has definite value in interpretation or simulation of environmental processes. It is often the only option as the necessary sensitive, selective, and noninvasive analytical techniques for measuring metal ion and metal complex concentrations are still, to a great extent, unavailable.

Detailed knowledge of chemical speciation is essential to a full understanding of bioavailability and toxicity of heavy metal ions, and to their adsorption, sedimentation, and transport phenomena in soils, rivers, and aquifers. The optimization of many industrial chemical processes, as in hydrometallurgy and pulp and paper processing, relies on a detailed understanding of speciation in often-complicated multicomponent, multiphase systems.

2. OBJECTIVES

This review is concerned with the Hg^{2+}– Cl^-, OH^-, CO_3^{2-}, SO_4^{2-}, and PO_4^{3-} systems. Each review in this series will provide critically evaluated equilibrium data applicable to environmental waters at low ionic strength. Such values are derived from data reported in the IUPAC Stability Constants database, *SC-Database* [2003PET], and extrapolated to zero ionic strength ($I_m = 0$ mol kg^{-1}) using appropriate specific ion interaction theory (SIT) functions [97GRE]. A consequence of this SIT approach, which typically utilized published constants measured at $I_c = 0.5$–3.0 mol dm^{-3}, is the generation of empirical functions that permit the calculation of $\log_{10} K_n$ values at intermediate values of I_m as may be relevant in industrial or environmental situations.

For each metal–ligand combination, the review will

- identify the most reliable publications and stability constants;
- identify (and reject) unreliable stability constants;
- establish correlations between the selected data on the basis of ionic strength dependence, using the SIT functions;
- establish recommended values of $\beta_{p,q,r}°$ and K_{s0} at 25 °C (298.15 K) and $I_m = 0$ mol kg^{-1};
- identify the most reliable value of the reaction enthalpy $\Delta_r H_m$ for each equilibrium reaction and establish recommended values at 25 °C and $I_m = 0$ mol kg^{-1};
- provide the user with the numerical relationships required to interpolate values of $\beta_{p,q,r}$ and $\Delta_r H_m$ at $I_m > 0$ mol kg^{-1}; and
- provide examples of SIT plots for $\beta_{p,q,r}$ and $\Delta_r H_m$ extrapolations, and examples of distribution diagrams for binary and multicomponent systems.

Literature values for metal–ligand "stability constants" [2003PET], or "formation constants" [97INC], are typically determined in ionic media of nominally fixed and (comparatively) high ionic strength. The reported constants, designated by $\beta_{p,q,r}$ or K_n, are valid at a single ionic strength. Most frequently, they are reported on the amount concentration (molarity) scale as "equilibrium concentration products" in which [species i] refers to the (amount) concentration, c, of species i in a system at equilibrium (see Appendix 1A). These concentration products are related to the standard (state) equilibrium constants, $\beta_{p,q,r}°$ and $K_n°$, the "equilibrium activity products", by $\beta_{p,q,r}° = \beta_{p,q,r}(\lim I_c \to 0$ mol dm$^{-3})$ and $K_n° = K_n(\lim I_c \to 0$ mol dm$^{-3})$. This is a consequence of the usual thermodynamic standard state convention for solutions: that activity coefficients of solute species approach 1 as the ionic strength (or concentration) approaches zero. As noted in the "Orange Book" [97INC], stability constants are as well defined thermodynamically as those referring to pure water (the equilibrium activity products); they simply refer to a different relative activity scale (standard state).

In this document, to facilitate the use of the SIT functions, reported values of stability constants $\beta_{p,q,r}$ and K_n were initially converted to the molality scale. The limiting values at $I_m = 0$ mol kg^{-1} ($\beta_{p,q,r}°$ and $K_n°$) were then obtained by weighted linear regression against I_m using the SIT equations to describe the ionic strength dependence of ion activity coefficients. The weighting (uncertainty) assigned to each value followed the guidelines in [92GRE, Appendix C].

Consistent with common practice, the quotients $\beta_{p,q,r}$ and K_n are referred to as "stability constants" (whether defined on the molarity or molality scale), while the "equilibrium activity products", $\beta_{p,q,r}°$ and $K_n°$, are referred to as the "standard (state) equilibrium constants"; see Appendix 1A.

All reactions described in this document refer to aqueous solution, e.g.,

$$Hg^{2+}(aq) + Cl^-(aq) + H_2O \rightleftharpoons HgOHCl(aq) + H^+(aq)$$
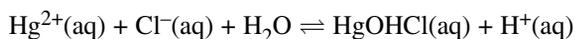
For simplicity, the suffix (aq) is not used in equations or when referring to specific species unless that species has zero net charge, in which case the phase is specified, e.g., HgOHCl(aq) and HgO(s). Further, throughout this document "amount concentration" is abbreviated to "concentration", the units being mol dm^{-3} ($\approx$ mol l^{-1}, or M).

3. SUMMARY OF RECOMMENDED VALUES

Tables 1–5 provide a summary of the standard equilibrium constants, reaction enthalpies, and reaction ion interaction coefficients, $\Delta\varepsilon$, for the formation of Hg^{2+} complexes with inorganic anions. These were derived from the critical evaluation of available literature data [2003PET] and application of SIT functions. See Section 5.3 for definition of the terms "Recommended" (R) and "Provisional" (P) used in the tables and Section 5.1 for a description of the selection and evaluation process. The log $\beta_{p,q,r}°$, log $K_n°$, and log $*\beta_{p,q,r}°$ values, and the reaction enthalpies, $\Delta_r H_m°$, are for 298.15 K, 1 bar (10^5 Pa) and infinite dilution ($I_m = 0$ mol kg^{-1}). Note that none of the values for the Hg^{2+}– PO$_4^{3-}$ system are assigned Recommended or Provisional status, and neither of the values for the Hg^{2+}– SO$_4^{2-}$ system is Recommended, nor applies at $I_m = 0$ mol kg^{-1}. See Appendix 1A for definitions of the symbols used for stability constants.

Table 1 Recommended values for the Hg^{2+}– OH$^-$ system at 298.15 K, 1 bar, and $I_m = 0$ mol kg^{-1}. R = Recommended; P = Provisional. $\Delta\varepsilon$ values for ClO$_4^-$ medium.

Reaction		
Hg^{2+} + H$_2$O $\rightleftharpoons$ HgOH$^+$ + H$^+$	$\log_{10} *K_1°$ = −3.40 ± 0.08	R
	$\Delta\varepsilon$ = −(0.14 ± 0.03) kg mol^{-1}	
Hg^{2+} + 2H$_2$O $\rightleftharpoons$ Hg(OH)$_2$(aq) + 2H$^+$	$\log_{10} *\beta_2°$ = −5.98 ± 0.06	R
	$\Delta\varepsilon$ = − (0.14 ± 0.02) kg mol^{-1}	
	$\Delta_r H_m°$ = (51.5 ± 1.8) kJ mol^{-1}	R
Hg^{2+} + 3H$_2$O $\rightleftharpoons$ Hg(OH)$_3^-$ + 3H$^+$	$\log_{10} *\beta_3°$ = −21.1 ± 0.3	P
HgO(s) + H$_2$O $\rightleftharpoons$ Hg(OH)$_2$(aq)	$\Delta_r H_m°$ = (26.2 ± 1.8) kJ mol^{-1}	R
HgO(s) + 2H$^+$ $\rightleftharpoons$ Hg^{2+} + H$_2$O	$\log_{10} *K_{s0}°$ = 2.37 ± 0.08	R
	$\Delta_r H_m°$ = −(25.3 ± 0.2) kJ mol^{-1}	R

Table 2 Recommended values for the Hg^{2+}– Cl$^-$ system at 298.15 K, 1 bar, and $I = 0$ mol kg^{-1}. R = Recommended; P = Provisional. $\Delta\varepsilon$ values for NaClO$_4$ medium.

Reaction		
Hg^{2+} + Cl$^-$ $\rightleftharpoons$ HgCl$^+$	$\log_{10} K_1°$ = 7.31 ± 0.04	R
	$\Delta\varepsilon$ = −(0.22 ± 0.04) kg mol^{-1}	
	$\Delta_r H_m°$ = −(21.3 ± 0.7) kJ mol^{-1}	R
Hg^{2+} + HgCl$_2$(aq) $\rightleftharpoons$ 2HgCl$^+$	$\log_{10} K°$ = 0.61 ± 0.03	R
	$\Delta\varepsilon$ = −(0.02 ± 0.02) kg mol^{-1}	
	$\Delta_r H_m°$ = (6.5 ± 1.7) kJ mol^{-1}	R
Hg^{2+} + 2Cl$^-$ $\rightleftharpoons$ HgCl$_2$(aq)	$\log_{10} \beta_2°$ = 14.00 ± 0.07	R
	$\Delta\varepsilon$ = −(0.39 ± 0.03) kg mol^{-1}	
	$\Delta_r H_m°$ = −(49.1 ± 1.0) kJ mol^{-1}	R

(continues on next page)

Table 2 (*Continued*).

Reaction		
$HgCl_2(aq) + Cl^- \rightleftharpoons HgCl_3^-$	$\log_{10} K_3^\circ = 0.925 \pm 0.09$	R
	$\Delta\varepsilon = (0.01 \pm 0.05)$ kg mol^{-1}	
	$\Delta_r H_m^\circ = (0.5 \pm 2.5)$ kJ mol^{-1}	P
$HgCl_3^- + Cl^- \rightleftharpoons HgCl_4^{2-}$	$\log_{10} K_4^\circ = 0.61 \pm 0.12$	R
	$\Delta\varepsilon = (0.003 \pm 0.06)$ kg mol^{-1}	
	$\Delta_r H_m^\circ = -(10.5 \pm 2.5)$ kJ mol^{-1}	P
$Hg^{2+} + Cl^- + H_2O \rightleftharpoons HgOHCl(aq) + H^+$	$\log_{10} \beta^\circ = 4.27 \pm 0.35$	P

Table 3 Recommended values[1] for the $Hg^{2+}-CO_3^{2-}$ system at 298.15 K, 1 bar, and $I_m = 0$ mol kg^{-1}. R = Recommended; P = Provisional.

Reaction		
$Hg(OH)_2(aq) + CO_2(g) \rightleftharpoons HgCO_3(aq) + H_2O$	$\log_{10} K^\circ = -0.70 \pm 0.20$	R
$Hg(OH)_2(aq) + HCO_3^- \rightleftharpoons Hg(OH)CO_3^- + H_2O$	$\log_{10} K^\circ = 0.98 \pm 0.10$	R
$Hg(OH)_2(aq) + CO_2(g) + H^+ \rightleftharpoons HgHCO_3^+ + H_2O$	$\log_{10} K^\circ = 3.63 \pm 0.10$	R
$HgCO_3 \cdot 2HgO(s) + 3H_2O \rightleftharpoons 3Hg(OH)_2(aq) + CO_2(g)$	$\log_{10} K_s = -11.27 \pm 0.35$	P

[1]The value for $\log_{10} K_s$ refers to $I_c = 3.0$ mol dm^{-3} (NaClO$_4$).

Table 4 Selected values for the $Hg^{2+}-PO_4^{3-}$ system at 298.15 K, 1 bar, and $I_c = 3$ mol dm^{-3} NaClO$_4$.

Reaction	
$Hg^{2+} + HPO_4^{2-} \rightleftharpoons HgHPO_4(aq)$	$\log_{10} K = 8.8 \pm 0.2$
$Hg^{2+} + HPO_4^{2-} \rightleftharpoons HgPO_4^- + H^+$	$\log_{10} K = 3.25 \pm 0.2$
$Hg_3(PO_4)_2(s) + 2H^+ \rightleftharpoons 3Hg^{2+} + 2HPO_4^{2-}$	$\log_{10} {}^*K_s = -24.6 \pm 0.6$
$(HgOH)_3PO_4(s) + 4H^+ \rightleftharpoons 3Hg^{2+} + HPO_4^{2-} + 3H_2O$	$\log_{10} {}^*K_s = -9.4 \pm 0.8$
$HgHPO_4(s) \rightleftharpoons Hg^{2+} + HPO_4^{2-}$	$\log_{10} K_s = -13.1 \pm 0.1$

Table 5 Selected stability constants for the $Hg^{2+}-SO_4^{2-}$ system at 298.15 K, 1 bar, and $I_c = 0.50$ mol dm^{-3} NaClO$_4$.

Reaction		
$Hg^{2+} + SO_4^{2-} \rightleftharpoons HgSO_4(aq)$	$\log_{10} K_1 = 1.4 \pm 0.1$	P
$Hg^{2+} + 2SO_4^{2-} \rightleftharpoons Hg(SO_4)_2^{2-}$	$\log_{10} \beta_2 = 2.4$	[a]

[a] = of doubtful value, unknown uncertainty.

Tables 6 and 7 report Recommended values for the protonation constants for CO_3^{2-} and PO_4^{3-}. These are supplementary data that are required to complete speciation calculations on the related Hg^{2+} systems. These data, and the reaction ion interaction coefficients, $\Delta\varepsilon$, are also derived from the critical evaluation of published stability constants [2003PET] and application of SIT functions. However, the reader is alerted to the fact that NaCl medium and different activity coefficient relationships are used for these two systems (see Sections 7.1 and 7.2).

Table 6 Recommended values for the $H^+ - CO_3^{2-}$ system at 298.15 K, 1 bar, and $I_m = 0$ mol kg^{-1}. R = Recommended; P = Provisional. $\Delta\varepsilon$ values for NaCl medium.

Reaction		
$H^+ + CO_3^{2-} \rightleftharpoons HCO_3^-$	$\log_{10} K_1° = 10.336 \pm 0.005$	R
	$\Delta\varepsilon^1 \quad = -(0.116 \pm 0.002)$ kg mol^{-1}	
$H^+ + HCO_3^- \rightleftharpoons H_2CO_3*^3$	$\log_{10} K_2° = 6.355 \pm 0.003$	R
	$\Delta\varepsilon^2 \quad = -(0.092 \pm 0.002)$ kg mol^{-1}	

[1]Based on regression analysis yielding $a_jB = 1.117 \pm 0.015$. With $a_jB = 1.50$, $\log_{10} K_1° = 10.248 \pm 0.002$, and $\Delta\varepsilon = -(0.078 \pm 0.001)$ kg mol^{-1}. See Section 7.1.
[2]Based on regression analysis yielding $a_jB = 1.136 \pm 0.022$. With $a_jB = 1.50$, $\log_{10} K_2° = 6.317 \pm 0.001$, and $\Delta\varepsilon = -(0.072 \pm 0.001)$ kg mol^{-1}.
[3]$[H_2CO_3*] = [CO_2(aq)] + [H_2CO_3]$.

Table 7 Recommended values for the $H^+ - PO_4^{3-}$ system at 298.15 K, 1 bar, and $I_m = 0$ mol kg^{-1}. R = Recommended; P = Provisional. $\Delta\varepsilon$ values for NaCl medium.

Reaction		
$H^+ + PO_4^{3-} \rightleftharpoons HPO_4^{2-}$	$\log_{10} K_1° = 12.338 \pm 0.028$	R
	$\Delta\varepsilon^1 \quad = -(0.078 \pm 0.019)$ kg mol^{-1}	
$H^+ + HPO_4^{2-} \rightleftharpoons H_2PO_4^-$	$\log_{10} K_2° = 7.200 \pm 0.008$	R
	$\Delta\varepsilon^2 \quad = -(0.061 \pm 0.016)$ kg mol^{-1}	
$H^+ + H_2PO_4^- \rightleftharpoons H_3PO_4$	$\log_{10} K_3° = 2.141 \pm 0.010$	R
	$\Delta\varepsilon^3 \quad = -(0.043 \pm 0.017)$ kg mol^{-1}	

[1]Based on regression analysis yielding $a_jB = 1.204 \pm 0.090$. With $a_jB = 1.50$, $\log_{10} K_1° = 12.277 \pm 0.019$, and $\Delta\varepsilon = -(0.029 \pm 0.008)$ kg mol^{-1}. See Section 7.2.
[2]Based on regression analysis yielding $a_jB = 1.160 \pm 0.083$. With $a_jB = 1.50$, $\log_{10} K_2° = 7.191 \pm 0.008$, and $\Delta\varepsilon = -(0.011 \pm 0.007)$ kg mol^{-1}.
[3]Based on regression analysis yielding $a_jB = 1.352 \pm 0.235$. With $a_jB = 1.50$, $\log_{10} K_2° = 2.138 \pm 0.009$, and $\Delta\varepsilon = -(0.033 \pm 0.006)$ kg mol^{-1}.

The abbreviations used to describe the experimental methods are as follows.

emf   emf measurements using electrodes utilizing redox equilibria
sol   solubility determination
gl   pH measurement by glass electrode
con   conductivity
dis   distribution between immiscible solvents
ise   emf measurements using an ion selective electrode
cal   calorimetry
sp   spectrophotometry

4. Hg(II) SOLUTION CHEMISTRY

Mercury has two common cations in aqueous solution, a di-ion, Hg_2^{2+}, composed of two singly charged ions, and a doubly charged Hg^{2+}. Of these, Hg(II) is the dominant form in most aqueous solutions. Diagrams of pH-potential boundaries indicate that Hg(I) is stable only within a narrow band of E_H values in acid solutions [66ZOU]. The hydrolysis reactions of Hg(II) are significant at pH > 1 [86BAE], and these reactions must be taken into account in all equilibrium studies of Hg^{2+}-ligand systems. At low

aqueous mercury concentrations ($\leq$0.01 mmol dm^{-3}), the dominant hydrolysis species formed are monomers HgOH$^+$ and Hg(OH)$_2$(aq), while Hg(OH)$_3^-$ forms at pH > 13. At higher mercury concentrations, evidence for the formation of the dimer, Hg$_2$(OH)$_2^{2+}$, has been reported [62AHa, 77SJb].

5. DATA EVALUATION METHODS

5.1 Data evaluation criteria

The majority of anion complexation studies of Hg(II) have utilized the potentiometric technique and have been carried out using sodium perchlorate as the ionic medium. A few have used [Ca,Mg](ClO$_4$)$_2$ or [Na,K]NO$_3$, but the propensity of Hg^{2+} to form stable chloro complexes precludes use of chloride media.

In this review, stability constant and reaction enthalpy data published for 25 °C and a wide range of ionic strengths (I_c or I_m) have been used in weighted linear regression analyses to determine values valid at 298.15 K and I_m = 0 mol kg^{-1}. Literature data have been accepted as "reliable" (designated "reported" in relevant tables), and thus included in the regression analysis, when all, or in some cases most, of the following requirements have been met:

i.   full experimental details are reported (solution stoichiometry, electrode calibration method, temperature, ionic strength, error analysis);
ii.   the equilibrium model is considered to be complete (including hydrolysis reactions);
iii. data are for an essentially noncomplexing medium; and
iv.   the experimental method and numerical analysis are considered to have minimal systematic errors.

These are not the usual IUPAC criteria for selection of published data that are used in the calculation of "Recommended" and "Provisional" values at a single ionic strength [2001PRa], but they permit utilization of a larger data set for the adopted ionic strength correlations.

Most of the uncertainties reported in the literature reflect analytical and numerical precision, but do not include systematic errors. We assign an additional uncertainty to each selected value that reflects our estimation of accuracy and reliability of the experimental methods. The data selected for use in the SIT analyses for Hg^{2+} complexes are recorded in Tables A2-1 through A2-15 in Appendix 2. The tables record only those data that have met our selection criteria. The column headed log$_{10}$ K (reported) contains the "accepted" stability constant data, on the molar scale, as published. The column headed log$_{10}$ K (accepted) contains the same data converted to the molal scale (to facilitate SIT analysis). It indicates our assigned uncertainties, which are based on the reliability and systematic uncertainties of the data. In the SIT regression analysis, the constants are weighted according to these assigned uncertainties. References that contain data rejected from our analysis are recorded in the footnotes to relevant tables. Each reference carries superscript(s) that refer to the reasons for rejection of the data according to the alphabetic list below.

Reasons for rejection of specific references include:

a.   data are for temperature(s) other than 25 °C, data cannot be corrected to 25 °C, or the temperature is not defined;
b.   data for Hg^{2+} complexation are for a medium other than (Na)ClO$_4$;
c.   the ionic strength has not been held constant;
d.   experimental details are incomplete;
e.   the equilibrium model is incomplete;
f.   electrode calibration details are missing;
g.   incomplete experimental data;
h.   the description of the numerical analysis of measurement data is incomplete;

i.   the correction for competing equilibria [e.g., formation of $Hg(OH)_2(aq)$] is inadequate; and
j.   value(s) appear to be in error when compared with results from more than one other reliable laboratory.

Of this list, a and b do not necessarily question the quality of the data, but merely indicate that the data has not been used in the present review. The remaining reasons, however, place doubt in relation to the validity of the data in question.

5.2 Methods for numerical extrapolation of data to $I_m = 0$ mol kg^{-1}

For many reactions, equilibrium measurements cannot be made accurately, or at all, in dilute solutions (which would permit calculation of standard state values by application of simple activity coefficient relationships). Such is the case for reactions involving formation of weak complexes or ions of high charge. For these systems, precise equilibrium data can only be obtained in the presence of an inert electrolyte of sufficiently high concentration to ensure that reactant activity coefficients are reasonably constant. The associated short-range, weak, noncoulombic interactions between the reactant species and electrolyte anions or cations must be considered. They may be described in terms of ion pair formation (as required when the Debye–Hückel theory or the empirical Davies equation is used for activity coefficients). Alternatively, they can be quantified by inclusion of empirical specific ion interaction coefficients, $\varepsilon(i,k)$, within the activity coefficient expression, as in the Brønsted–Guggenheim–Scatchard (SIT) model [97PUI], which is adopted in this review:

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

In this model, the ionic strength is expressed on the molality scale, I_m. The advantage of SIT is that the activity coefficient expressions are valid over a very wide range of concentrations. In contrast, the Debye–Hückel and Davies equations are limited to $I_m \lesssim 0.03$ mol kg^{-1} and < 0.1 mol kg^{-1}, respectively. The ionic strength dependence of stability constants discussed in this report does not require empirical relationships more complex than eq. 1. Use of Pitzer equations would require adoption of data that have not undergone critical review. The present critical assessment of data could, however, be used to refine the Pitzer model for its application to complex, multicomponent systems.

The following general reaction is assumed (omitting most charges for simplicity):

$$p\text{M} + q\text{L} + r\text{H}_2\text{O} \rightleftharpoons \text{M}_p\text{L}_q(\text{OH})_r + r\text{H}^+$$
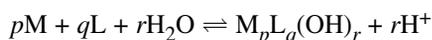
If the stability constant $\beta_{p,q,r}$ is determined in an ionic medium (containing the 1:1 electrolyte NX of ionic strength I_m mol kg^{-1}) and expressed in units of relative molality [m(species i)/$m°$, where the standard molality $m° = 1$ mol kg^{-1}] it is related to the corresponding value at zero ionic strength, $\beta_{p,q,r}°$:

$$\log_{10} \beta_{p,q,r} = \log_{10} \beta_{p,q,r}° + p\log_{10} \gamma_m(\text{M}) + q\log_{10} \gamma_m(\text{L}) + r\log_{10} a(\text{H}_2\text{O})$$
$$- \log_{10} \gamma_m(\text{p,q,r}) - r\log_{10} \gamma_m(\text{H}^+) \tag{2}$$

where $\gamma_m(p,q,r)$ refers to the species $\text{M}_p\text{L}_q(\text{OH})_r$.

Substitution of eq. 1 into 2, and the assumption that the concentration of NX is much greater than that of each reactant (such that $I_m = m_k$), gives

$$\log_{10} \beta_{p,q,r} - \Delta z^2 D - r\log_{10} a(\text{H}_2\text{O}) = \log_{10} \beta_{p,q,r}° - \Delta\varepsilon I_m \tag{3}$$

where

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

and

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

In this review, the term a_jB is set at 1.5 $kg^{1/2}$ $mol^{-1/2}$, except for the systems $H^+ - CO_3^{2-}$ and $H^+-PO_4^{3-}$, in which it is treated as a variable in the regression analysis using eq. 3. The term $\log_{10} a(H_2O)$ is near constant for most studies of equilibrium in dilute aqueous solutions where the ionic medium is in large excess; also, $\log_{10} a(H_2O) \to 0$ as $I_m \to 0$ mol kg^{-1}. For a 1:1 electrolyte (NX), this term can be calculated from the solution osmotic coefficient, Φ_m, if the minor electrolyte species (the reacting ions) are neglected, whence $I_m \approx m(NX)$:

$$\log_{10} a(H_2O) = -2m(NX)\Phi_m/M_W(\ln 10)$$

Values for the osmotic coefficient of $NaClO_4$ media are available in [59ROB]; these provide the relationship $\log_{10} a(H_2O) = -(0.01378 \pm 0.00003)(I_m/\text{mol kg}^{-1})$ for $NaClO_4$ media at 25 °C (298.15 K), $I_m = 0$ to 3.5 mol kg^{-1}.

The application of SIT to the selected literature stability constants involves graphical extrapolation of $\log_{10} \beta_{p,q,r} - \Delta z^2 D - r\log_{10} a(H_2O)$ to $m_k = 0$ (or $I_m = 0$ mol kg^{-1} for a system with a large excess of 1:1 electrolyte), using eq. 3. The intercept at $I_m = 0$ mol kg^{-1} gives the standard equilibrium constant $\log_{10} \beta_{p,q,r}°$, and the slope provides the reaction ion interaction coefficient (slope = $-\Delta\varepsilon$) as defined in eq. 3. If the regression line slope is negative, then $\Delta\varepsilon$ is positive. Conversely, the value of the stability constant $\beta_{p,q,r}$ at a specific ionic strength, I_m, can be calculated from $\beta_{p,q,r}°$ if the value of the empirical parameter $\Delta\varepsilon$ is known. Thus, this review reports values for both $\log_{10} \beta_{p,q,r}°$ and $\Delta\varepsilon$. [It is noted that in eq. 3, D is a function of I_m, whereas the ion interaction term (i.e., $\Sigma_k \varepsilon(i,k) m_k$; eq. 1) is a function of m_k; however, $m_k \approx I_m$ for a medium containing excess 1:1 electrolyte.]

The weighted linear regression analyses using SIT are represented graphically and are recorded in Appendix 3 (e.g., Fig. A3-1). The SIT regressions used values that resulted from independent analyses of experimental datum points (population values). Some values have very strong experimental bases, other have weaker grounds, some are based on a few, others on a large number of datum points, and the experimental methods also may differ. These differences were taken into account in the regression analyses by assigning appropriate weights to each value, according to [92GRE, Appendix C]. A specific regression analysis could only include values that belong to the same "parent distribution", which means they must be "consistent" with each other. In this document, "consistency" was established by propagating the uncertainties of the regression results (at $I_m = 0$ mol kg^{-1}) back to high ionic strengths, viz. the dotted lines in Fig. A3-1. If the initial SIT analysis revealed values for which the uncertainty ranges did not overlap with the area between the dotted lines, they were considered to be inconsistent with the population; thus, they were removed (as outliers) or, if justified, their uncertainties were increased accordingly. For the figures in Appendix 3, the error propagation calculation that determined the confidence limits that are shown used the errors on $\log_{10} \beta_{p,q,r}°$, and on $\Delta\varepsilon$ obtained in the final SIT regression.

5.3 Criteria for the assignments: "Recommended" and "Provisional"

Criteria for assigning equilibrium data as "Recommended" or "Provisional" (previously "Tentative") were based on those used in more recent IUPAC critical reviews [97SJa, 97LPa, 2001PRa]. In most examples in this work, an equilibrium constant $\log_{10} \beta_{p,q,r}°$ was classified as "Recommended" if the standard deviation, σ, (obtained from the SIT regression) was ≤0.2, and as "Provisional" if $0.2 \leq \sigma \leq 0.4$. Values for $\Delta_r H_m°$ obtained from the SIT regression were assigned as "Recommended" if $\sigma \leq 2.0$ kJ mol^{-1}, and as "Provisional" if $2.0 \leq \sigma \leq 5.0$ kJ mol^{-1}. In some cases, the assignment "Provisional" was necessary because there were too few "accepted" data to allow a reliable regression analysis. However, in others more subjective judgement was used when, for example, further experimental confirmation was needed or the result is, despite good coincidence of experimental data, an unexpected one.

6. EVALUATION OF EQUILIBRIUM CONSTANTS (HOMOGENEOUS REACTIONS)

6.1 The Hg^{2+}– OH^- system

The speciation diagram for the Hg^{2+}– OH^- system, based on the Recommended values recorded in Table 1 for stability constants at $I_m = 0$ mol kg^{-1}, is shown in Fig. 1. Results outside the pH range 2 to 12 should be viewed with caution as activity coefficients may deviate significantly from 1.0.
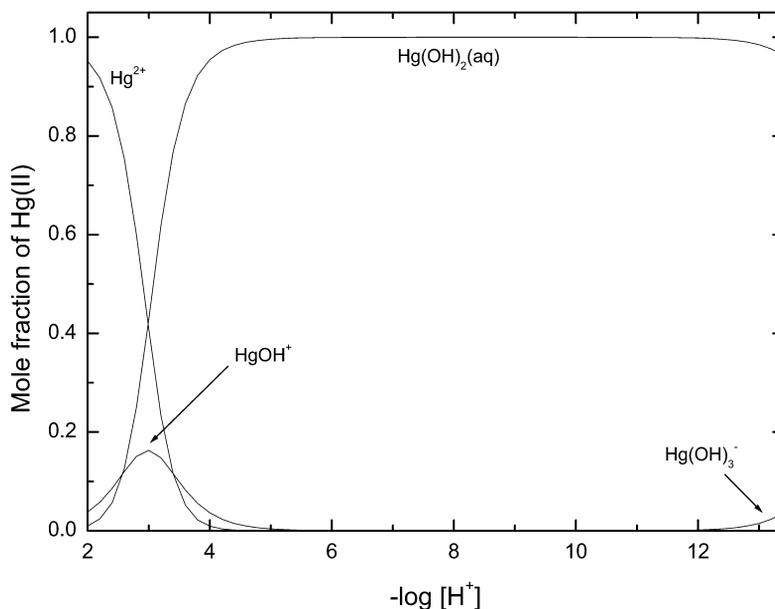
Fig. 1 Speciation diagram for the binary Hg(II) hydroxide system as obtained from the Recommended stability constants at $I_m = 0$ mol kg^{-1} (Table 1). This diagram is applicable for Hg(II) concentrations ≤ 0.01 mmol dm^{-3}. Results outside the –log [H$^+$] range of 2 to 12 should be viewed with caution as activity coefficients deviate from 1.0.

6.1.1 Formation of HgOH$^+$

Formation of the first mononuclear hydrolysis species is described by eq. 4,

$$Hg^{2+} + H_2O \rightleftharpoons HgOH^+ + H^+ \tag{4}$$

Data selected for the SIT analysis, to determine the stability constant at zero ionic strength (the standard equilibrium constant) and the reaction interaction coefficient $\Delta\varepsilon(4)$, are listed in Table A2-1, along with references and our assigned uncertainties. The selected data refer to perchlorate media and 25 °C. References for rejected data are shown in the footnote, along with the reasons for rejection, designated by the superscript letters specified in Section 5.1. The uncertainties assigned to the selected data are used to determine the weight for each respective value. The weighted linear regression (Fig. A3-1) involves the expression

$$\log_{10} *K_1 + 2D - \log_{10} a(H_2O) = \log_{10} *K_1° - \Delta\varepsilon I_m$$

that is derived from eqs. 3 and 4 ($\Delta z^2 = -2$) and which yields $\log_{10} *K_1°$ from the intercept and $-\Delta\varepsilon$ from the slope. It indicates reasonable consistency among the data and provides the Recommended value

$$\log_{10} *K_1° \text{ (eq. 4, 298.15 K)} = -3.40 \pm 0.08$$

This value is identical to that selected by Baes and Mesmer [86BAE] in their review of the hydrolysis of metal ions; their value was based on a smaller and older set of stability constants. The value for $\Delta\varepsilon(4)$ is $-(0.14 \pm 0.03)$ kg mol^{-1}. The values for $\varepsilon(Hg^{2+},ClO_4^-) = (0.34 \pm 0.03)$ kg mol^{-1} and $\varepsilon(H^+,ClO_4^-) = (0.14 \pm 0.02)$ kg mol^{-1} [97GRE] lead to $\varepsilon(HgOH^+,ClO_4^-) = (0.06 \pm 0.05)$ kg mol^{-1}.

6.1.2 Formation of Hg(OH)$_2$(aq)

Formation of the second mononuclear hydrolysis species is described by eq. 5,

$$Hg^{2+} + 2H_2O \rightleftharpoons Hg(OH)_2(aq) + 2H^+ \tag{5}$$
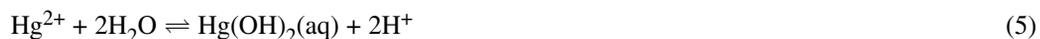
Data selected for the SIT analysis, and our estimated uncertainties, are listed in Table A2-2. References for rejected data are shown in the footnote. The selected stability constants were determined at 25 °C in sodium or calcium perchlorate media of constant ionic strength. Figure A3-2 illustrates that there is a relatively large scatter of data at high ionic strength. It appears that the data obtained from calcium perchlorate media [62AHa] and from solubility experiments [61DTa] may be less reliable than the other data obtained at $I_c = 3.0$ mol dm^{-3}. The experimental methodology used by [62AHa] resulted in some changes in the ionic strength, whereas the work of [61DTa] potentially suffers from lack of characterization of the solid phase. The Recommended constant at zero ionic strength, derived from the weighted linear regression, is

$$\log_{10} {}^*\beta_2^\circ \text{ (eq. 5, 298.15 K)} = -5.98 \pm 0.06$$

The reaction ion interaction coefficient $\Delta\varepsilon(5) = -(0.14 \pm 0.02)$ kg mol^{-1}. The values for $\varepsilon(Hg^{2+},ClO_4^-) = (0.34 \pm 0.03)$ kg mol^{-1} and $\varepsilon(H^+,ClO_4^-) = (0.14 \pm 0.02)$ kg mol^{-1} [97GRE] lead to $\varepsilon(Hg(OH)_2,Na^+,ClO_4^-) = -(0.08 \pm 0.05)$ kg mol^{-1}. This value is consistent with that reported by [90CIA], $-(0.06 \pm 0.05)$ kg mol^{-1}. The standard equilibrium constant recommended in this review is somewhat more positive than that evaluated by Baes and Mesmer [86BAE] ($\log_{10} {}^*\beta_2^\circ = -6.17$), but in good agreement with the value proposed by Ciavatta [90CIA] ($\log_{10} {}^*\beta_2^\circ = -6.01$).

6.1.3 Formation of Hg(OH)$_3^-$, Hg$_2$OH^{3+}, and Hg$_2$(OH)$_2^{2+}$

Reliable stability constant data have been reported for the formation of Hg(OH)$_3^-$, Hg$_2$OH^{3+}, and Hg$_2$(OH)$_2^{2+}$ (Table A2-3). However, there are insufficient data for a SIT analysis. From the stability constant for Hg(OH)$_3^-$ determined at $I_m = 0$ mol kg^{-1} [38GHa] and the stability constant for Hg(OH)$_2$ ($\log_{10} {}^*\beta_2^\circ = -5.98$), the stepwise stability constant $\log_{10} {}^*K_3^\circ = -15.13$ is calculated. This species will form only in highly alkaline solutions; it is unlikely to be environmentally important. The species Hg$_2$OH^{3+} and Hg$_2$(OH)$_2^{2+}$ will form only at relatively high Hg(II) concentrations (ca. 0.005 mol dm^{-3}); they also are unlikely to be environmentally important.

There has been some conjecture in relation to the stoichiometry of the Hg$_n$(OH)$_n^{n+}$ species. Sjöberg [77SJb] found evidence for Hg$_2$(OH)$_2^{2+}$, consistent with the above. In contrast, Baes and Mesmer [86BAE], in recalculating the data of Ahlberg [62AHa], concluded that the polymeric species is Hg$_3$(OH)$_3^{3+}$. Regardless of the stoichiometry, evidence for this polymer has only been found in 3 mol dm^{-3} perchlorate media and, as such, it is not possible to determine a stability constant at zero ionic strength. The polymeric species Hg$_4$(OH)$_3^{5+}$, also postulated [62AHa], has not been identified in any other study; as such, its existence is not accepted by this review.

6.2 The Hg^{2+}– Cl$^-$ system

The speciation diagram for the Hg^{2+}– Cl$^-$ system, based on the Recommended values for stability constants at $I_m = 0$ mol kg^{-1} (Table 2), is shown in Fig. 2, which represents the situation in which hydrolysis is suppressed (pH < 2). Results for values of $\log_{10}$ [Cl$^-$] > -2.0 should be viewed with caution as activity coefficients may deviate significantly from 1.0. Formation of the chloro complexes in aqueous solution is described by eqs. 6–9

$$Hg^{2+} + Cl^- \rightleftharpoons HgCl^+ \tag{6}$$

$$Hg^{2+} + 2Cl^- \rightleftharpoons HgCl_2(aq) \tag{7}$$

$$HgCl_2(aq) + Cl^- \rightleftharpoons HgCl_3^- \tag{8}$$

$$HgCl_3^- + Cl^- \rightleftharpoons HgCl_4^{2-} \tag{9}$$

The 1:1 and 1:2 chloro complexes of Hg(II) are among the most stable of metal-chloro complexes formed.

Many of the early stability constant data are not reliable because the constant ionic strength protocol was not employed. Furthermore, the simultaneous presence of $HgCl_2$, $HgCl_3^-$, and $HgCl_4^{2-}$ was not recognized, which led to erroneous evaluations. A comprehensive investigation of the Hg(I) and Hg(II) chloride system was undertaken by Sillén in the 1940s. Since $[Hg^{2+}]$ cannot be measured directly with a Hg electrode, due to formation of Hg(I), Sillén developed an indirect but very precise emf method based on measurement of the redox potential for Hg(II)/Hg(I) in the presence of $Hg_2Cl_2(s)$. These experiments, performed at 25.0 °C, $I_c = 0.5$ mol dm^{-3} (NaClO$_4$) and pH = 2 (to avoid hydrolysis), are described in detail in [46SIL].
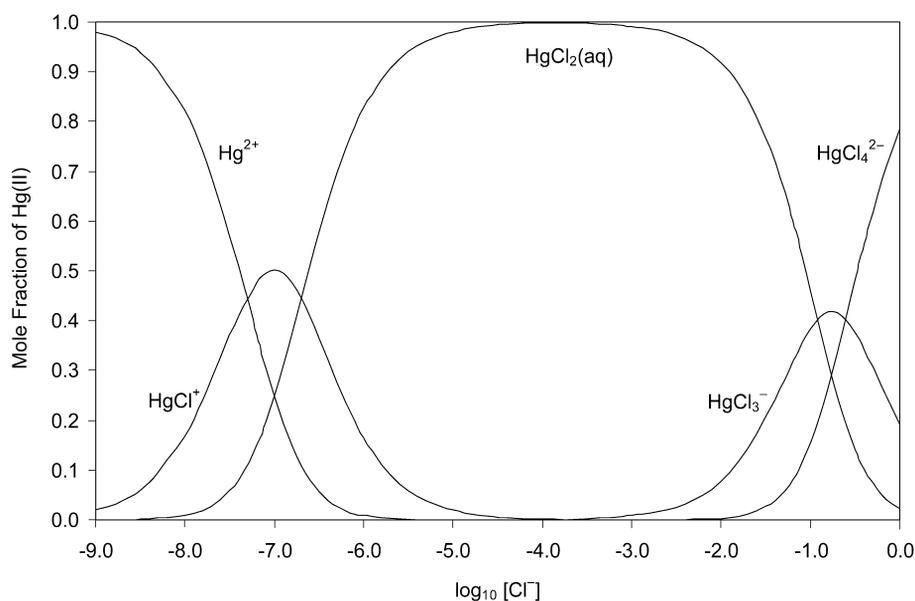
Fig. 2 Speciation diagram of the binary Hg(II) chloride system as obtained from the Recommended stability constants at $I_m = 0$ mol kg^{-1}, Table 2. Hydrolysis is suppressed (pH < 2 is assumed). Results for –log [Cl$^-$] > –2.0 should be viewed with caution as activity coefficients deviate from 1.0.

6.2.1 Formation of HgCl$^+$

Data selected for the SIT analysis, to determine the stability constant at zero ionic strength (the standard equilibrium constant) and the ion interaction coefficient $\Delta\varepsilon$ for reaction 6, are listed in Table A2-4, along with our assigned uncertainties. The selected data all refer to NaClO$_4$ media and 25 °C. The weighted linear regression (Fig. A3-3) shows that there is reasonable consistency between the data and results in the Recommended standard constant

$$\log_{10} K_1^\circ \text{ (eq. 6, 298.15 K)} = 7.30 \pm 0.05$$

The reaction ion interaction coefficient based on this regression is $\Delta\varepsilon(6) = -(0.22 \pm 0.04)$ kg mol^{-1}, which is in excellent agreement with that calculated from tabulated ε values [97GRE] for the reactant and product species, $\Delta\varepsilon(6) = -(0.18 \pm 0.06)$ kg mol^{-1}.

Formation of HgCl$^+$ is also expressed by reaction 10

$$Hg^{2+} + HgCl_2(aq) \rightleftharpoons 2HgCl^+ \tag{10}$$

The emf method elaborated by Sillén [46SIL, 47SIL] yields a redox titration curve that goes through a maximum of dE/dc (where c is the concentration of titrant) when the concentration of HgCl$^+$ is at a maximum, because the measured emf is a function of [HgCl$^+$] alone. This results in precise log K values for equilibrium 10. The selected values for 25 °C and (Na,H)ClO$_4$ media are listed in Table A2-5. With the exception of one solvent extraction (distribution) study [57MAa], all values result from application of Sillén's emf method. The weighted linear regression (Fig. A3-4) results in the recommended value of:

$$\log_{10} K° \text{ (eq. 10, 298.15 K)} = 0.61 \pm 0.03$$

The reaction ion interaction coefficient is $\Delta\varepsilon(10) = -(0.02 \pm 0.02)$ kg mol^{-1}.

6.2.2 Formation of HgCl$_2$(aq)

Data selected for the SIT analysis of reaction 7 are listed in Table A2-6. The weighted linear regression (Fig. A3-5) shows that there is reasonable consistency between the data and results in the Recommended standard constant

$$\log_{10} \beta_2° \text{ (eq. 7, 298.15 K)} = 14.00 \pm 0.07$$

The resulting reaction ion interaction coefficient is $\Delta\varepsilon(7) = -(0.39 \pm 0.03)$ kg mol^{-1}.

From the reported values $\varepsilon(Hg^{2+},ClO_4^-) = (0.34 \pm 0.03)$ kg mol^{-1}, $\varepsilon(HgCl^+,ClO_4^-) = (0.19 \pm 0.02)$ kg mol^{-1}, and $\varepsilon(Cl^-,Na^+) = (0.03 \pm 0.01)$ kg mol^{-1} [97GRE], $\Delta\varepsilon(10)$ gives $\varepsilon(HgCl_2,Na^+,ClO_4^-) = (0.06 \pm 0.05)$ kg mol^{-1} and $\Delta\varepsilon(7)$ gives $\varepsilon(HgCl_2,Na^+,ClO_4^-) = (0.01 \pm 0.04)$ kg mol^{-1}. Both values are consistent with that reported by [90CIA], (0.06 ± 0.03) kg mol^{-1}.

The evaluated constants for reactions 6, 7, and 10 define an energy cycle that is consistent within experimental error. From the relationship $2\log_{10} K_1°(6) = \log_{10} K°(10) + \log_{10} \beta_2°(7)$, we derive the Recommended standard constant

$$\log_{10} K_1° \text{ (eq. 6, 298.15 K)} = 7.31 \pm 0.04$$

which is consistent with that derived from the SIT analysis (Section 6.2.1).

6.2.3 Formation of HgCl$_3^-$ and HgCl$_4^{2-}$

The stepwise formation constants for the 1:3 and 1:4 Hg(II) chloro complexes are much smaller than those for the 1:1 and 1:2 complexes. Thus, comparatively large chloride concentrations are required for them to form (Fig. 2). Nevertheless, their stabilities are such that they always exist in aqueous solution simultaneously, in equilibrium with HgCl$_2$(aq). Data selected for the SIT analyses for reactions 8 and 9 are listed in Table A2-7. The weighted linear regression analyses (Figs. A3-6 and A3-7) indicate excellent consistency between the data. They result in the Recommended standard constants ($I_m = 0$ mol kg^{-1}):

$$\log_{10} K_3° \text{ (eq. 8, 298.15 K)} = 0.92_5 \pm 0.09$$

$$\log_{10} K_4° \text{ (eq. 9, 298.15 K)} = 0.61 \pm 0.12$$

The resulting reaction ion interaction coefficients are $\Delta\varepsilon(8) = (0.01 \pm 0.05)$ kg mol^{-1} and $\Delta\varepsilon(9) = -(0.00_3 \pm 0.05)$ kg mol^{-1}. From these, we derive new ε values: $\varepsilon(Na^+, HgCl_3^-) = (0.05 \pm 0.07)$ kg mol^{-1} and $\varepsilon(Na^+, HgCl_4^{2-}) = (0.08 \pm 0.09)$ kg mol^{-1}.

The first value is in the range expected for +1/–1 interactions, whereas for the +1/–2 category, ε values are usually negative, cf. [92GRE, Table B.4].

The SIT analysis used only data obtained for $NaClO_4$ media and 25 °C. However, the results of the refractometric investigation of Barcza [76BAb] in 1.0 mol dm^{-3} $NaNO_3$ solution ($\log_{10} K_3 = 0.89$), and Dubinskii and Shul'man's $\log_{10} K_3$ value in 0.4 mol dm^{-3} $HClO_4$ solution [70DSe] (0.96), agree well with our selected values.

6.2.4 Other binary Hg(II) chloro complexes

The formation of Hg(II) chloro complexes higher than 1:4 has not been observed in aqueous solution. However, Linhart [15LIa, 16LIa] suggested the existence of the dimeric complexes Hg_2Cl_4(aq), $Hg_2Cl_5^-$, and $Hg_2Cl_6^{2-}$ from distribution measurements with total Hg(II) concentrations up to 0.29 mol dm^{-3}. Tourneux [34TOa] also reported the formation of dimeric anionic complexes, but the ionic strength was varied substantially and it is difficult to distinguish medium effects from weak complexation. Ciavatta and Grimaldi [68CGb] varied the total Hg(II) concentration from 0.038 to 0.19 mol dm^{-3} [$I_c = 1.0$ mol dm^{-3} (Na)ClO$_4$] and found no evidence for polynuclear Hg(II)– Cl$^-$ complexes. It is thus inferred that the binary Hg(II) chloride system in acidic aqueous solution is fully characterized by the complexes HgCl$^+$, HgCl$_2$(aq), HgCl$_3^-$, and HgCl$_4^{2-}$.

6.3 The Hg^{2+}– OH^-– Cl^- system: Formation of HgOHCl(aq)

Sjöberg [77SJb] made a detailed investigation of the ternary system Hg^{2+}– OH^-– Cl^-, varying the component concentrations over large ranges. He found evidence for the formation of HgOHCl(aq) in solution at pH 3 to 9 and for $\log_{10}$ [Cl$^-$] in the range –1 to –7 (reaction 11):

$$HgCl_2(aq) + H_2O \rightleftharpoons HgOHCl(aq) + Cl^- + H^+ \tag{11}$$

At a total concentration [Hg]$_T$ > 10 mmol dm^{-3}, the polynuclear complexes $Hg_2(OH)Cl_2^+$ and $Hg_3(OH)_2Cl^{3+}$ also formed. Other authors investigating the hydrolysis of HgCl$_2$ [65PIa, 68CGa, 76CGb] also observed the formation of HgOHCl(aq). Table A2-8 records the reported stability constants. Considering the different ionic strengths, and the possible systematic uncertainties that are undoubtedly larger than those reported, the three values for HgOHCl(aq) formation are remarkably consistent.

Extrapolation of the stability constants to zero ionic strength is not possible because of the scarcity of data. However, the importance of reaction 11 demands that an estimate be made for $\log_{10} \beta$ for reaction 12 at $I_m = 0$ mol kg^{-1}.

$$Hg^{2+} + Cl^- + H_2O \rightleftharpoons HgOHCl(aq) + H^+ \tag{12}$$

This can be effected by use of eq. 3, an estimated value for $\Delta\varepsilon(12)$ in $NaClO_4$ media:

$$\Delta\varepsilon(12) = \varepsilon(HgOHCl,Na^+,ClO_4^-) + \varepsilon(H^+,ClO_4^-) - \varepsilon(Hg^{2+},ClO_4^-) - \varepsilon(Cl^-,Na^+) \tag{13}$$

and the value calculated for log $\beta(12)$ at I_m =3.503 m [log $\beta(12) = 4.12$], derived from the data in Tables A2-6 and A2-8. In eq. 13, the value for $\varepsilon(HgOHCl,Na^+,ClO_4^-)$ is not known, but can be estimated from $\varepsilon(HgOHCl,Na^+,ClO_4^-) = \frac{1}{2} [\varepsilon(Hg(OH)_2,Na^+,ClO_4^-) + \varepsilon(HgCl_2,Na^+,ClO_4^-)]$. Based on the average of ε values derived in this work, and those from [90CIA], this yields $\varepsilon(HgOHCl,Na^+,ClO_4^-) = -(0.01 \pm 0.09)$ kg mol^{-1}, and hence $\Delta\varepsilon(12) = -(0.24 \pm 0.10)$ kg mol^{-1}. From eq. 3, the value calculated for $\log_{10} \beta°$ (eq. 12, 298.15 K) is 4.27 $\pm$ 0.35.

6.4 The Hg^{2+}– CO_3^{2-} system

Figures 3a and 3b present speciation diagrams for the Hg^{2+}– H^+– CO_2 system, based on a CO_2 fugacity $f(CO_2)$ of 370 µbar and 1 bar, respectively, and our Recommended standard constants at $I_m = 0$ mol kg^{-1} (Tables 1 and 3).
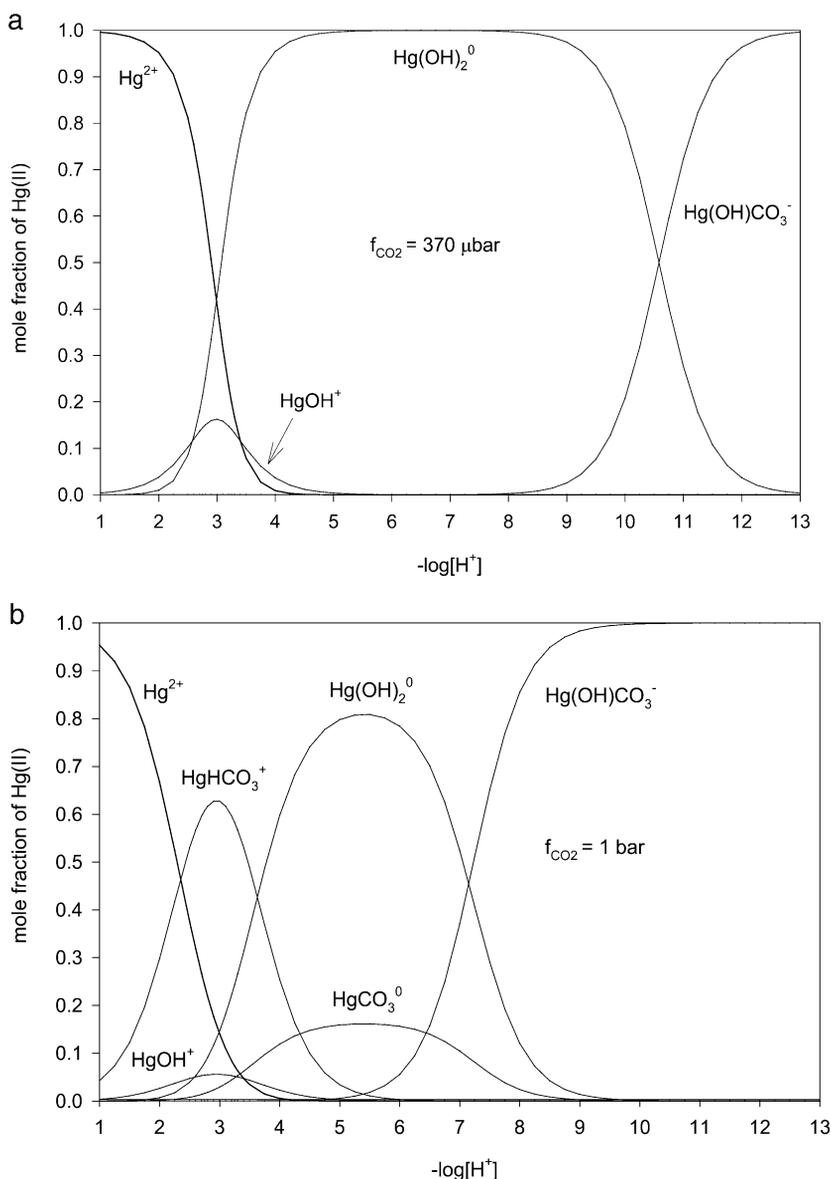
Fig. 3 Speciation diagrams for the Hg^{2+}– H^+– CO_2 system as obtained from the selected stability constants reported in Tables 1 and 3 and calculated for (a) $f(CO_2) = 370$ microbar and (b) $f(CO_2) = 1$ bar. These diagrams are applicable for Hg(II) concentrations below ≤0.01 mmol dm^{-3}. Results outside the $-\log[H^+]$ range of 2 to 12 should be viewed with caution as activity coefficients deviate from 1.0.

Equilibrium constants for the formation of $HgOH^+$ and $HgCO_3(aq)$ are of a similar magnitude. However, the ratio of concentrations $[Hg(OH)_2(aq)]/[HgOH^+]$ is >1 over a wide pH range; thus, experimental evaluation of $Hg^{2+}-CO_3^{2-}$ equilibria requires accurate corrections for the coformation of $Hg(OH)_2(aq)$, the predominant Hg(II) hydroxy complex in the pH region relevant to environmental systems.

The only reported equilibrium studies of aqueous Hg(II) interactions with carbonate are those of Hietanen and Högfeldt [76HHa, 76HHb] at 25 °C (3.0 mol dm^{-3} $NaClO_4$) and of Bilinski et al. [80BMb] at 25 °C (0.5 mol dm^{-3} $NaClO_4$). The former results, summarized in Table A2-9, are somewhat lacking in precision, but are regarded as more reliable than the latter. Extrapolation to zero ionic strength is not possible. However, the derived isocoulombic reactions shown in Table A2-10 should have minimal dependence on ionic strength. Consequently, the isocoulombic equilibrium constants shown in Table A2-10, based on the Table A2-9 values, have been used as Recommended values appropriate to $I_m = 0$ mol kg^{-1}, 25 °C, and 1 bar total pressure.

To assess the influence of CO_2 on Hg(II) speciation in natural waters, equilibrium with the atmosphere [CO_2 fugacity, $f(CO_2)$, equal to 370 μbar] is assumed. From the data in Table A2-10 for reactions 14 and 15, $I_c = 3.0$ mol dm^{-3}:

$$HgOH^+ + CO_2(g) \rightleftharpoons HgHCO_3^+ \tag{14}$$

$$Hg(OH)_2(aq) + CO_2(g) \rightleftharpoons HgCO_3(aq) + H_2O \tag{15}$$

the following calculated concentration ratios, relevant to natural waters, are independent of pH: $[HgHCO_3^+]/[HgOH^+] = 10^{-2.4}$ (reaction 14) and $[HgCO_3(aq)]/[Hg(OH)_2(aq)] = 10^{-4.1}$ (reaction 15).

For reaction 16,

$$Hg(OH)_2(aq) + HCO_3^- \rightleftharpoons Hg(OH)CO_3^- + H_2O \tag{16}$$

$[Hg(OH)CO_3^-]/[Hg(OH)_2(aq)] = 10^{0.98} [HCO_3^-]$; this indicates that $Hg(OH)CO_3^-$ is significant relative to $Hg(OH)_2(aq)$ only at very high HCO_3^- concentrations.

The data in Table A2-10 provide relationships between the concentrations of $HgHCO_3^+$, $HgCO_3(aq)$, and $Hg(OH)CO_3^-$. Since $[HgHCO_3^-]/[HgCO_3] = 10^{4.33} [H^+]$, it follows that $HgCO_3(aq)$ is a dominant species above pH 4.3, independent of $f(CO_2)$. Since $[Hg(OH)CO_3^-]/[HgCO_3] = 10^{1.68}$ $[HCO_3^-]/f(CO_2)$, the species $Hg(OH)CO_3^-$ can be dominant relative to $HgCO_3(aq)$ in natural waters. For $f(CO_2) = 370$ μbar, the ratio $[Hg(OH)CO_3^-]/[HgCO_3]$ is greater than unity when the HCO_3^- concentration exceeds approximately 8 μmol dm^{-3}.

6.5 The $Hg^{2+}-PO_4^{3-}$ system

For the $Hg^{2+}-H^+-PO_4^{3-}$ system, there are a limited number of data at $I_c = 3.0$ mol dm^{-3} $NaClO_4$. A SIT analysis is not possible; the selected data are neither "Recommended" nor "Provisional" (Table 4). Potentiometric study of $Hg^{2+}-PO_4^{3-}$ equilibria is confounded by the low solubility of $HgHPO_4(s)$, $Hg_3(PO_4)_2(s)$, and $(HgOH)_3PO_4(s)$. A single paper [75QDa] reports the formation of two rather stable, water-soluble Hg(II)-phosphate complexes, $HgHPO_4(aq)$ and $HgPO_4^-$ at 25 °C, 3.0 mol dm^{-3} $NaClO_4$, reactions 17 and 18 (Table 4).

$$Hg^{2+} + HPO_4^{2-} \rightleftharpoons HgHPO_4(aq) \tag{17}$$

$$Hg^{2+} + HPO_4^{2-} \rightleftharpoons HgPO_4^- + H^+ \tag{18}$$

By using the protonation constants for phosphate ion under identical conditions [69BSb], stability constants can be derived for reactions 19 and 20:

$$Hg^{2+} + H^+ + PO_4^{3-} \rightleftharpoons HgHPO_4(aq) \tag{19}$$

$$Hg^{2+} + PO_4^{3-} \rightleftharpoons HgPO_4^{-} \tag{20}$$

viz. $\log_{10} \beta$ (eq. 19, 298.15 K) = 19.65 ± 0.2 and $\log_{10} K_1$ (eq. 20, 298.15 K) = 14.1 ± 0.2, respectively.

Despite the lack of "Recommended" values, the importance of phosphate as a water pollutant necessitates further discussion. At sufficiently high concentrations (e.g., total concentrations $[Hg^{2+}]_T$ = 5×10^{-5} mol dm^{-3} and $[PO_4^{3-}]_T = 5 \times 10^{-3}$ mol dm^{-3}) Hg(II) speciation is dominated by the two water-soluble complexes, HgHPO$_4$ and HgPO$_4^{-}$, over a wide pH range (Fig. 4), with Hg(OH)$_2$(aq) dominating at pH > 7. The three Hg(II)-phosphate solid phases form at higher concentrations of Hg(II) or phosphate, with HgO(s) forming at pH > 9.4 (Fig. 5).
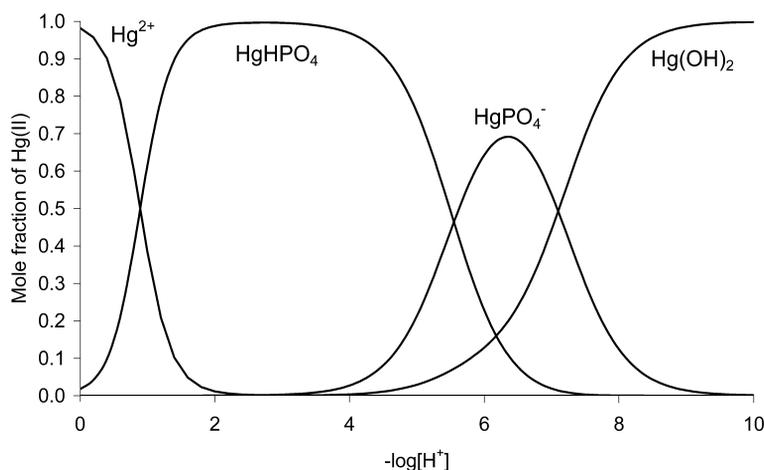
Fig. 4 Speciation diagram for the Hg^{2+}– H$^+$– PO$_4^{3-}$ system (total concentrations $[Hg^{2+}]_T = 5 \times 10^{-5}$ mol dm^{-3} and $[PO_4^{3-}]_T = 5 \times 10^{-3}$ mol dm^{-3}) as obtained from the selected stability constants reported in Table 4 (I_c = 3 mol dm^{-3} NaClO$_4$).
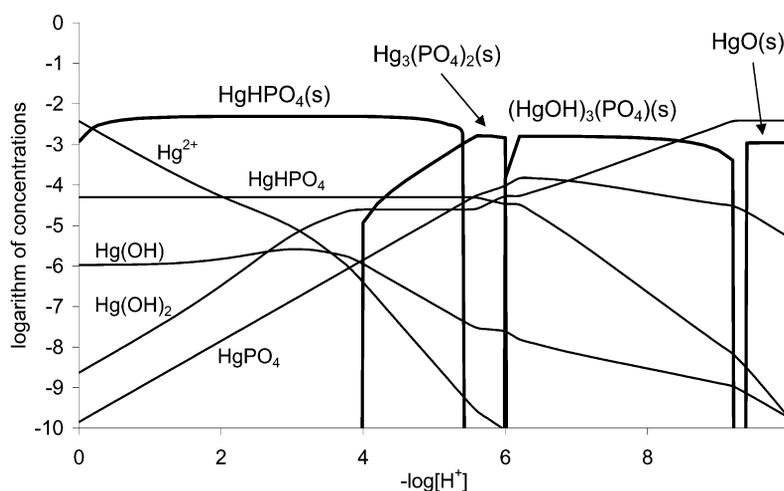
Fig. 5 Speciation diagram for soluble and insoluble species in the Hg^{2+}– H$^+$– PO$_4^{3-}$system (total concentrations $[Hg^{2+}]_T = 5 \times 10^{-3}$ mol dm^{-3} and $[PO_4^{3-}]_T = 5 \times 10^{-3}$ mol dm^{-3}) as obtained from the selected stability and solubility constants reported in Table 4 (I_c = 3 mol dm^{-3} NaClO$_4$). Solid phases shown by bold lines.

6.6 The Hg^{2+}– SO_4^{2-} system

For the interactions between cations and strongly hydrated polyvalent anions such as SO_4^{2-}, CO_3^{2-}, and PO_4^{3-}, special care must be taken in the interpretation of experimental data. This is because such systems may involve the formation of both inner-sphere ("contact") and outer-sphere ("solvent separated" and "solvent shared") complexes. A detailed consideration shows that under such circumstances, the common spectroscopic methods (UV–vis, NMR, and Raman) probe different equilibrium processes from those determined by traditional methods such as potentiometry and conductivity. Thus, constants obtained for such systems by different experimental methods may not be comparable. This is discussed in more detail in Appendix 1B, using SO_4^{2-} as an example.

Only three papers report quantitative measurements for the Hg^{2+}– H^+– SO_4^{2-} system, all at similar I_c, so a SIT analysis is not possible. The selected data (Table 5), neither of which is "Recommended", refer to $I_c = 0.5$ mol dm^{-3} (NaClO$_4$). Stability constants listed in more recent publications [see, e.g., 93MOR] appear to be derived from these papers. The small stability constants indicate that formation of sulfate complexes will not be a major feature of Hg(II) speciation in typical environmental fresh waters (total concentration $[SO_4^{2-}]_T \approx 10^{-4}$ M), even though the constants should increase considerably with decreasing I [2001KRA].

None of the published data for Hg^{2+}– SO_4^{2-} complexation is fully satisfactory. Surprisingly, no quantitative IR or Raman study of this system appears to have been made [2002RUD]. The investigation considered most reliable is that of Infeldt and Sillén [46ISa] who used mercury electrode [Hg/Hg(I),Hg(II)] potentiometry to measure K_1 and β_2. The values obtained (Table A2-11) were based on the stability constants for the Hg(I)– SO_4^{2-} system, determined in the same paper. Because of solubility problems, only a limited range of concentrations could be investigated. Using the UV band of Hg^{2+}(aq) in a study of the substitution kinetics of Co(III) complexes, Posey and Taube [57PTa] reported just three spectrophotometric measurements of K_1 (reaction 23):

$$Hg^{2+} + SO_4^{2-} \rightleftharpoons Hg(SO_4)(aq) \tag{21}$$

Although conditions were favorable, with the ratio of total concentrations $[SO_4^{2-}]_T/[Hg^{2+}]_T \leq 30$, no higher order complexes were detected. The values reported for K_1 [46ISa, 57PTa] are in fair agreement, but their average (Table 5) must be regarded as "Provisional", pending further investigation.

The reported value of β_2 [46ISa], although qualitatively confirmed [57KSb], is considered doubtful because of: (i) possible activity coefficient variation resulting from significant replacement of the NaClO$_4$ medium by Na$_2$SO$_4$ at constant I, (ii) the failure of [57PTa] to detect such a complex under conditions favorable to its formation, and (iii) the absence of evidence for such species in related, but much better characterized, metal(II)– SO_4^{2-} systems.

7. SPECIATION IN 2-COMPONENT SYSTEMS: H^+– L

Examples of speciation calculations for the selected Hg^{2+}-ligand systems are given in Figs. 1–5. For those ligands that are the conjugate bases of weak acids (CO_3^{2-}, PO_4^{3-}), the calculations require values for the ligand protonation constants under the same conditions of ionic strength and medium. To this end, this review also presents an analysis of available data for the required ligand protonation reactions.

7.1 The H^+– CO_3^{2-} system

Table 6 records the Recommended standard stability (protonation) constants for the CO_3^{2-} protonation reactions at 25 °C and $I_m = 0$ mol kg^{-1}, based on weighted linear regression analyses of an extensive series of selected data for NaCl media (Table A4-1a). The data for NaClO$_4$ media are fewer (Table A4-1b) and provide a much inferior regression.

The ionic strength dependence of $\log_{10} K_n$ for reactions 22 and 23 (in which $[H_2CO_3{}^*] = [CO_2(aq)] + [H_2CO_3])$

$$H^+ + CO_3{}^{2-} \rightleftharpoons HCO_3{}^- \tag{22}$$

$$H^+ + HCO_3{}^- \rightleftharpoons H_2CO_3{}^* \tag{23}$$

highlights two limitations of SIT. Firstly, Scatchard [76SCA] used the Debye–Hückel term a_jB as an empirical parameter and set it to the value 1.5 $kg^{1/2}$ $mol^{-1/2}$, which was found to minimize the ionic strength dependence of derived $\varepsilon(i,k)$ values for a wide, but necessarily limited, range of systems. Secondly, there is evidence that SIT interaction coefficients may be concentration-dependent [97GRE, p. 332], a factor not taken into account in the simple theory.

SIT regression analyses for reactions 22 and 23 based on $a_jB = 1.5$ $kg^{1/2}$ $mol^{-1/2}$ indicate distinct curvature at low values of I_m, a feature that becomes apparent because of the large number of data available for NaCl media (Figs. A4-1a and A4-2a). In contrast, by allowing a_jB to vary, that is, by treating the term D in eq. 3 as a fitting parameter, there is a significant improvement in goodness of fit (Figs. A4-1b and A4-2b). Most importantly, the values for $\log_{10} K_n{}^\circ$ obtained from the regressions are now consistent with the body of results reported for $I_m = 0$ mol kg^{-1} (Table A4-1a) and based on reliable emf or conductivity data determined at low I_m with or without added electrolyte. This consistency is an important validation of the empirical approach adopted here.

For reaction 22, the weighted linear regression analysis gave the Recommended value:

$$\log_{10} K_1{}^\circ \text{ (eq. 22, 298.15 K)} = 10.336 \pm 0.005$$

and $a_jB = 1.117 \pm 0.015$ $kg^{1/2}$ $mol^{-1/2}$ and $\Delta\varepsilon(22) = -(0.116 \pm 0.002)$ kg mol^{-1}, where uncertainties are expressed as ± one standard deviation. For reaction 23, the weighted linear regression analysis gave the Recommended value:

$$\log_{10} K_2{}^\circ \text{ (eq. 23, 298.15 K)} = 6.355 \pm 0.003$$

and $a_jB = 1.136 \pm 0.022$ $kg^{1/2}$ $mol^{-1/2}$ and $\Delta\varepsilon(23) = -(0.092 \pm 0.002)$ kg mol^{-1}. The Recommended values for $\log_{10} K_1{}^\circ$ and $\log_{10} K_2{}^\circ$ are in excellent agreement with the CODATA values [89COX], viz. 10.33 ± 0.02 and 6.354 ± 0.02, where uncertainties are assumed to be ± two standard deviations. In contrast, there is poorer agreement between the CODATA values and those calculated by using $a_jB = 1.5$ $kg^{1/2}$ $mol^{-1/2}$ in the SIT regression analysis (10.248 ± 0.002 and 6.317 ± 0.001).

The deviations from linearity which arise when a_jB is fixed at 1.5 $kg^{1/2}$ $mol^{-1/2}$ could relate either to inadequacies in the treatment of activity coefficients, or to weak ion pairing that occurs between Na^+ and $CO_3{}^{2-}$ or $HCO_3{}^-$, or both. On the latter point. it is noted that deviation (Figs. A4-1a and A4-2a) is greater for $CO_3{}^{2-}$ protonation (K_1) than for $HCO_3{}^-$ protonation (K_2), consistent with the relative strength of possible ion pair interactions [2003PET]. The same trend is noted for protonation of $PO_4{}^{3-}$, $HPO_4{}^2$, and $H_2PO_4{}^-$ in NaCl media (Section 7.2, Figs. A4-3a to A4-5a and [2003PET]). However, it is inappropriate to mix the ion pair theory and SIT theory in attempting an empirical analysis of these data. In SIT, ion pairing should contribute to the derived values of $\Delta\varepsilon$. In the current treatment, it will be reflected in the empirical values for $\Delta\varepsilon$ and a_jB. Indeed, it is noted that the empirical values for a_jB increase toward the SIT empirical value of 1.5 as the charge on the conjugate base decreases.

7.2 The H^+– $PO_4{}^{3-}$ system

Table A4-2 contains an extensive series of selected data for NaCl, KCl, $NaClO_4$, and $NaNO_3$ media. Table 7 records the Recommended stability constants for the $PO_4{}^{3-}$ protonation reactions at 25 °C and $I_m = 0$ mol kg^{-1}. As there are comparatively few data for $NaClO_4$ media, the regression analyses were based on the selected data for NaCl media.

Regression analyses were carried out for each of the stepwise equilibria:

$$H^+ + PO_4^{3-} \rightleftharpoons HPO_4^{2-} \tag{24}$$

$$H^+ + HPO_4^{2-} \rightleftharpoons H_2PO_4^- \tag{25}$$

$$H^+ + H_2PO_4^- \rightleftharpoons H_3PO_4 \tag{26}$$

Figures A4-3 to A4-5 show the weighted linear regression analyses for NaCl media. Analogous to that for reactions 22 and 23, the SIT regression analyses for reactions 24 to 26 based on $a_jB = 1.5$ kg$^{1/2}$ mol$^{-1/2}$ indicate curvature at low values of I_m (the derived values for $\Delta\varepsilon$, and $\log_{10} K_n°$ are shown in the footnotes to Table 7). By allowing a_jB to vary in the term D (eq. 3), there were again significant improvements in goodness of fit and improved agreement with the literature values reported for $I_m = 0$ (corr). The weighted linear regression analyses using data for NaCl media gave the values for $\Delta\varepsilon$ and a_jB, and the Recommended values of $\log_{10} K_n°$, shown in Table 7:

$$\log_{10} K_1°(\text{eq. 24, 298.15 K}) = 12.338 \pm 0.028$$

$$\log_{10} K_2°(\text{eq. 25, 298.15 K}) = 7.200 \pm 0.008$$

$$\log_{10} K_3°(\text{eq. 26, 298.15 K}) = 2.141 \pm 0.010$$

The Recommended values for $\log_{10} K_1°$, $\log_{10} K_2°$, and $\log_{10} K_3°$ are in excellent agreement with the CODATA values [89COX], viz. 12.35 ± 0.03, 7.212 ± 0.013, and 2.14 ± 0.03. In contrast, there is poorer agreement between the CODATA values and those calculated by using $a_jB = 1.5$ kg$^{1/2}$ mol$^{-1/2}$ in the SIT regression analysis, particularly for $\log_{10} K_1°$ (12.277 ± 0.019).

Regression analyses (not shown) using the less extensive data set for KCl media gave values for $\log K_n°$ consistent with those obtained from extrapolation in NaCl medium, but different ion interaction coefficients (Table A4-3). The latter arises because of the dependence of the term $\Delta\varepsilon = \varepsilon(\text{cation}, H_nPO_4^{(3-n)-}) - \varepsilon(H^+, \text{anion}) - \varepsilon(\text{cation}, H_{n-1}PO_4^{(4-n)-})$ for the reaction $H^+ + H_{n-1}PO_4^{(4-n)-} \rightleftharpoons H_nPO_4^{(3-n)-}$ on the nature of the medium anion and cation. The selected data for NaCl and KCl media include a significant number of values for $I_m = 0$ mol kg^{-1}, each of which was derived from a series of experimental $\log_{10} K_n$ values that are of high precision. For example, in [61VQa] 35 values were used between $I_c = 0$ and 0.5 mol dm^{-3}, in [65PEa] 15 between $I_c = 0.002$ and 0.16 mol dm^{-3}, in [58GRc] 10 between $I_c = 0.02$ and 0.11 mol dm^{-3}, in [43BAa] 43 between $I_c = 0.01$ and 0.45 mol dm^{-3}, in [51BAb] 46 between $I_c = 0.01$ and 0.36 mol dm^{-3}, and in [49MCb] 36 between $I_c = 0.002$ and 0.1 mol dm^{-3}. In some cases (e.g. [61VQa], [49MCa]), no inert electrolyte was used, while in others the inert electrolyte concentration was a minor component at most medium concentrations studied.

The data reported in Table A4-2 for $I_m = 0$ mol kg^{-1} show very good consistency, especially for $\log K_2°$ and $\log K_3°$; in general, these studies involved low concentrations of phosphate and background salt. In contrast, the protonation constants reported at other ionic strengths can be rather divergent for identical conditions. In part, this is related to experimental errors in determining [H$^+$] in strongly alkaline (and acidic) solutions corresponding to the first (and third) protonation processes. The H$^+$-phosphate system is thought to be subject to other equilibrium processes that become increasingly important at higher concentrations of PO$_4^{3-}$ and background electrolyte.

The reported protonation constants are strongly dependent on the experimental conditions used (total concentration [PO$_4^{3-}$]$_T$, medium electrolyte concentration, and nature). One interpretation is that at [PO$_4^{3-}$]$_T$ > 0.01 mol dm^{-3} weakly hydrogen-bonded "dimeric" species {H$_x$[PO$_4$]$_2^{(6-x)-}$, x = 2–6} form over a wide pH range. The species are not well characterized, and the equilibrium constants reported for their formation ($\log K_{xy}$, reaction 27)

$$H_xPO_4^{x-3} + H_yPO_4^{y-3} = H_{x+y}(PO_4)_2^{(x+y)-6} \tag{27}$$

are of low precision because the associations are weak. Recommended or Provisional values cannot be specified. The average $\log K_{xy}$ values for reaction 27 at $I = 3$ mol dm^{-3} are: $\log K_{33} = -0.2 \pm 0.5$, $\log K_{23} = -0.08 \pm 0.5$, $\log K_{22} = -0.57 \pm 0.6$, $\log K_{12} = 0.25 \pm 0.5$, $\log K_{11} = -0.7 \pm 0.5$ [69CHc, 73FAa,

73IVd, 74FGb, 74FER, 91CIb]. From these values, it is inferred that the formation of hydrogen-bonded entities will not be significant under environmental conditions; such equilibria should be taken into account only at $[PO_4^{3-}]_T > 0.05$ mol dm^{-3}. The existence of H-bonded aggregates has qualitative support from laser Raman spectroscopy [79PAa, 87CER, 89RUL, 98SHA] and IR spectroscopy [2000BAR] and less support from potentiometry [73IVd, 73FAa, 74FGb, 74FER, 83DGa, 91CIb], isopiestic measurements [75WOO], osmotic coefficient measurements [76PSf], solution X-ray analysis [85WER], NMR [78LEN], and X-ray diffraction of alkali metal salts with formula $MH_5P_2O_8$ [71PHI]. However, the existence of two-dimensional dimer species (as distinct from three-dimensional H-bonded species [91RUD]) is not conclusive.

The formation of ion pairs, such as $M(HPO_4)^-$, between alkali metal ions and protonated orthophosphate anions has been suggested [56SAa, 63SGd, 83DGa, 88MFa, 91DDa, 95VAS]. Although the effect of such ion pair formation is generally reflected in the corresponding specific ion interaction coefficients, consideration of these equilibria may be pertinent when a "true" speciation is needed in the presence of high concentrations of alkali metal salts. It should be noted that problems may occur in measuring such association, along the lines discussed in Appendix 1B.

8. EVALUATION OF EQUILIBRIUM CONSTANTS FOR HETEROGENEOUS REACTIONS

Available data refer to reactions of pure crystalline phases used in the laboratory. Amorphous phases, which may form more rapidly, will do so at different pH or pL and have different (generally higher) solubility.

8.1 The Hg^{2+}– OH^- system: Solubility of HgO(s)

HgO(s) exists in three forms, two orthorhombic (red and yellow) and one hexagonal. Crystallographically they are similar; the red and yellow forms have identical X-ray diffraction patterns [86BAE]. The orthorhombic form is stable at 25 °C. The three forms have similar standard solubility products ($K_{s2}°$, Table A2-12). Solubility data are available for solutions in which the dominant solution species of Hg(II) is cationic (Hg^{2+}), neutral [$Hg(OH)_2$] or anionic [$Hg(OH)_3^-$]. The majority have been corrected to $I_m = 0$ mol kg^{-1}.

The standard solubility product, $\log_{10} K_{s2}°$, reported for reaction 28

$$HgO(s) + H_2O \rightleftharpoons Hg(OH)_2(aq) \tag{28}$$

is -3.62 ± 0.05 (average from [02SCa, 20FUa, 38GHa, 61AHb]), -3.63 ± 0.05 (average from [38GHa, 61AHb]), and -3.59 ± 0.05 [61AHb] for the red, yellow, and hexagonal forms, respectively. For HgO(red), $\log_{10} K_{s2}°$ agrees with that for 3 mol dm^{-3} $NaClO_4$ (-3.69 ± 0.03 [61DTa]), as expected for a reaction involving no ions ($\Delta z^2 = 0$). For reaction 29,

$$HgO(s) + 2H^+ \rightleftharpoons Hg^{2+} + H_2O \tag{29}$$
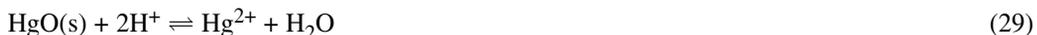
$\log_{10} *K_{s0}°$ can be calculated from $\log_{10} K_{s2}°$(eq. 28) and $\log_{10} *\beta_2°$:

$\log_{10} *K_{s0}°$ (eq. 29 HgO(red), 298.15 K) = 2.36 ± 0.08

$\log_{10} *K_{s0}°$ (eq. 29 HgO(yellow), 298.15 K) = 2.35 ± 0.08

$\log_{10} *K_{s0}°$ (eq. 29 HgO(hex.), 298.15 K) = 2.39 ± 0.08

As these values agree within error estimates, a single value is Recommended:

$\log_{10} *K_{s0}°$ (eq. 29, 298.15 K) = 2.37 ± 0.08

This is in reasonable agreement with that determined from measurements on HgO(red) in 3 mol dm^{-3} NaClO$_4$ (2.62 ± 0.10 [61DTa]) and that calculated from $\log_{10}$ *K_{s1}° (–0.77, [39GHa]) for HgO(red), reaction 30,

$$HgO(s) + H^+ \rightleftharpoons HgOH^+ \tag{30}$$

and $\log_{10}$ *K_1 recommended in the present review (viz. $\log_{10}$ *K_{s0}° = 2.63).

Data in Table A2-12 can be used to calculate $\log_{10}$ *β_3° for reaction 31

$$Hg^{2+} + 3H_2O \rightleftharpoons Hg(OH)_3^- + 3H^+ \tag{31}$$

$$HgO(s) + H_2O + OH^- \rightleftharpoons Hg(OH)_3^- \tag{32}$$

by utilizing the standard solubility constant for reaction 32 ($\log_{10} K_{s3}$° = –4.43) and the values for $\log_{10}$ *β_2° (–5.98), pK_w, and $\log_{10} K_{s2}$°:

$$\log_{10}\ {}^*\beta_3°(\text{eq. } 31) = \log_{10} K_{s3}°(\text{eq. } 32) - pK_w + \log_{10}\ {}^*\beta_2°(\text{eq. } 5) - \log_{10} K_{s2}°(\text{eq. } 28)$$

The derived value [utilizing the data for both red and yellow HgO(s)], is

$$\log_{10}\ {}^*\beta_3° (\text{eq. } 31, 298.15\ \text{K}) = -20.8 \pm 0.3$$

It is assigned as Provisional. It is consistent with that (–21.11) determined from the solubility data of Garrett and Hirschler [38GHa]. The error estimate has been selected so that it covers this latter value and also reflects the difficulty of determining the constant from measurements in strongly alkaline solutions.

8.2 The Hg^{2+}– Cl$^-$ system: Solubility of HgCl$_2$(s)

Solid HgCl$_2$ is very soluble in water. Reported values for the solubility at 25 °C are 0.263 mol dm^{-3} [03SHa, 73ACa] and 0.2659 mol dm^{-3} [39THO]. Because of its large stability field, dissociation of HgCl$_2$(aq) occurs to only a very small extent in pure water (cf. Fig. 2). Thus, the solubility corresponds to the equilibrium constant for the intrinsic solubility, reaction 33:

$$HgCl_2(s) \rightleftharpoons HgCl_2(aq) \tag{33}$$

i.e., $\log_{10} K_{s2}$°(eq. 33) = –0.58 (average of reported values). As no charged species is involved, no pronounced dependency on ionic strength is expected. An increase or decrease in the concentration of Cl$^-$ will enhance HgCl$_2$(s) solubility. Because of its high solubility, HgCl$_2$(s) is not significant in the environmental behavior of mercury. However, it is noted that Hg(II) can be reduced to Hg(I) under environmental conditions, leading to the formation of Hg$_2$Cl$_2$(s), which has a much lower solubility [49SIL].

8.3 The Hg^{2+}– CO$_3$$^{2-}$ system: Solubility of HgCO$_3$·2HgO(s)

Hg(OH)$_2$ is dominant relative to Hg(II)-carbonate species over a wide range of pH and f(CO$_2$). Therefore, it is useful to consider the solubility of HgCO$_3$·2HgO(s) in terms of aqueous Hg(OH)$_2$ concentrations. The Provisional standard solubility product $\log_{10} K_s$° shown in Table 3 for I_c = 3.0 mol dm^{-3} NaClO$_4$ indicates that the concentration of aqueous Hg(OH)$_2$ in equilibrium with HgCO$_3$·2HgO(s) will exceed 175 μmol dm^{-3} even at a CO$_2$ fugacity of one atmosphere. Thus, it is unlikely that HgCO$_3$·2HgO(s) will set bounds on the concentration of Hg(II) in natural waters. A SIT analysis was not possible.

8.4 The Hg^{2+}– PO$_4$$^{3-}$ system

The solubility products $\log_{10}$ $^{*}K_s$ and $\log_{10} K_s$ for the dissolution of the Hg(II) phosphates, reactions 34–36, are given in Table 4 (I_c = 3 mol dm^{-3} NaClO$_4$).

$$Hg_3(PO_4)_2(s) + 2H^+ \rightleftharpoons 3Hg^{2+} + 2HPO_4^2 \tag{34}$$

$$(HgOH)_3PO_4(s) + 4H^+ \rightleftharpoons 3Hg^{2+} + HPO_4^{2-} + 3H_2O \tag{35}$$

$$HgHPO_4(s) \rightleftharpoons Hg^{2+} + HPO_4^{2-} \tag{36}$$
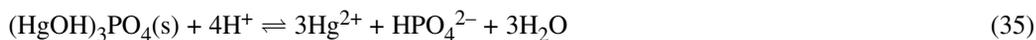
As shown in Fig. 5, (i) these solid phases form as a function of pH when the total concentrations of Hg^{2+} and phosphate are sufficiently high, (ii) HgHPO$_4$(s) is likely to be the least soluble phase at environmental pH, and (iii) it will form from equimolar solution when the concentration of Hg^{2+} is >40 μmol dm^{-3}. Thus, it is unlikely to be important in pristine or moderately polluted systems.

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

The most reliable enthalpy data are derived from calorimetric measurements. If the values are sufficiently consistent and cover an adequate range of ionic strength, then an extrapolation to I_m = 0 mol kg^{-1} is possible. Heats of reaction determined at constant ionic strength contain contributions from mixing and dilution. By extrapolation to I_m = 0 mol kg^{-1} these contributions are eliminated. The extrapolation is achieved by use of the SIT procedure adapted to enthalpy format, as described by Grenthe et al. [97GRE]. The relevant equation, including the term for water, at sufficiently high electrolyte concentration I_m, is:

$$\Delta_r H_m - 0.75\Delta(z^2)A_L\sqrt{I_m}\,(1 + 1.5\sqrt{I_m})^{-1} - rL_1 = \Delta_r H_m° - RT^2 I_m \Delta\varepsilon_L \tag{37}$$

$$L_1 = M_W\,[-A_L(t - 2\ln t - 1/t)/(1.5)^2 + RT^2 \upsilon_N z_N m^2 \varepsilon_L(N,X)]$$

$$t = 1 + 1.5\sqrt{I_m}$$

Δz^2 is the stoichiometric sum of the charge squares for the product species minus the reactant species. Values for the Debye–Hückel parameter for enthalpy, A_L, are listed by Pitzer [91PIT]; at 25 °C and 10^5 Pa, A_L = 1.986 kJ kg$^{1/2}$ mol$^{-3/2}$. The Debye–Hückel term may be denoted by $\Psi(I_m)$ as in [80VKb] and [78VAS]. A weighted linear regression of $[\Delta_r H_m - \Psi(I_m) - rL_1]$ against I_m yields $\Delta_r H_m°$ as the intercept and $(-RT^2\Delta\varepsilon_L)$ as the slope.

9.1 The Hg^{2+}– OH$^-$ system

There are few reported studies of reaction enthalpies for the hydrolysis of Hg(II). The enthalpy change for dissolution of HgO(s) (yellow) in perchloric acid solutions over a range of concentrations (reaction 29) was studied by [59SLd] and [62LGa]. The data selected for the SIT analysis are listed in Table A2-13. (The datum at the highest ionic strength from each study was not selected. There is concern about the applicability of SIT to the data obtained from these high ionic strength measurements: 5.524 mol dm^{-3} [59SLd] and 8.76 mol dm^{-3} [62LGa]). The weighted linear regression (Fig. A3-8) indicates excellent consistency among the data. It results in the Recommended standard reaction enthalpy (I_m = 0 mol kg^{-1}):

$$\Delta_r H_m° \text{ (eq. 29, 298.15 K)} = -(25.3 \pm 0.2) \text{ kJ mol}^{-1}$$

The reaction interaction coefficient for the enthalpy is $\Delta\varepsilon_L(29) = -(1.24 \pm 0.07) \times 10^{-3}$ kg mol^{-1} K^{-1}.

Aurivillius and von Heidenstam [61AHb] reported the standard solubility constant, $\log_{10} K_{s2}^{\circ}$ (for reaction 28) for red, yellow, and hexagonal HgO(s), in the temperature range 25–60 °C, $I_m = 0$ (corr). They obtained values in good agreement with earlier ones [02SCa, 17KOa, 20FUa, 38GHa, 59SAa]. If $\Delta_r H_m^{\circ}(K_{s2}^{\circ})$ is temperature-independent in the range studied, then the van't Hoff relationship can be used to obtain $-\Delta_r H_m^{\circ}/2.303R$ and $\Delta_r S_m^{\circ}/2.303R$. The solubility constant data for yellow HgO(s) [61AHb], $\log_{10} K_{s2}^{\circ}$, were plotted against $1/T$ (Fig. A3-9); the regression indicated that $\Delta_r H_m^{\circ}$ has a small dependence on temperature over the range studied. The value determined for $\Delta_r H_m^{\circ}(K_{s2}^{\circ})$ is (26.8 ± 3.5) kJ mol^{-1}. Similar calculations for red and hexagonal HgO(s) led to $\Delta_r H_m^{\circ}$ values of (26.0 ± 2.7) and (26.1 ± 3.5) kJ mol^{-1}, respectively. As the three $\Delta_r H_m^{\circ}$ values agree within error limits, the weighted average is Recommended for the enthalpy change of reaction 28:

$\Delta_r H_m^{\circ}$(eq. 28, 298.15 K) = (26.2 ± 1.8) kJ mol^{-1}

This value, combined with $\Delta_r H_m^{\circ}$(eq. 29, 298.15 K), gives the Recommended enthalpy change for reaction 5:

$\Delta_r H_m^{\circ}$(eq. 5, 298.15 K) = $\Delta_r H_m^{\circ}$(eq. 28, 298.15 K) – $\Delta_r H_m^{\circ}$(eq. 29, 298.15 K)

$\Delta_r H_m^{\circ}$(eq. 5, 298.15 K) = (51.5 ± 1.8) kJ mol^{-1}

This value is consistent with those determined by [58ASa] and [67AKb] in 0.1 mol dm^{-3} NaNO$_3$ and 3 mol dm^{-3} NaClO$_4$, respectively.

Enthalpies of reaction for zero ionic strength cannot be determined for other reactions due to the paucity of data.

9.2 The Hg^{2+}– Cl$^-$ system

Data selected for the SIT analysis of enthalpies for reactions 6, 7, and 10 are listed in Table A2-14. These result from calorimetric measurements in 0.5 to 3.0 mol dm^{-3} (Na,H)ClO$_4$ media, except for those of Vasil'kevich and Shilov [66VAS] who determined $\Delta_r H_m$ for reaction 10 from the temperature dependence of $\log_{10} K(T)$ determined by emf measurements between 0 and 35 °C. Additional data for reactions 6 and 7 are reported by Vasil'ev, Kozlovskii, and Mokeev [80VKb] at 40 and 60 °C in 0.5, 1.0, and 3.0 mol dm^{-3} NaClO$_4$.

The reported uncertainties, in general, result from data evaluation statistics and seldom include systematic errors. We considered it justified to give each accepted value the same weight in the analysis. The weighted linear regression analyses for reactions 6 and 7, Figs. A3-10 and A3-11, indicate excellent consistency between the data. They result in Recommended values for the standard enthalpy change, $I_m = 0$ mol kg^{-1}:

$\Delta_r H_m^{\circ}$(eq. 6, 298.15 K) = $-(21.3 \pm 0.7)$ kJ mol^{-1}

$\Delta_r H_m^{\circ}$(eq. 7, 298.15 K) = $-(49.1 \pm 1.0)$ kJ mol^{-1}

The specific ion interaction coefficients for the reaction enthalpy, derived from the slope of the regression lines, are $\Delta \varepsilon_L$(eq. 6, 298.15 K) = $(0.06 \pm 0.51) \times 10^{-3}$ kg mol^{-1} K^{-1} and $\Delta \varepsilon_L$(eq. 7, 298.15 K) = $-(1.11 \pm 0.77) \times 10^{-3}$ kg mol^{-1} K^{-1}. A SIT analysis is not possible for reaction 10, but $\Delta_r H_m^{\circ}$(eq. 10) can be calculated from the Recommended values for $\Delta_r H_m^{\circ}$(eq. 6) and $\Delta_r H_m^{\circ}$(eq. 7): $\Delta_r H_m^{\circ}$(eq. 10, 298.15 K) = (6.5 ± 1.7) kJ mol^{-1}; this value is Recommended.

The selected values for the enthalpy changes for reactions 8 and 9 are listed in Table A2-15. The large medium effect for the isocoulombic equilibrium 8 is surprising, cf., [97PUI, p. 439]. Since the number of independent determinations is small we assign comparatively high uncertainties of ± 3 kJ mol^{-1}. The SIT regression analyses, Figs. A3-12 and A3-13, indicate excellent consistency between the data. They result in Provisional values for the standard enthalpy change, $I_m = 0$ mol kg^{-1}:

$\Delta_r H_m°$(eq. 8, 298.15 K) = (0.5 ± 2.5) kJ mol^{-1}

$\Delta_r H_m°$(eq. 9, 298.15 K) = –(10.5 ± 2.5) kJ mol^{-1}

The specific ion interaction coefficients for the reaction enthalpy are $\Delta\varepsilon_L$(eq. 8, 298.15 K) = (1.8 ± 1.7) × 10^{-3} kg mol^{-1} K^{-1} and $\Delta\varepsilon_L$(eq. 9, 298.15 K) = –(0.9 ± 1.7) × 10^{-3} kg mol^{-1} K^{-1}.

10. SPECIATION IN MULTICOMPONENT SYSTEMS: Hg^{2+}– H^+– Cl^-– CO_3^{2-}– PO_4^{3-}– SO_4^{2-}

As an aid to the user, this section presents results from speciation calculations for model freshwater systems. In each case, the required stability constants have been calculated from the values in Tables 1 to 7, after correction for ionic strength effects (D term; eq. 1) and water activity, $a(H_2O)$, according to eq. 38:

$$\log_{10} \beta_{p,q,r} = \log_{10} \beta_{p,q,r}° + \Delta z^2 D + r\log_{10} a(H_2O) - \Delta\varepsilon I_m \tag{38}$$

In this equation, Δz^2 is defined by the stoichiometry:

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

for the reaction

$$pM + qL + rH_2O \rightleftharpoons M_pL_q(OH)_r + rH^+$$
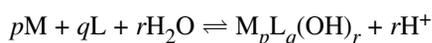
The resultant values of $\log_{10} \beta_{p,q,r}$ were then converted to the molarity scale. The calculation of $\log_{10} \beta_{p,q,r}$ at the required ionic strength and its correction to the molarity scale are conveniently done by using the program SIT, which is included in *SC-Database* [2003PET] and in the *Sol-Eq* tutorials [98PET]. The water activity term for a 1:1 electrolyte (NX) can be calculated from the solution osmotic coefficient as described in Section 5.2.

It should be noted that the $\Delta\varepsilon$ values given in this review generally apply to $NaClO_4$ media (although values for the H^+– CO_3^{2-} system are for NaCl media, while values for both NaCl and KCl media are given for the system H^+– PO_4^{3-}). For calculations in freshwater media, which are normally of low ionic strength, (i) the use of $\Delta\varepsilon$ ($NaClO_4$) values will have minimal effect, and (ii) the activity of water can be set equal to one.

The speciation calculations have been effected using the program SOLGASWATER [79ERI] utilizing a recent modified Windows version WinSGW (<www.chem.umu.se/dep/inorgchem>). In the calculations, this program recalculates the different stability constants from $I_m = 0$ mol kg^{-1} to the effective ionic strength by using eq. 39

$$\log_{10} \beta_{p,q,r} = \log_{10} \beta_{p,q,r}° + \Delta z^2 A[\sqrt{I_m}(1 + 1.5\sqrt{I_m})^{-1} - 0.3\,I_m] \tag{39}$$

which is considered to be an adequate approximation for solutions of low ionic strength.

10.1 Freshwater in equilibrium with CO_2(g)

The chemical composition of an average freshwater was taken from Morel and Hering [93MOR]. Typical total concentrations are: $[Cl^-]_T = 0.23$ mmol dm^{-3}, $[SO_4^{2-}]_T = 0.42$ mmol dm^{-3}, and $[HPO_4^{2-}]_T = 0.7$ μmol dm^{-3}. The total concentration of Hg(II) was set to 1 nmol dm^{-3}, and it was assumed that the system was in equilibrium with air having a CO_2 fugacity of 370 μbar. Furthermore, –log $[H^+]$ was allowed to vary between 4.0 and 8.5. The result of this calculation is visualized as a distribution diagram in Fig. 6. This diagram indicates that the predominating species with increasing pH are $HgCl_2$(aq), HgOHCl(aq), and $Hg(OH)_2$(aq), with all other species formed in negligible amounts. The formation of
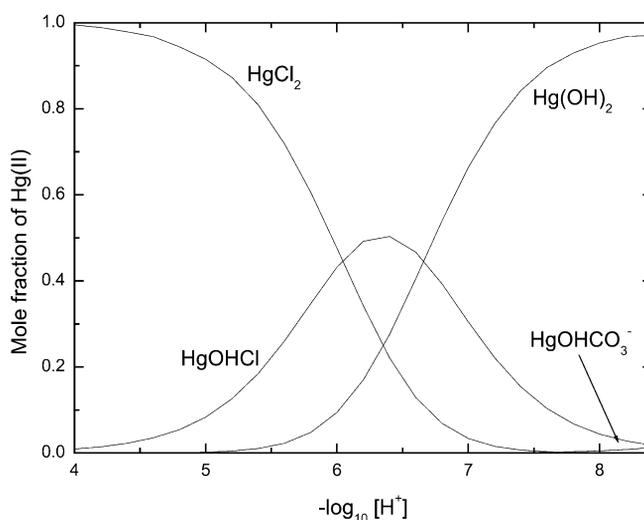
Fig. 6 Speciation diagram for the $Hg^{2+}-H^+-Cl^--CO_2-HPO_4^{2-}-SO_4^{2-}$ system with total concentrations $[Cl^-]_T$ = 0.23 mmol dm^{-3}, $[SO_4^{2-}]_T$ = 0.42 mmol dm^{-3}, and $[HPO_4^{2-}]_T$ = 0.7 μmol dm^{-3}. The total concentration of Hg(II) was set to 1 nmol dm^{-3}, and it was assumed that the system was in equilibrium with air having a CO_2 fugacity of 370 μbar. Log $K_{10}[CO_2(g) \rightleftharpoons CO_2(aq)]$ = –1.5 [93MOR]. All other formation constants are according to Tables 1 to 7.

$HgOHCO_3^-$ is significant only in alkaline solutions and is formed to ca. 1 % of $[Hg^{2+}]_T$ at –log $[H^+]$ = 8.5.

It is concluded from this calculation that the major Hg(II) species formed in the absence of strongly complexing organic ligands are given by the ternary system $Hg^{2+}-OH^--Cl^-$. None of the possible Hg(II)-containing solid phases forms under the specified conditions.

10.2 Freshwater with varying chloride concentrations

It is obvious from the calculation presented above that the critical parameters with respect to the inorganic speciation of Hg(II) are pH and the total chloride concentration. Changes in these variables are found in the mixing zone of fresh- and saltwater (estuaries). By varying the concentration $[Cl^-]_{free}$ between 10^{-5} and 10^{-2} mol dm^{-3}, at a constant alkalinity of 0.1 mmol dm^{-3} (–log $[H^+]$ = 7.22) in an open CO_2 system, the influence of Cl^- on the Hg(II) speciation can be illustrated, as in Fig. 7. $Hg(OH)_2(aq)$ is found to predominate with $[Cl^-]_{free} < 10^{-3.1}$ mol dm^{-3}. Within the range $10^{-2.9} < [Cl^-]_{free} < 10^{-2.4}$ mol dm^{-3}, HgOHCl(aq) prevails and with $[Cl^-]_{free} > 10^{-2.4}$ mol dm^{-3}, $HgCl_2(aq)$ is the predominating species.
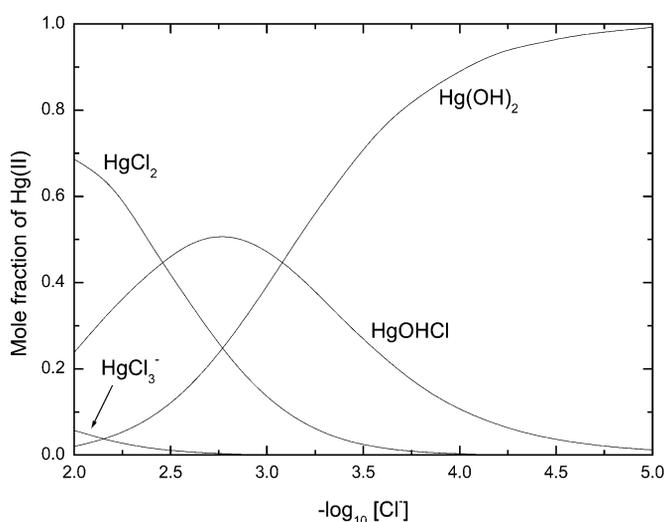
Fig. 7 Speciation diagram for the $Hg^{2+}- H^+- Cl^-- CO_2- HPO_4^{2-}- SO_4^{2-}$ system. Concentrations as in Fig. 6 except for pH, which is kept constant at 7.22, and $[Cl^-]_{free}$ which was allowed to vary between 10^{-5} and 10^{-2} mol dm^{-3}.

10.3 Summary

The speciation calculations indicate that the two-coordinated, uncharged species $HgCl_2(aq)$, $HgOHCl(aq)$, and $Hg(OH)_2(aq)$ play a dominant role in the speciation of Hg(II) in freshwater media. Thus, the accuracy of the equilibrium data ($I_m = 0$ mol kg^{-1}) for formation of $Hg(OH)_2$ (reaction 5), $HgCl_2$ (reaction 7), and HgOHCl (reaction 12) is crucial to the reliability of speciation calculations.

This review has established that the data selected for the SIT analysis of reactions 5 and 7 show reasonable consistency and yield the Recommended values at 25 °C, $I_m = 0$ mol kg^{-1}: $\log_{10} {}^*\beta_2° = -5.98 \pm 0.06$ [$Hg^{2+} + 2H_2O \rightleftharpoons Hg(OH)_2(aq) + 2H^+$] and $\log_{10} \beta_2° = 14.00 \pm 0.07$ [$Hg^{2+} + 2Cl^- \rightleftharpoons HgCl_2(aq)$]. It was necessary to derive a value of $\log_{10} \beta°$ for reaction 12. This was achieved by use of a thermodynamic cycle and a calculated value for $\Delta\varepsilon(12)$. These calculations (Section 6.3) gave $\Delta\varepsilon(12) = -(0.24 \pm 0.10)$ kg mol^{-1} and $\log \beta°(12) = 4.27 \pm 0.35$ (25 °C, $I_m = 0$ mol kg^{-1}).

A test of consistency of the values for $\log_{10} {}^*\beta_2°$, $\log_{10} \beta_2°$, and $\log \beta°(12)$ is afforded by consideration of reaction 40, which links the three species that dominate the inorganic speciation of Hg(II) in freshwater media:

$$HgCl_2(aq) + Hg(OH)_2(aq) \rightleftharpoons 2HgOHCl(aq) \tag{40}$$

From the Recommended values for $\log_{10} {}^*\beta_2°$, $\log_{10} \beta_2°$ and the derived value for $\log \beta°(12)$ we calculate $\log K_{10}(40) = 0.52$. This value is close to the statistical value of $\log_{10} K = 0.60$ for reaction 40. Similar observations were made by [68CGa] and [76SJb] using data for 1.0 and 3.0 mol dm^{-3} $NaClO_4$ media, respectively. The corresponding values reported for $\log K_{10}(40)$ were 0.48 and 0.50. This apparent independence with ionic strength is consistent with the approximation that the interaction coefficient, ε, for uncharged species, is close to zero. This, in combination with $\Delta z^2 = 0$, will give $\log K_{10} = \log K_{10}°$ for reaction 40 (cf. eq. 38).

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79ERI   G. Eriksson. *Anal. Chim. Acta* **112**, 375 (1979).
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2001PRa   K. I. Popov, H. Rönkkömäki, L. H. J. Lajunen. *Pure Appl. Chem.* **73**, 1641 (2001).

2002BUC   R. Buchner, T. Chen, G. T. Hefter. *Book of Abstracts, 17th IUPAC Conference on Chemical Thermodynamics*, Rostock, pp. 86 & 96 (2002).

2003PET   L. D. Pettit and K. J. Powell. *SC-Database*, IUPAC Stability Constants Database, Release 5, IUPAC; Academic Software, Otley, UK (2003).

2003RUD   W. W. Rudolph, G. Irmer, G. T. Hefter. *Phys. Chem. Chem. Phys.* **5**, 5253 (2003).

2004BUC   R. Buchner, T. Chen, G. T. Hefter. *J. Phys. Chem. B* **108**, 2365 (2004).

APPENDIX 1A

Stability constants and equilibrium constants

For a general reaction (with charges for M and L omitted),

$$p\text{M} + q\text{L} + r\text{H}_2\text{O} \rightleftharpoons \text{M}_p\text{L}_q(\text{OH})_r + r\text{H}^+$$
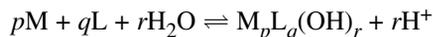
The cumulative stability (formation) constant can be defined in terms of component species amount concentrations, c or [species i], at equilibrium: $[\text{M}_p\text{L}_q(\text{OH})_r][\text{H}^+]^r/[\text{M}]^p[\text{L}]^q$ or in terms of species molalities, m, at equilibrium: $m(\text{M}_p\text{L}_q(\text{OH})_r)m(\text{H}^+)^r/m(\text{M})^p m(\text{L})^q$. Throughout this document, "amount concentration" is abbreviated to "concentration", the units being mol dm^{-3} ($\approx$ mol l^{-1}, or M).

   The stability constant is numerically valid only at the measurement ionic strength. Stability constants are most frequently determined and reported [2003PET] on the concentration scale (molarity) and under experimental conditions of essentially constant and (comparatively) high ionic strength, I_c. In the present work, these constants are initially converted to the molality scale. The resultant stability constant, $\beta_{p,q,r}$, is related to the standard (state) equilibrium constant $\beta_{p,q,r}°$ via the species activity coefficients:

$$\beta_{p,q,r}° = a(\text{M}_p\text{L}_q(\text{OH})_r)\,a(\text{H}^+)^r/a(\text{M})^q a(\text{L})^q$$

$$= \gamma_m(\text{M}_p\text{L}_q(\text{OH})_r)m(\text{M}_p\text{L}_q(\text{OH})_r)\,\gamma_m(\text{H}^+)^r m(\text{H}^+)^r/\gamma_m(\text{M})^p m(\text{M})^p\,\gamma_m(\text{L})^q m(\text{L})^q$$

$$= m(\text{M}_p\text{L}_q(\text{OH})_r)m(\text{H}^+)^r/m(\text{M})^p m(\text{L})^q \cdot \gamma_m(\text{M}_p\text{L}_q(\text{OH})_r)\gamma_m(\text{H}^+)^r/\gamma_m(\text{M})^p\gamma_m(\text{L})^q$$

$$= \beta_{p,q,r} \cdot \gamma_m[\text{M}_p\text{L}_q(\text{OH})_r]\gamma_m(\text{H}^+)^r/\gamma_m(\text{M})^p\gamma_m(\text{L})^q$$

   The stability constant and equilibrium constant are dimensionless if expressed in terms of *relative* molalities or activities: $a(\text{A}) = \gamma_m(\text{A})m(\text{A})/m°$, where the standard molality $m° = 1$ mol kg^{-1}. It follows that ionic strength, I_m or I_c, is also dimensionless when calculated from *relative* molalities or *relative* concentrations, $c/c°$.

   The term $\gamma_m(\text{M}_p\text{L}_q(\text{OH})_r)\gamma_m(\text{H}^+)^r/\gamma_m(\text{M})^p\gamma_m(\text{L})^q$ is a function of I_m and has the value 1.0 in the limit $I_m \to 0$ mol kg^{-1}. This permits a regression of $\log_{10} \beta_{p,q,r}$ against I_m, using appropriate empirical relationships. In this work, the SIT equations were used to obtain the value for the standard (state) equilibrium constant, $\beta_{p,q,r}°$, at $I_m = 0$ mol kg^{-1}.

Nomenclature for stability constants

The following examples use the molarity scale, as this is the scale adopted in the majority of literature, as reported in [2003PET].

   In the case where $p = 1$ and $r = 0$, $\beta_{p,q,r}$ is simplified to $\beta_q = [\text{ML}_q]/[\text{M}][\text{L}]^q$; for example, reaction 7.

   For the stepwise addition of one ligand molecule:

$$\text{ML}_{n-1} + \text{L} \rightleftharpoons \text{ML}_n$$

the symbol K_n is used:

$$K_n = [\text{ML}_n]/[\text{ML}_{n-1}][\text{L}]$$

for example, reactions 6 or 8.

   For reactions in which $p = 1$, $q = 0$, and $r \geq 1$, the metal ion hydrolysis reactions 4 and 5, *β_r or *K_n terminology is used. In these reactions, the component species is the protonated ligand (H$_2$O), from which a bound ligand (OH$^-$) and proton are produced:

$$\text{Hg}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Hg(OH)}_2 + 2\text{H}^+$$
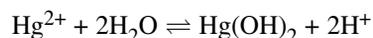
$*\beta_2 = [Hg(OH)_2][H^+]^2/[Hg^{2+}]$

For reactions in which $p \neq 1$, $q = 0$, and $r \geq 1$, the metal ion hydrolysis reactions to form $Hg_p(OH)_r$, $*\beta_{p,r}$ terminology is used:

$2Hg^{2+} + 2H_2O \rightleftharpoons Hg_2(OH)_2^{2+} + 2H^+$
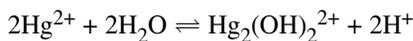
$*\beta_{2,2} = [Hg_2(OH)_2^{2+}][H^+]^2/[Hg^{2+}]^2$

Solubility constants K_{s0} are used to describe the equilibrium of solids with their simple component ions in solution:

$HgX_2(s) \rightleftharpoons Hg^{2+} + 2X^-$ $\qquad\qquad\qquad K_{s0} = [Hg^{2+}][X^-]^2$

The constant K_{sn} indicates that the solid dissolves in a solution containing the ligand to produce a complex species ML_n, for example, reaction 32:

$HgO(s) + H_2O + OH^- \rightleftharpoons Hg(OH)_3^-$ $\qquad\qquad K_{s3} = [Hg(OH)_3^-]/[OH^-]$

When the solid dissolves by reaction with protons to produce the metal species and protonated ligand, the symbol $*K_{s0}$ is used, for example, reaction 29.

APPENDIX 1B

Complex formation by polyvalent anions (SO_4^{2-}, PO_4^{3-}, CO_3^{2-})

Although the following comments focus on the sulfate ion, such considerations apply to all strongly hydrated anions, including carbonate and phosphate. Because of their relatively high charge/radius ratios, such ions are strongly hydrated and tend to retain their solvent sheaths when interacting with cations. For example, the "absolute" enthalpy of hydration of the sulfate ion, ca. -1140 kJ mol^{-1} [85MAR], is 2 to 4 times greater than those for halide ions. The formation of complex species involving such anions is believed to occur via the following stepwise mechanism [62EIG]: (i) formation of a double solvent-separated ion pair ("outer sphere", 2SIP) in which the primary hydration sheaths of both ions remain more or less intact, followed by (ii) a solvent-shared ("bridged", SIP) and (iii) a contact ("inner sphere", CIP) ion pair:

$$M^{m+}(aq) + L^{l-}(aq) \rightleftharpoons [M^{m+}(OH_2)(OH_2)L^{l-}](aq) \rightleftharpoons [M^{m+}(OH_2)L^{l-}](aq) \rightleftharpoons [ML]^{(m-l)+}(aq)$$

free hydrated ions   2SIP   SIP   CIP
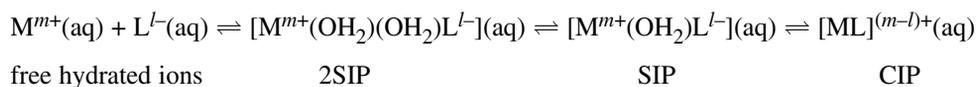
The detection of the individual ion pairs, and hence the quantitative characterization of each reaction step in the above sequence, is difficult. Ultrasonic absorption and related relaxation techniques detect the *equilibria* rather than individual *species* [62EIG, 66ATK]. However, the simultaneous existence and realistic concentration dependences of the three ion-pair species has recently been established for several cation-sulfate systems by dielectric spectroscopy [2002BUC, 2004BUC], following earlier indicative results [65POa, 92BAR].

Spectroscopic techniques (UV–vis, NMR, IR and Raman) can detect CIPs but in general cannot distinguish between the 2SIP, SIP, and free hydrated ions. Such techniques will thus measure the equilibrium:

$$\{\text{free hydrated ions} + 2SIP + SIP\} \rightleftharpoons CIP \tag{41}$$
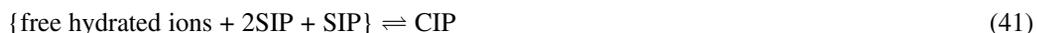
In contrast, thermodynamic (potentiometric) and conductivity measurements do not distinguish between dissolved species that have the same stoichiometry, but differ in their degree of hydration [79HEP]. Thus, only the *overall* equilibrium between free hydrated ions and the sum of 2SIP, SIP, and CIP is determined by such techniques:

$$\text{free hydrated ions} \rightleftharpoons \{2SIP + SIP + CIP\} \tag{42}$$

Clearly, equilibria 41 and 42 are different; thus, the "stability constants" obtained from typical spectroscopic measurements (associated with equilibrium 41) *should not* be equated with those obtained by potentiometric and conductivity measurements (equilibrium 42). For speciation calculations, it will normally be the "overall" constant, corresponding to equilibrium 42, which is required. For more detailed considerations, the microconstants associated with the individual steps in the full scheme, as measured by relaxation techniques [62EIG, 2002BUC, 2004BUC], would be required.

Another difficulty regarding the stability constants of species formed from highly charged ions such as sulfate concerns the most appropriate means for their extrapolation (or correction) to infinite dilution. A sound theoretical treatment of activity coefficients for higher-valent electrolyte solutions has proven elusive, and all current theories require the use of empirical parameters [91PIT]. In the SIT model [97GRE], ionic strength-dependent interaction parameters must be invoked for sulfate systems [92GRE], thereby losing the simplicity of this approach. Malatesta and Zamboni [97MAL] showed that it is possible to describe the activities of divalent metal-sulfate solutions as a function of I without invoking ion-association, provided that log K_1 < ca. 2. However, as the thermodynamic [2001KRA], spectroscopic [98PYE, 2003RUD], and other [62EIG, 2002BUC, 2004BUC] evidence for the existence of metal-sulfate complexes in aqueous solution is overwhelming, this only indicates the difficulties of finding a physically realistic model to explain the activity coefficients of such systems.

APPENDIX 2

Selected equilibrium constants

For explanation of superscripts on footnote references, see Section 5.1.

Table A2-1 Selected equilibrium constants for the reaction: $Hg^{2+} + H_2O \rightleftharpoons HgOH^+ + H^+$.

| Method | Ionic medium | | $t/°C$ | $Log_{10} *K_1$ (reported) | $Log_{10} *K_1$ (accepted)[2] | Ref.[3] |
	Amount[1] concn./mol dm^{-3}	Molality/ mol kg^{-1}				
gl	0.5 NaClO$_4$	0.513	25	−3.70 ± 0.07	−3.69 ± 0.1	52HSa
sol	3.0 NaClO$_4$	3.503	25	−3.37 ± 0.19	−3.30 ± 0.19	61DTa
gl	3.0 NaClO$_4$	3.503	25	−3.55 ± 0.06	−3.48 ± 0.1	62AHa
gl	3.0 (ClO$_4^-$)	3.419	25	−3.49 ± 0.06	−3.43 ± 0.1	62AHa
gl	0.5 NaClO$_4$	0.513	25	−3.68	−3.67 ± 0.1	63KOb
gl	1.0 NaClO$_4$	1.052	25	−3.84 ± 0.1	−3.82 ± 0.2	68CGa
gl	1.0 NaClO$_4$	1.052	25	−3.65 ± 0.1	−3.63 ± 0.2	70CGc
gl	3.0 NaClO$_4$	3.503	25	−3.58 ± 0.02	−3.51 ± 0.05	77SJb
gl	3.0 NaClO$_4$	3.503	25	−3.48 ± 0.03	−3.41 ± 0.08	79CFb

[1]Traditional term: "molar concentration" or "molarity".
[2]Constants corrected from concentration to molality units and including our assigned errors.
[3]References for rejected data: [17KOa][a], [39GHa][j], [41BJa][a], [54GOa][b], [78THa][b], [87GGc][b].

Table A2-2 Selected equilibrium constants for the reaction: $Hg^{2+} + 2H_2O \rightleftharpoons$ $Hg(OH)_2(aq) + 2H^+$.

| Method | Ionic medium | | $t/°C$ | $Log_{10} *\beta_2$ (reported) | $Log_{10} *\beta_2$ (accepted)[1] | Ref.[2] |
	Amount concn./mol dm^{-3}	Molality/ mol kg^{-1}				
gl	0.5 NaClO$_4$	0.513	25	−6.30 ± 0.05	−6.28 ± 0.1	52HSa
sol	3 NaClO$_4$	3.503	25	−6.44 ± 0.08	−6.31 ± 0.08	61DTa
gl	3 NaClO$_4$	3.503	25	−6.21 ± 0.02	−6.08 ± 0.06	62AHa
gl	3 (ClO$_4^-$)	3.419	25	−5.96 ± 0.02	−5.85 ± 0.1	62AHa
gl	0.5 NaClO$_4$	0.513	25	−6.25	−6.23 ± 0.1	63KOb
gl	1 NaClO$_4$	1.052	25	−6.38 ± 0.05	−6.34 ± 0.1	68CGa
gl	1 NaClO$_4$	1.052	25	−6.29 ± 0.05	−6.25 ± 0.1	70CGc
gl	3 (NaClO$_4$)	3.503	25	−6.228 ± 0.004	−6.09 ± 0.02	77SJb
gl	3 (NaClO$_4$)	3.503	25	−6.18 ± 0.02	−6.05 ± 0.06	79CFb

[1]Constants corrected from concentration to molality units and including our assigned errors.
[2]References for rejected data: [17KOa][a,c], [38GHa][a,c], [39GHa][a,c], [41BJa][a], [54GOa][b], [58ASa][a,b], [59NHa][a,b], [78THa][b], [87GGc][b].

Table A2-3 Equilibrium constants for the formation of $Hg(OH)_3^-$, Hg_2OH^{3+}, and $Hg_2(OH)_2^{2+}$.

Method	Ionic medium		$t/°C$	Log_{10} $^*\beta$ (reported)	Ref.
	Amount concn./mol dm^{-3}	Molality/ mol kg^{-1}			
$Hg^{2+} + 3H_2O \rightleftharpoons Hg(OH)_3^- + 3H^+$ ($^*\beta_3$)					
sol	var.	0 (corr.)	25	–21.11	38GHa
$2Hg^{2+} + H_2O \rightleftharpoons Hg_2OH^{3+} + H^+$ ($^*\beta_{2,1}$)					
gl	3 NaClO$_4$	3.503	25	–2.67 ± 0.03	62AHa
gl	3 (ClO$_4^-$)	3.419	25	–2.67 ± 0.03	62AHa
$2Hg^{2+} + 2H_2O \rightleftharpoons Hg_2(OH)_2^{2+} + 2H^+$ ($^*\beta_{2,2}$)					
gl	3 NaClO$_4$	3.503	25	–5.16 ± 0.09	62AHa
gl	3 (ClO$_4^-$)	3.419	25	–4.95 ± 0.08	62AHa
gl	3 NaClO$_4$	3.503	25	–4.84 ± 0.02	77SJb

Table A2-4 Selected equilibrium constants for the reaction: $Hg^{2+} + Cl^- \rightleftharpoons HgCl^+$.

Method	Ionic medium		$t/°C$	$Log_{10} K_1$ (reported)	$Log_{10} K_1$ (accepted)[1]	Ref.[2]
	Amount concn./mol dm^{-3}	Molality/ mol kg^{-1}				
emf	0.5 NaClO$_4$	0.513	25	6.74 ± 0.02	6.73 ± 0.05	47LJa
dis	0.5 NaClO$_4$	0.513	25	6.56 ± 0.2	6.55 ± 0.30	57MAa
emf	0.5 NaClO$_4$	0.513	25	6.62	6.61 ± 0.20	63HIa
emf	3.0 NaClO$_4$	3.503	25	7.07 ± 0.15	7.00 ± 0.15	65ARa
emf	1.0 NaClO$_4$	1.051	25	6.72 ± 0.02	6.70 ± 0.05	68CGb
gl	3.0 NaClO$_4$	3.503	25	7.22 ± 0.06	7.15 ± 0.13	77SJb[3]

[1]Constants corrected from concentration to molality units and including our assigned errors.
[2]Reference for rejected data: [55DWb][a,c,g].
[3]$Log_{10} K_1$ calculated from $log_{10} K_2$ and $log_{10} \beta_2$, reported by Sjöberg [77SJb].

Table A2-5 Selected equilibrium constants for the reaction: $Hg^{2+} + HgCl_2(aq) \rightleftharpoons 2HgCl^+$.

Method	Ionic medium		$t/°C$	$Log_{10} K$ (reported)	$Log_{10} K$ (accepted)[1]	Ref.[2]
	Amount concn./mol dm^{-3}	Molality/ mol kg^{-1}				
emf	0.5 NaClO$_4$	0.513	25	0.255 ± 0.03	0.255 ± 0.05	46SIL
dis	0.5 NaClO$_4$	0.513	25	0.26 ± 0.03	0.26 ± 0.05	57MAa
emf	3.0 NaClO$_4$	3.503	25	0.17 ± 0.03	0.17 ± 0.05	65ARa
emf	0.5 NaClO$_4$	0.513	25	0.255 ± 0.02	0.255 ± 0.05	66VAS
emf	1.0 NaClO$_4$	1.051	25	0.22 ± 0.01	0.22 ± 0.05	68CGa

[1]Constants corrected from concentration to molality units and including our assigned errors.
[2]References for rejected data: [53PEc][a,d], [66VAS][a].

Table A2-6 Selected equilibrium constants for the reaction: $Hg^{2+} + 2Cl^- \rightleftharpoons HgCl_2(aq)$.

Method	Ionic medium		$t/°C$	$Log_{10} \beta_2$ (reported)	$Log_{10} \beta_2$ (accepted)[1]	Ref.[2]
	Amount concn./mol dm^{-3}	Molality/ mol kg^{-1}				
emf	0.5 NaClO$_4$	0.513	25	13.22 ± 0.02	13.20 ± 0.08	47LJa
dis	0.5 NaClO$_4$	0.513	25	12.86 ± 0.3	12.84 ± 0.30	57MAa
emf	0.5 NaClO$_4$	0.513	25	12.99	12.97 ± 0.15	63HIa
emf	3.0 NaClO$_4$	3.503	25	13.98 ± 0.02	13.85 ± 0.08	65ARa
emf	1.0 NaClO$_4$	1.051	25	13.23 ± 0.02	13.19 ± 0.08	68CGa
gl	3.0 NaClO$_4$	3.503	25	14.00 ± 0.03	13.87 ± 0.08	77SJb

[1]Constants corrected from concentration to molality units and including our assigned errors.
[2]References for rejected data: [55DWb][a,c,g], [66VAS][a].

Table A2-7 Selected equilibrium constants for the formation of $HgCl_3^-$ and $HgCl_4^{2-}$ at 25 °C.

Method	Ionic medium		$t/°C$	$Log_{10} K$ (reported)	$Log_{10} K$ (accepted)[1]	Ref.[2]
	Amount concn./mol dm^{-3}	Molality/ mol kg^{-1}				
$HgCl_2 + Cl^- \rightleftharpoons HgCl_3^-$ (K_3)						
emf	0.5 NaClO$_4$	0.513	25	0.85 ± 0.15	0.84 ± 0.20	47LJa
dis	0.5 NaClO$_4$	0.513	25	0.95 ± 0.03	0.94 ± 0.10	57MAa
cal	3.0 NaClO$_4$	3.503	25	1.08 ± 0.34	1.01 ± 0.40	65ARa
emf	3.0 NaClO$_4$	3.503	25	0.75 ± 0.12	0.68 ± 0.20	65ARa
emf	1.0 NaClO$_4$	1.051	25	1.00 ± 0.01	0.98 ± 0.20	68CGb
dis	0.5 NaClO$_4$	0.513	25	0.85	0.84 ± 0.30	70SIa
gl	3.0 NaClO$_4$	3.503	25	1.07 ± 0.03	1.00 ± 0.20	77SJb
cal	0.5 NaClO$_4$	0.513	25	1.03 ± 0.13	1.02 ± 0.30	82VKa
cal	1.0 NaClO$_4$	1.051	25	0.96 ± 0.11	0.94 ± 0.30	82VKa
cal	2.0 NaClO$_4$	2.212	25	1.08 ± 0.14	1.04 ± 0.30	82VKa
sp	0.5 NaClO$_4$	0.513	20	0.81 ± 0.10	0.80 ± 0.30[3]	84GAc
$HgCl_3^- + Cl^- \rightleftharpoons HgCl_4^{2-}$ (K_4)						
emf	0.5 NaClO$_4$	0.513	25	1.00 ± 0.16[4]	0.99 ± 0.20	47LJa
dis	0.5 NaClO$_4$	0.513	25	1.05 ± 0.06	1.04 ± 0.20	57MAa
cal	3.0 NaClO$_4$	3.503	25	1.09 ± 0.36	1.02 ± 0.40	65ARa
emf	3.0 NaClO$_4$	3.503	25	1.38 ± 0.12	1.31 ± 0.20	65ARa
emf	1.0 NaClO$_4$	1.051	25	0.97 ± 0.03	0.95 ± 0.20	68CGb
dis	0.5 NaClO$_4$	0.513	25	1.00	0.99 ± 0.30	70SIa
gl	3.0 NaClO$_4$	3.503	25	1.07 ± 0.05	1.00 ± 0.20	77SJb
cal	0.5 NaClO$_4$	0.513	25	0.95 ± 0.16	0.94 ± 0.30	82VKa
cal	1.0 NaClO$_4$	1.051	25	1.03 ± 0.15	1.01 ± 0.30	82VKa
cal	2.0 NaClO$_4$	2.212	25	1.03 ± 0.21	0.99 ± 0.30	82VKa

[1]Constants corrected from concentration to molality units and including our assigned errors.
[2]References for rejected data: [53PEc][a,d,i], [55DWb][a,c,g], [63EMb][a], [70DSe][b], [73ACa][b,c], [76BAb][b].
[3]The correction from 20 to 25 °C using the Provisional reaction enthalpy (–0.3 kJ mol^{-1} at I_c = 0.5 mol dm^{-3}) is not visible in the first two digits (exactly, $\log_{10} K_3$ amounts to 0.809).
[4]Reported as [$\log_{10} K_3$(6) + $\log_{10} K_4$(7)] = (1.85 ± 0.05). With an uncertainty of ±0.15 in $\log_{10} K_3$(6), this results in ±0.16 in $\log_{10} K_4$(7).

Table A2-8 Equilibrium constants for the system Hg^{2+}– OH^-– Cl^- at 25 °C.

| Method | Ionic medium | | $t/°C$ | $Log_{10} K$ (reported) | Ref. |
	Amount concn./mol dm^{-3}	Molality/ mol kg^{-1}			
$HgCl_2 + H_2O \rightleftharpoons HgOHCl(aq) + Cl^- + H^+$					
gl	Self medium	0 (corr.)	25	-9.92 ± 0.02[1]	65PIa
gl	1.0 NaClO$_4$	1.052	25	-9.56 ± 0.05	68CGa
gl	3.0 NaClO$_4$	3.503	25	-9.87 ± 0.02	77SJb
$2HgCl_2(aq) + H_2O \rightleftharpoons Hg_2(OH)Cl_2^+ + 2Cl^- + H^+$					
gl	3.0 NaClO$_4$	3.503	25	-15.25 ± 0.01	77SJb
$3HgCl_2(aq) + 2H_2O \rightleftharpoons Hg_3(OH)_2Cl^{3+} + 5Cl^- + 2H^+$					
gl	3.0 NaClO$_4$	3.503	25	-37.79 ± 0.02	77SJb

[1]The constant reported was $\log_{10} K° = (4.08 \pm 0.02)$ for the equilibrium $HgCl_2 + OH^- \rightleftharpoons HgOHCl^+ + Cl^-$.

Table A2-9 Selected equilibrium constants for the Hg^{2+}-carbonate system at 25 °C.

| Method | Ionic medium | | $t/°C$ | $Log_{10} K$ (reported) | $Log_{10} K$ (accepted)[1] | Ref. |
	Amount concn./mol dm^{-3}	Molality/ mol kg^{-1}				
$Hg^{2+} + CO_3^{2-} \rightleftharpoons HgCO_3(aq)$ (K_1)						
sol	3 NaClO$_4$	3.503	25	10.65 ± 0.20	10.58 ± 0.20	76HHb[2]
$Hg^{2+} + H_2O + CO_3^{2-} \rightleftharpoons Hg(OH)CO_3^- + H^+$						
sol	3 NaClO$_4$	3.503	25	4.40 ± 0.10	4.40 ± 0.10	76HHb[2]
$Hg^{2+} + H^+ + CO_3^{2-} \rightleftharpoons HgHCO_3^+$						
sol	3 NaClO$_4$	3.503	25	15.05 ± 0.10	14.92 ± 0.10	76HHb[2]

[1]Constants corrected from concentration to molality units and including our assigned errors.
[2]Reference for rejected data: [80BMb]^j.

Table A2-10 Selected equilibrium constants for isocoulombic reactions in the Hg(II)– H^+– $CO_2(g)$ system at 25 °C.

| Method | Ionic medium | | $t/°C$ | $Log_{10} K$ (reported) | $Log_{10} K$ (accepted)[1] | Ref. |
	Amount concn./mol dm^{-3}	Molality/ mol kg^{-1}				
$HgCO_3(aq) + HCO_3^- \rightleftharpoons Hg(OH)CO_3^- + CO_2(g)$						
sol	3 NaClO$_4$	3.503	25	1.75 ± 0.20	1.68 ± 0.20	76HHb[2]
$HgCO_3(aq) + H^+ \rightleftharpoons HgHCO_3^+$						
sol	3 NaClO$_4$	3.503	25	4.40 ± 0.20	4.33 ± 0.20	76HHb[2]
$Hg(OH)_2(aq) + HCO_3^- \rightleftharpoons Hg(OH)CO_3^- + H_2O$						
sol	3 NaClO$_4$	3.503	25	1.05 ± 0.10	0.98 ± 0.10	76HHb[2]
$Hg(OH)_2(aq) + CO_2(g) + H^+ \rightleftharpoons HgHCO_3^+ + H_2O$						
sol	3 NaClO$_4$	3.503	25	3.70 ± 0.10	3.63 ± 0.10	76HHb[2]
$Hg(OH)_2(aq) + CO_2(g) \rightleftharpoons HgCO_3(aq) + H_2O$						
sol	3 NaClO$_4$	3.503	25	-0.70 ± 0.20	-0.70 ± 0.20	76HHb[2]

(*continues on next page*)

Table A2-10 (*Continued*).

| Method | Ionic medium | | $t/°C$ | $\text{Log}_{10} K$ (reported) | $\text{Log}_{10} K$ (accepted)[1] | Ref. |
	Amount concn./mol dm^{-3}	Molality/ mol kg^{-1}				
HgOH$^+$ + CO$_2$(g) $\rightleftharpoons$ HgHCO$_3^+$						
sol	3 NaClO$_4$	3.503	25	1.05 ± 0.10	1.05 ± 0.10	76HHb[2]
Hg(OH)$_3^-$ + CO$_2$(g) $\rightleftharpoons$ Hg(OH)CO$_3^-$ + H$_2$O						
sol	3 NaClO$_4$	3.503	25	7.98 ± 0.10	7.98 ± 0.10	76HHb[2]

[1]Constants corrected from concentration to molality units and including our assigned errors.
[2]Reference for rejected data: [80BMb]^j.

Table A2-11 Experimental stability constants reported for the Hg^{2+}– SO$_4^{2-}$ system at 25 °C.

| Method | Ionic medium | $t/°C$ | $\text{Log}_{10} K$ (reported)[1] | Ref. |
	Amount concn./mol dm^{-3}			
Hg^{2+} + SO$_4^{2-}$ $\rightleftharpoons$ Hg(SO$_4$)(aq) (K_1)				
emf	0.50 NaClO$_4$	25	1.34 ± 0.02	46ISa
sp	0.33 NaClO$_4$	25	1.42 ± 0.01[2]	57PTa
Hg^{2+} + 2SO$_4^{2-}$ $\rightleftharpoons$ Hg(SO$_4$)$_2^{2-}$ (β_2)				
emf	0.50 NaClO$_4$	25	2.43 ± 0.03	46ISa
emf	Var. (SO$_4^{2-}$)	25	1.29 – 1.81[3]	57KSb

[1]Uncertainties as given in the original publications.
[2]Same value also reported by these authors for I_c = 0.43 mol dm^{-3} NaClO$_4$.
[3]No uncertainties given.

Table A2-12 Selected solubility product (solubility constant) data for HgO(s) at 25 °C.

| Method | Ionic medium | | $t/°C$ | $\text{Log}_{10} K$ (reported) | $\text{Log}_{10} K$ (accepted)[1] | Ref. |
	Amount concn./mol dm^{-3}	Molality/ mol kg^{-1}				
HgO(s) (red) + H$_2$O $\rightleftharpoons$ Hg(OH)$_2$(aq) (K_{s2})[2]						
sol	var.	0 (corr.)	25	–3.57	–3.57 ± 0.05	02SCa
sol	var.	0 (corr.)	25	–3.63 ± 0.02	–3.63 ± 0.05	20FUa
sol	var.	0 (corr.)	25	–3.64 ± 0.01	–3.64 ± 0.05	38GHa
sol	var.	0 (corr.)	25	–3.65 ± 0.01	–3.65 ± 0.05	61AHb
sol	3 NaClO$_4$	3.503	25	–3.75 ± 0.01	–3.69 ± 0.03	61DTa
HgO(s) (red) + 2H$^+$ $\rightleftharpoons$ Hg^{2+} + H$_2$O (*K_s)[3]						
sol	3 NaClO$_4$	3.503	25	2.69 ± 0.10	2.62 ± 0.10	61DTa
HgO(s) (red) + H$_2$O + OH$^-$ $\rightleftharpoons$ Hg(OH)$_3^-$ ($K_{s3}°$)						
sol	var.	0 (corr.)	25	–4.30	–4.43 ± 0.09	20FUa
sol	var.	0 (corr.)	25	–4.49	–4.43 ± 0.09	38GHa
HgO(s) (yellow) + H$_2$O $\rightleftharpoons$ Hg(OH)$_2$(aq) ($K_{s2}°$)[4]						
sol	var.	0 (corr.)	25	–3.63 ± 0.003	–3.63 ± 0.05	38GHa
sol	var.	0 (corr.)	25	–3.63 ± 0.01	–3.63 ± 0.05	61AHb

Table A2-12 (*Continued*).

Method	Ionic medium		$t/°C$	$\mathrm{Log}_{10}\,K$ (reported)	$\mathrm{Log}_{10}\,K$ (accepted)[1]	Ref.
	Amount concn./mol dm^{-3}	Molality/ mol kg^{-1}				
HgO(s) (yellow) + H$_2$O + OH$^-$ ⇌ Hg(OH)$_3^-$ ($K_{s3}°$)						
sol	var.	0 (corr.)	25	–4.51	–4.43 ± 0.09	38GHa
HgO(s) (hex.) + H$_2$O ⇌ Hg(OH)$_2$(aq) ($K_{s2}°$)						
sol	var.	0 (corr.)	25	–3.59 ± 0.01	–3.59 ± 0.05	61AHb

[1]Constants corrected from concentration to molality units and including our assigned errors.
[2]References for rejected data: [17KOa][a], [59SAa][a].
[3]References for rejected data: [17KOa][a], [39GHa][a], [61DTa][a,j].
[4]Reference for rejected data: [59NHa][a,b,i].

Table A2-13 Selected enthalpies for the reaction HgO(s) (yellow) + 2H$^+$ ⇌ Hg^{2+} + H$_2$O (*K_{s0}) at 25 °C, HClO$_4$ media.

Method	Ionic medium		$t/°C$	$\Delta_r H_m$/kJ mol^{-1} (reported)	$\Delta_r H_m$/kJ mol^{-1} (accepted)[1]	Ref.
	Amount concn./mol dm^{-3}	Molality/ mol kg^{-1}				
HgO(s) (yellow) + 2H$^+$ ⇌ Hg^{2+} + H$_2$O (*K_{s0})						
cal	1.12 HClO$_4$	1.183	25	–22.79 ± 0.04	–22.8 ± 0.2	59SLd
cal	2.215 HClO$_4$	2.465	25	–21.41 ± 0.04	–21.4 ± 0.2	59SLd
cal	3.336 HClO$_4$	3.927	25	–20.07 ± 0.04	–20.1 ± 0.2	59SLd
cal	4.236 HClO$_4$	5.223	25	–19.24 ± 0.08	–19.2 ± 0.2	59SLd
cal	0.876 HClO$_4$	0.915	25	–23.54 ± 0.13	–23.5 ± 0.2	62LGa

[1]Reported values with our assigned errors.

Table A2-14 Selected reaction enthalpies for the formation of HgCl$^+$ and HgCl$_2$(aq), 25 °C, NaClO$_4$ media.

Method	Ionic medium		$t/°C$	$\Delta_r H_m$/kJ mol^{-1} (reported)	$\Delta_r H_m$/kJ mol^{-1} (accepted)[1]	Ref.[2]
	Amount concn./mol dm^{-3}	Molality/ mol kg^{-1}				
Hg^{2+} + Cl$^-$ ⇌ HgCl$^+$ (K_1)						
cal	0.5 NaClO$_4$	0.513	25	–23.0 ± 0.8	–23.0 ± 1.0	64CIa
cal	3.0 NaClO$_4$	3.503	25	–24.2 ± 1.0	–24.2 ± 1.0	65ARa
cal	1.0 NaClO$_4$	1.051	25	–23.2 ± 0.5	–23.2 ± 1.0	75CGe
cal	0.5 NaClO$_4$	0.513	25	–23.6 ± 0.3	–23.6 ± 1.0	80VKb
cal	1.0 NaClO$_4$	1.051	25	–24.4 ± 0.3	–24.4 ± 1.0	80VKb
cal	2.0 NaClO$_4$	2.212	25	–24.6 ± 0.3	–24.6 ± 1.0	80VKb
Hg^{2+} + HgCl$_2$(aq) ⇌ 2 HgCl$^+$						
emf	0.5 NaClO$_4$	0.513	25	–3.1		66VAS

(*continues on next page*)

Table A2-14 (*Continued*).

| Method | Ionic medium | | $t/°C$ | $\Delta_r H_m/\text{kJ mol}^{-1}$ (reported) | $\Delta_r H_m/\text{kJ mol}^{-1}$ (accepted)[1] | Ref.[2] |
	Amount concn./mol dm^{-3}	Molality/ mol kg^{-1}				
Hg^{2+} + 2 Cl$^-$ $\rightleftharpoons$ HgCl$_2$(aq) (β_2)						
cal	0.5 NaClO$_4$	0.513	25	−53.3 ± 0.4	−53.3 ± 1.5	64CIa
cal	3.0 NaClO$_4$	3.503	25	−51.4 ± 1.1	−51.4 ± 1.5	65ARa
?	0.5 NaClO$_4$	0.513	25	−51.5[3]		66VAS
cal	1.0 NaClO$_4$	1.051	25	−50.9 ± 1.1	−50.9 ± 1.5	75CGe
cal	0.5 NaClO$_4$	0.513	25	−51.8 ± 0.2	−51.8 ± 1.5	80VKb
cal	1.0 NaClO$_4$	1.051	25	−51.4 ± 0.2	−51.4 ± 1.5	80VKb
cal	2.0 NaClO$_4$	2.212	25	−50.5 ± 0.2	−50.5 ± 1.5	80VKb

[1]Reported values with our assigned errors.
[2]Reference for rejected data: [60GKb][b], [61MPa][c], [64CIa][a].
[3]This value is cited in [66VAS] and refers to an unavailable Russian report dated 1949.

Table A2-15 Selected reaction enthalpies for the formation of HgCl$_3^-$ and HgCl$_4^{2-}$, 25 °C, NaClO$_4$ media.

| Method | Ionic medium | | $t/°C$ | $\Delta_r H_m/\text{kJ mol}^{-1}$ (reported) | $\Delta_r H_m/\text{kJ mol}^{-1}$ (accepted)[1] | Ref.[2] |
	Amount concn./mol dm^{-3}	Molality/ mol kg^{-1}				
HgCl$_2$(aq) + Cl$^-$ $\rightleftharpoons$ HgCl$_3^-$ (K_3)						
cal	3.0 NaClO$_4$	3.503	25	−4.31 ± 0.88	−4.3 ± 3.0	65ARa
cal	1.0 NaClO$_4$	1.051	25	−1.0 ± 0.1	−1.0 ± 3.0	75CGe
cal	0.5 NaClO$_4$	0.513	25	−0.25 ± 0.08	−0.3 ± 3.0	82VKb
cal	1.0 NaClO$_4$	1.051	25	−0.71 ± 0.13	−0.7 ± 3.0	82VKb
cal	2.0 NaClO$_4$	2.212	25	−2.22 ± 0.13	−2.2 ± 3.0	82VKb
HgCl$_3^-$ + Cl$^-$ $\rightleftharpoons$ HgCl$_4^{2-}$ (K_4)						
cal	3.0 NaClO$_4$	3.503	25	−6.2 ± 1.0	−6.2 ± 3.0	65ARa
cal	1.0 NaClO$_4$	1.051	25	−7.6 ± 0.2	−7.6 ± 3.0	75CGe
cal	0.5 NaClO$_4$	0.513	25	−9.12 ± 0.13	−9.1 ± 3.0	82VKb
cal	1.0 NaClO$_4$	1.051	25	−9.04 ± 0.13	−9.0 ± 3.0	82VKb
cal	2.0 NaClO$_4$	2.212	25	−8.83 ± 0.13	−8.8 ± 3.0	82VKb

[1]Reported values with our assigned errors.
[2]Reference for rejected data: [60GKb][b].

APPENDIX 3
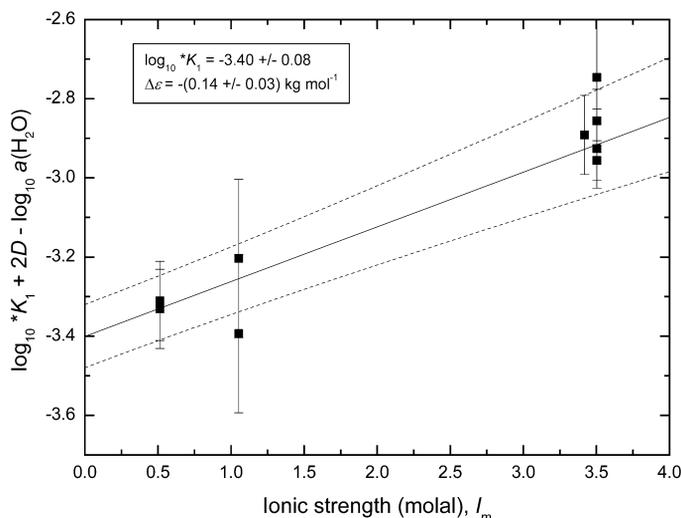
Fig. A3-1 Extrapolation to $I = 0$ of $\log_{10} *K_1 - \Delta(z^2)D - \log_{10} a(H_2O)$ (eq. 3, Section 5.2) for reaction 4 using selected data for $NaClO_4$ solution, 25 °C, Table A2-1. The error bounds are derived by using the uncertainty ranges of $\log_{10} *K_1°$ and $\Delta\varepsilon$ to recalculate $\log_{10} *K_1(I_m)$ up to $I_m = 4$ mol kg^{-1}.
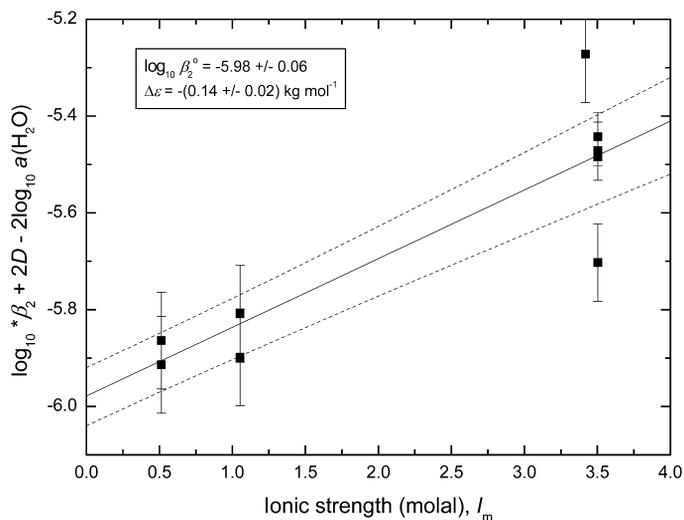
Fig. A3-2 Extrapolation to $I = 0$ of $\log_{10} *\beta_2 - \Delta(z^2)D - 2\log_{10} a(H_2O)$ for reaction 5 using selected data for $NaClO_4$ and $CaClO_4$ media, 25 °C (Table A2-2). The error bounds are derived by using the uncertainty ranges of $\log_{10} *\beta_2°$ and $\Delta\varepsilon$ to recalculate $\log_{10} *\beta_2(I_m)$ up to $I_m = 4$ mol kg^{-1}.
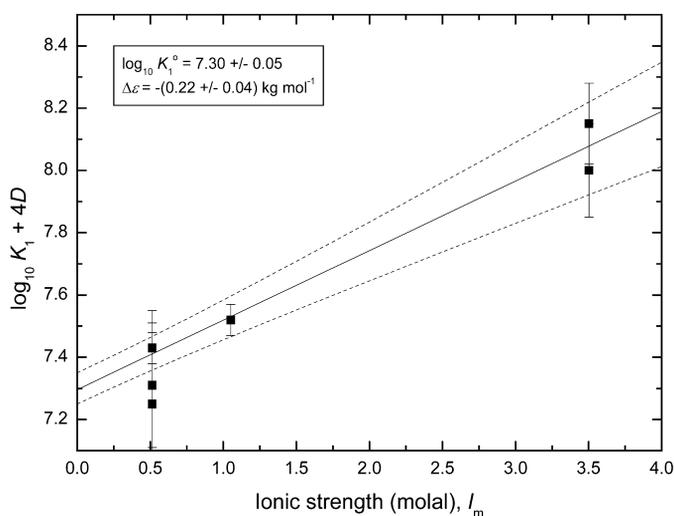
Fig. A3-3 Extrapolation to $I = 0$ of $\log_{10} K_1 - \Delta(z^2)D$ for reaction 6 using selected data (Table A2-4) at 25 °C for NaClO$_4$ media, pH ≈ 2 (pH ≈ 1.3 in [68CGb], pH ≈ 1 in [63HIa], pH variable in [77SJb]). The error bounds are derived by using the uncertainty ranges of $\log_{10} K_1^\circ$ and $\Delta\varepsilon$ to recalculate $\log_{10} K_1(I_m)$ up to $I_m = 4$ mol kg^{-1}.
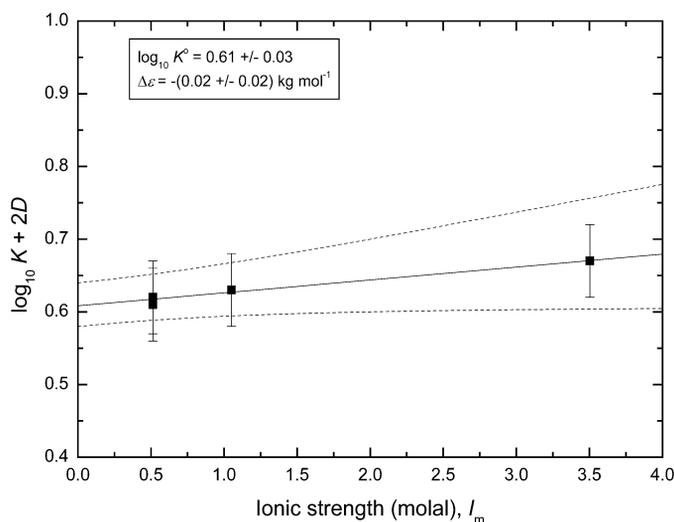
Fig. A3-4 Extrapolation to $I = 0$ of $\log_{10} K - \Delta(z^2)D$ for reaction 10 using selected data for (Na,H)ClO$_4$ media at pH ≈ 2 (pH ≈ 1.3 in [68CGb]), 25 °C (Table A2-5). The error bounds are derived by using the uncertainty ranges of $\log_{10} K^\circ$ and $\Delta\varepsilon$ to recalculate $\log_{10} K(I_m)$ up to $I_m = 4$ mol kg^{-1}.
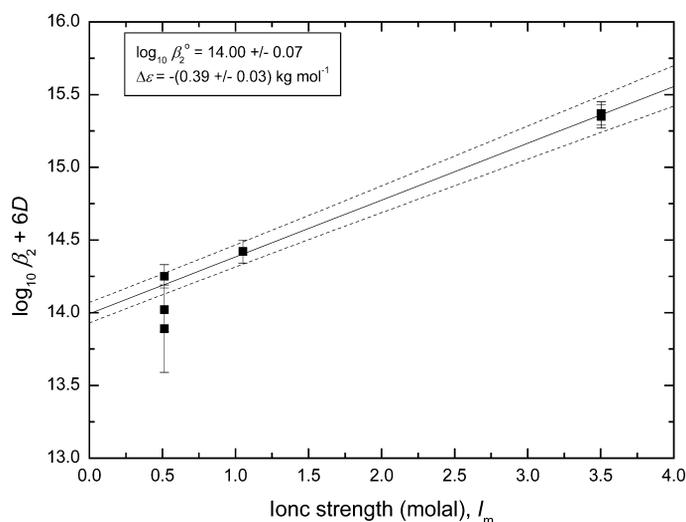
Fig. A3-5 Extrapolation to $I = 0$ of $\log_{10} \beta_2 - \Delta(z^2)D$ for reaction 7 using selected data for $NaClO_4$ media, 25 °C (Table A2-6); pH $\approx$ 1.3 in [68CGb], pH $\approx$ 1 in [63HIa], pH variable in [77SJb]. The error bounds are derived by using the uncertainty ranges of $\log_{10} \beta_2^\circ$ and $\Delta\varepsilon$ to recalculate $\log_{10} \beta_2(I_m)$ up to $I_m = 4$ mol kg^{-1}.
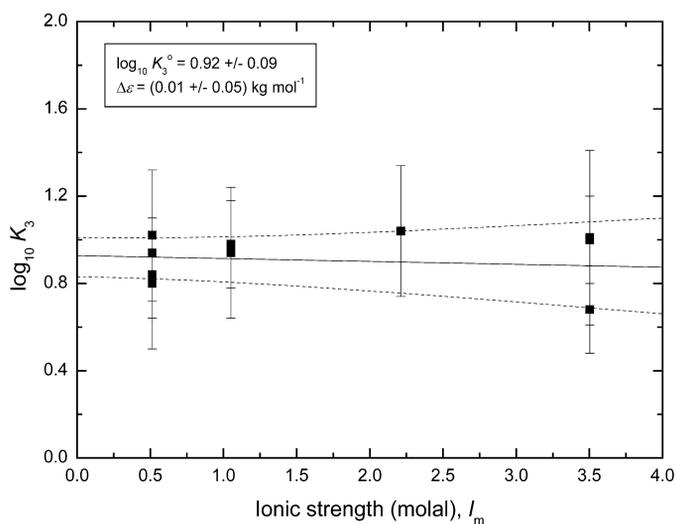
Fig. A3-6 Extrapolation to $I = 0$ of $\log_{10} K_3$ for reaction 8 ($\Delta(z^2)D = 0$) using selected data for $NaClO_4$ media containing varying and significant proportions of Cl$^-$; 25 °C (Table A2-7) The error bounds are derived by using the uncertainty ranges of $\log_{10} K_3^\circ$ and $\Delta\varepsilon$ to recalculate $\log_{10} K_3(I_m)$ up to $I_m = 4$ mol kg^{-1}.
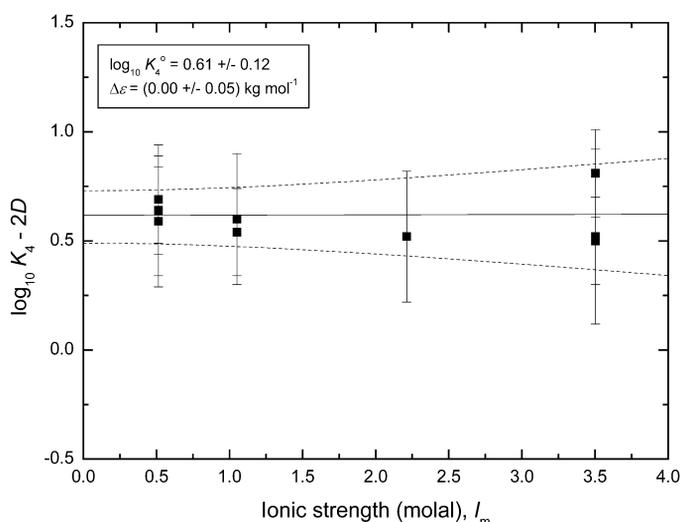
Fig. A3-7 Extrapolation to $I = 0$ of $\log_{10} K_4 - \Delta(z^2)D$ for reaction 9 using selected data for $NaClO_4$ media containing varying and significant proportions of Cl^-; 25 °C (Table A2-7). The error bounds are derived by using the uncertainty ranges of $\log_{10} K_4°$ and $\Delta\varepsilon$ to recalculate $\log_{10} K_4(I_m)$ up to $I_m = 4$ mol kg^{-1}.
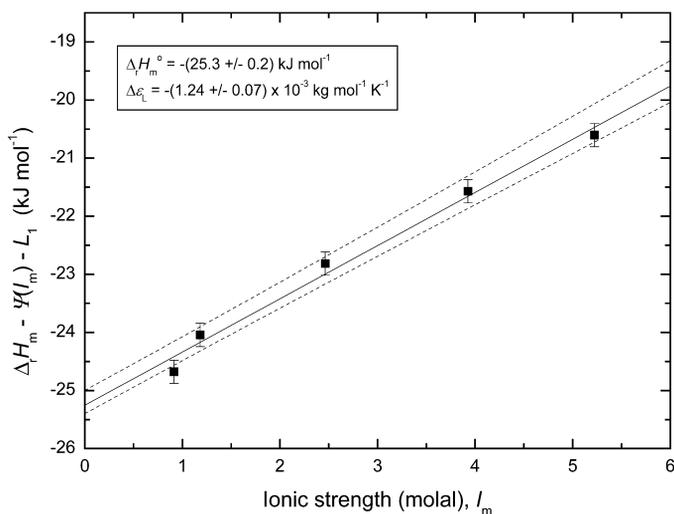
Fig. A3-8 Extrapolation of enthalpy data for reaction 29 to $I = 0$, according to eq. 37; $HClO_4$ media, 25 °C (Table A2-13). The error bounds are derived by using the uncertainty ranges of $\Delta_r H_m°$ and $\Delta\varepsilon_L$ to recalculate $\Delta_r H_m(I_m)$ up to $I_m = 6$ mol kg^{-1}.
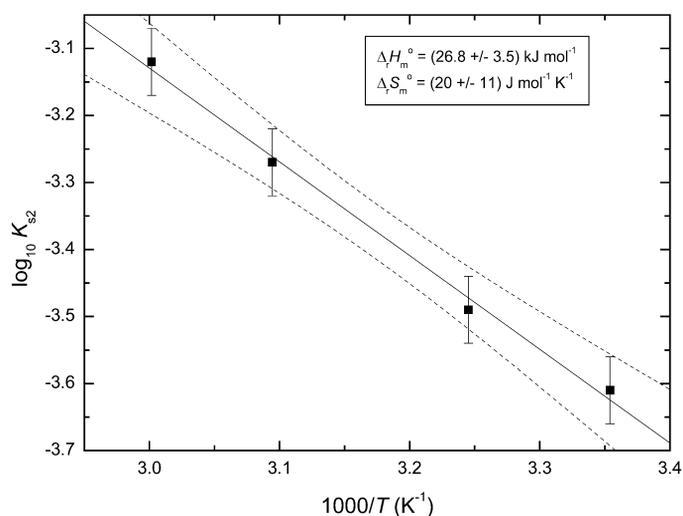
Fig. A3-9 Plot of $\log_{10} K_{s2}$ for reaction 28 (HgO(yellow)) against absolute temperature. The slope of the regression line is $-(\Delta_r H_m^\circ/2.303R)$ and the intercept $(\Delta_r S_m^\circ/2.303R)$. The error bounds are derived by using the uncertainty ranges of $\Delta_r H_m^\circ$ and $\Delta_r S_m^\circ$ to recalculate $\log_{10} K_{s2}(T)$.
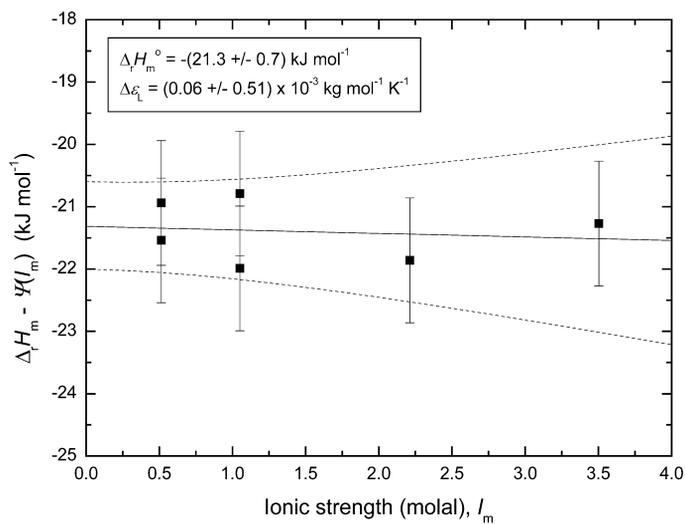
Fig. A3-10 Extrapolation to $I = 0$ of the enthalpy for reaction 6 in $NaClO_4$ solutions at pH ≈ 2 [65ARa], pH ≈ 1.3 [75CGe] and pH ≈ 1 [64CIa, 80VKb]; 25 °C (Table A2-14). The error bounds are derived by using the uncertainty ranges of $\Delta_r H_m^\circ$ and $\Delta\varepsilon_L$ to recalculate $\Delta_r H_m$ up to $I_m = 4$ mol kg^{-1}.
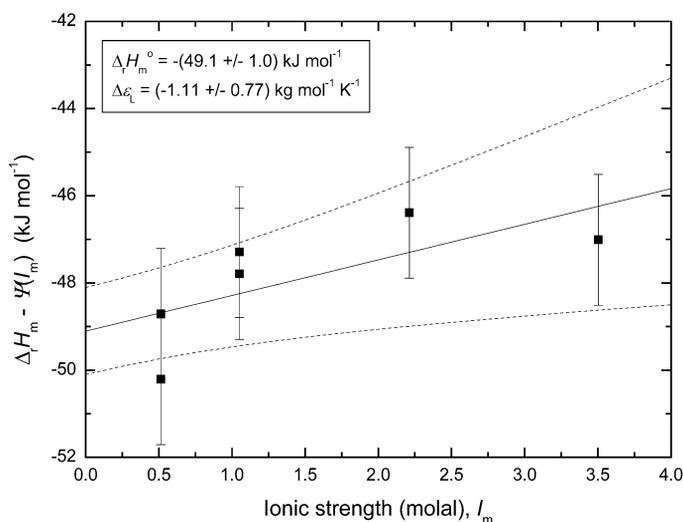
Fig. A3-11 Extrapolation to $I = 0$ of the enthalpy for reaction 7 in $NaClO_4$ solutions at pH $\approx$ 2 [65ARa], pH $\approx$ 1.3 [75CGe], and pH $\approx$ 1 [64CIa, 80VKb]; 25 °C (Table A2-14). The error bounds are derived by using the resulting uncertainty ranges of $\Delta_r H_m{}^\circ$ and $\Delta \varepsilon_L$ to recalculate $\Delta_r H_m$ up to $I_m = 4$ mol kg^{-1}.
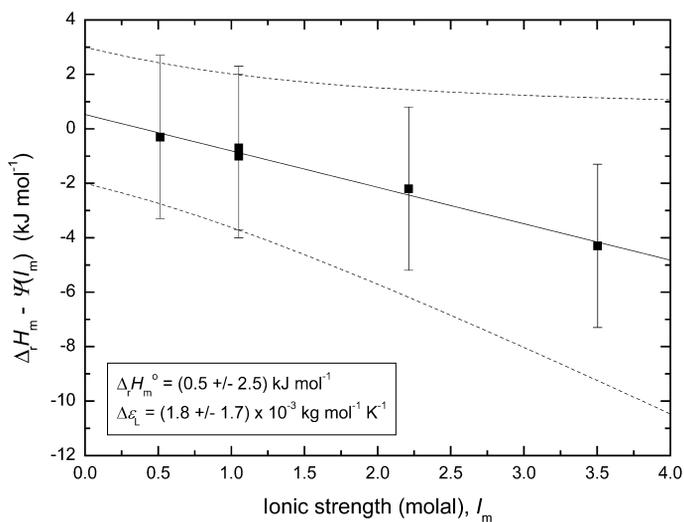
Fig. A3-12 Extrapolation to $I = 0$ of the enthalpy for reaction 8 in $NaClO_4$ solutions containing varying and significant proportions of Cl$^-$; 25 °C (Table A2-15). The error bounds are derived by using the uncertainty ranges of $\Delta_r H_m{}^\circ$ and $\Delta \varepsilon_L$ to recalculate $\Delta_r H_m$ to $I_m = 4$ mol kg^{-1}.
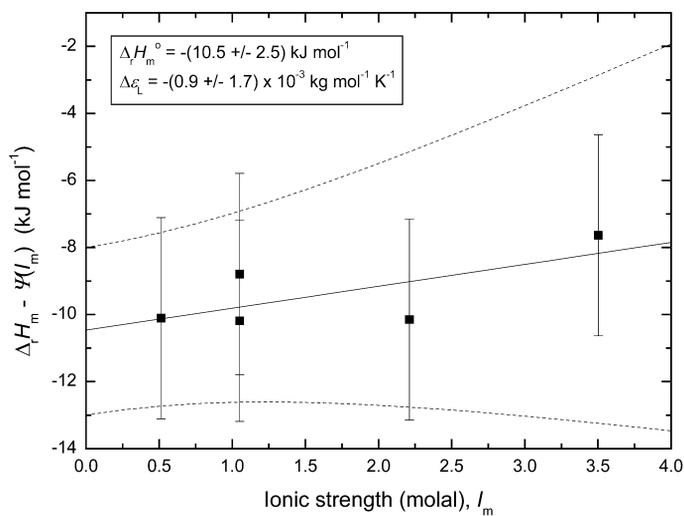
Fig. A3-13 Extrapolation to $I = 0$ of the enthalpy for reaction 9 in $NaClO_4$ solutions containing varying and significant proportions of Cl^-; 25 °C (Table A2-15). The error bounds are derived by using the uncertainty ranges of $\Delta_r H_m°$ and $\Delta\varepsilon_L$ to recalculate $\Delta_r H_m$ to $I_m = 4$ mol kg^{-1}.

APPENDIX 4

Equilibrium data for the H^+– CO_3^{2-} and H^+– PO_4^{3-} systems

Table A4-1a Selected experimental equilibrium constants for the protonation of carbonate anion. Data for 298.15 K and NaCl medium.

Method	Ionic medium molality/ mol kg^{-1}	$Log_{10} K$ (reported)		$Log_{10} K$ (accepted)[1]	Ref.[2]
$H^+ + CO_3^{2-} \rightleftharpoons HCO_3^-$					
emf	0	10.329		10.329 ± 0.005	41HSa[3]
gl	0.409	9.628	± 0.008	9.618 ± 0.008	72DHa[4]
gl	0.515	9.606	± 0.01	9.593 ± 0.01	72DHa[4]
gl	0.621	9.569	± 0.013	9.554 ± 0.013	72DHa[4]
gl	0.729	9.538	± 0.005	9.520 ± 0.005	72DHa[4]
gl	0.837	9.527	± 0.009	9.507 ± 0.009	72DHa[4]
gl	0.50	9.58	± 0.01	9.58 ± 0.01	82TMa
gl	0.70	9.53	± 0.01	9.53 ± 0.01	82TMa
gl	1.00	9.48	± 0.01	9.48 ± 0.01	82TMa
gl	1.50	9.44	± 0.01	9.44 ± 0.01	82TMa
gl	2.00	9.41	± 0.01	9.41 ± 0.01	82TMa
gl	2.50	9.43	± 0.01	9.43 ± 0.01	82TMa
gl	3.00	9.46	± 0.01	9.46 ± 0.01	82TMa
gl	3.50	9.46	± 0.01	9.46 ± 0.01	82TMa
gl	4.00	9.53	± 0.01	9.53 ± 0.01	82TMa
gl	4.50	9.56	± 0.01	9.56 ± 0.01	82TMa
gl	5.50	9.67	± 0.01	9.67 ± 0.01	82TMa
gl	6.00	9.71	± 0.01	9.71 ± 0.01	82TMa
gl	0.10	9.87	± 0.02	9.87 ± 0.02	93HMa
gl	0.50	9.62	± 0.02	9.62 ± 0.02	93HMa
gl	1.00	9.54	± 0.02	9.54 ± 0.02	93HMa
gl	2.00	9.47	± 0.02	9.47 ± 0.02	93HMa
gl	4.00	9.53	± 0.02	9.53 ± 0.02	93HMa
gl	6.00	9.74	± 0.02	9.74 ± 0.02	93HMa
gl	0.70	9.52		9.52 ± 0.02	85BMb[3,5]
gl	1.00	9.47		9.47 ± 0.02	85BMb[3,5]
gl	1.02	9.5068 ± 0.003		9.497 ± 0.003	98CHa[6]

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Table A4-1a (*Continued*).

Method	Ionic medium molality/ mol kg^{-1}	Log$_{10}$ K (reported)	Log$_{10}$ K (accepted)[1]	Ref.[2]
**H$^+$ + HCO$_3^-$ $\rightleftharpoons$ [CO$_2$(aq) + H$_2$CO$_3$]**				
emf	0	6.3519	6.3519 ± 0.005	43HDa[3]
emf	0	6.3514	6.3514 ± 0.005	45HBa[3]
emf	0.10	6.1157	6.1157 ± 0.005	45HBa[3]
emf	0.20	6.0567	6.0567 ± 0.005	45HBa[3]
emf	0.50	5.9824	5.9824 ± 0.005	45HBa[3]
emf	0.70	5.9635	5.9635 ± 0.005	45HBa[3]
emf	1.00	5.9443	5.9443 ± 0.005	45HBa[3]
gl	0.409	6.0385 ± 0.003	6.029 ± 0.003	72DHa[4]
gl	0.515	6.0315 ± 0.004	6.019 ± 0.004	72DHa[4]
gl	0.621	6.0105 ± 0.006	5.996 ± 0.006	72DHa[4]
gl	0.729	6.0005 ± 0.003	5.983 ± 0.003	72DHa[4]
gl	0.837	5.994 ± 0.002	5.974 ± 0.002	72DHa[4]
gl	0.50	5.997 ± 0.01	5.997 ± 0.01	82TMa
gl	0.70	5.984 ± 0.01	5.984 ± 0.01	82TMa
gl	1.00	5.970 ± 0.01	5.970 ± 0.01	82TMa
gl	1.50	5.964 ± 0.01	5.964 ± 0.01	82TMa
gl	2.00	5.968 ± 0.01	5.968 ± 0.01	82TMa
gl	2.50	5.992 ± 0.01	5.992 ± 0.01	82TMa
gl	3.50	6.046 ± 0.01	6.046 ± 0.01	82TMa
gl	4.00	6.092 ± 0.01	6.092 ± 0.01	82TMa
gl	4.50	6.130 ± 0.01	6.130 ± 0.01	82TMa
gl	5.50	6.227 ± 0.01	6.227 ± 0.01	82TMa
gl	6.00	6.264 ± 0.01	6.264 ± 0.01	82TMa
gl	0.10	6.106 ± 0.04	6.106 ± 0.04	93HMa
gl	0.50	5.992 ± 0.04	5.992 ± 0.04	93HMa
gl	1.00	5.940 ± 0.04	5.940 ± 0.04	93HMa
gl	2.00	5.979 ± 0.04	5.979 ± 0.04	93HMa
gl	4.00	6.058 ± 0.04	6.058 ± 0.04	93HMa
gl	6.00	6.185 ± 0.04	6.185 ± 0.04	93HMa

[1]Equilibrium constants corrected to molality units.
[2]References for rejected data: [61BNa][d], [71OPa][d], [74PHc][f,g], [98CHa][j].
[3]Errors assigned by reviewer.
[4]Original data reported in moles (kg solution)$^{-1}$.
[5]Personal communication.
[6]Original data reported in molar units.

Table A4-1b Selected experimental equilibrium constants for the protonation of carbonate anion. Data for 298.15 K and $NaClO_4$ medium.

Method	Ionic medium molality/ mol kg^{-1}	$Log_{10} K$ (reported)		$Log_{10} K$ (accepted)[1]		Ref.[2]
$H^+ + CO_3^{2-} \rightleftharpoons HCO_3^-$						
gl	1.00	9.57	± 0.02	9.57	± 0.02	58FNa
gl	3.50	9.56	± 0.02	9.56	± 0.02	58FNa
gl	3.00	9.57	± 0.02	9.57	± 0.02	77RGb
gl	0.304	9.76[3]		9.754	± 0.02	82BSa[3,4]
gl	0.101	9.95	± 0.03	9.947	± 0.03	82MAc[4]
gl	1.05	9.55	± 0.02	9.529	± 0.02	82MAc[4]
gl	0.72	9.55[3]		9.535	± 0.02	85BMb[3,4,5]
gl	1.05	9.50[3]		9.479	± 0.02	85BMb[3,4,5]
gl	0.68	9.53	± 0.01	9.53	± 0.01	87CBb
$H^+ + HCO_3^- \rightleftharpoons CO_2(g) + H_2O$						
gl	1.00	7.55	± 0.02	7.55	± 0.02	58FNa
gl	3.50	7.88	± 0.02	7.88	± 0.02	58FNa
gl	0.202	7.583		7.578	± 0.02	68SRe[3,4]
gl	3.00	7.800	± 0.004	7.800	± 0.004	77RGb
gl	0.304	7.53		7.524	± 0.02	82BSa[3,4]
gl	0.101	7.73	± 0.004	7.727	± 0.004	82MAc[4]
gl	0.68	7.56	± 0.01	7.56	± 0.01	87CBb

[1]Equilibrium constants corrected to molality units
[2]References for rejected data: [91BGa][f,j], [96FNa][f,j].
[3]Errors assigned by reviewer.
[4]Original data reported in molar units.
[5]Personal communication.

Table A4-2 Selected experimental equilibrium constants for the protonation of phosphate anion in various media. All data for 298.15 K.

| Method | Ionic medium | | $Log_{10} K$ (reported) | $Log_{10} K$ (accepted) | Ref.[2] |
	Reported[1]	Molality/ mol kg^{-1}			
$H^+ + PO_4^{3-} \rightleftharpoons HPO_4^{2-}$					
cal	0 corr[3]	0	12.39 ± 0.03	12.39 ± 0.15	66CIa
sp	0 corr[4]	0	12.375 ± 0.01	12.37 ± 0.05	61VQa
emf	0 corr	0	12.325	12.32 ± 0.05	29BUa
gl	3.00 M NaClO$_4$	3.503	10.72 ± 0.03	10.65 ± 0.05	71PEb
gl, emf	3.00 M NaClO$_4$	3.503	10.85 ± 0.01	10.78 ± 0.05	69BSb
gl	0.15 M NaCl	0.151	11.545 ± 0.005	11.54 ± 0.06	81VSa
gl	0.5 m NaCl	0.5	11.29 ± 0.06	11.29 ± 0.06	89HFa
gl	1.0 m NaCl	1.0	11.05 ± 0.015	11.05 ± 0.06	89HFa
gl	2.0 m NaCl	2.0	10.90 ± 0.01	10.90 ± 0.06	89HFa
gl	3.0 m NaCl	3.0	10.85 ± 0.015	10.85 ± 0.06	89HFa
gl	4.0 m NaCl	4.0	10.84 ± 0.01	10.84 ± 0.06	89HFa
gl	5.0 m NaCl	5.0	10.86 ± 0.01	10.86 ± 0.06	89HFa
gl	6.0 m NaCl	6.0	10.91 ± 0.01	10.91 ± 0.06	89HFa
gl	0.04 M NaCl	0.040	11.83	11.83 ± 0.06	91DDa
gl	0.16 M NaCl	0.161	11.49	11.49 ± 0.06	91DDa
gl	0.36 M NaCl	0.363	11.26	11.26 ± 0.06	91DDa
gl	0.64 M NaCl	0.649	11.10	11.09 ± 0.06	91DDa
gl	1.00 M NaCl	1.021	11.01	11.00 ± 0.06	91DDa
gl	0.04 M KCl	0.040	11.85	11.85 ± 0.06	91DDa
gl	0.16 M KCl	0.161	11.56	11.56 ± 0.06	91DDa
gl	0.36 M KCl	0.365	11.40	11.40 ± 0.06	91DDa
gl	0.64 M KCl	0.654	11.34	11.33 ± 0.06	91DDa
gl	1.00 M KCl	1.033	11.35	11.34 ± 0.06	91DDa
gl	0.20 M KCl	0.202	11.48 ± 0.01	11.48 ± 0.06	96AKa
gl	0.1 M NaNO$_3$	0.101	11.68 ± 0.05	11.68 ± 0.06	96SSa
gl	1.0 M (CH$_3$)$_4$NBr		11.10 ± 0.09	11.10 ± 0.10	61ICb

Table A4-2 (*Continued*).

Method	Ionic medium Reported[1]	Molality/ mol kg^{-1}	Log$_{10}$ K (reported)	Log$_{10}$ K (accepted)	Ref.[2]
H$^+$ + HPO$_4$$^{2-}$ ⇌ H$_2$PO$_4$$^-$					
gl	0 corr[5]		7.18 ± 0.02	7.18 ± 0.02	65PEa
emf	0 corr[6]		7.2002 ± 0.0002	7.20 ± 0.02	58GRc
emf	0 corr[7]		7.1988 ± 0.0002	7.20 ± 0.02	57ETa
emf	0 corr[8]		7.198 ± 0.001	7.20 ± 0.02	43BAa
emf	0 corr[9]		7.222 ± 0.002	7.22 ± 0.02	34GSa
emf	0 corr		7.205	7.20 ± 0.02	29BUa
gl	0.1 M NaClO$_4$	0.101	6.59	6.59 ± 0.10	76TDa
gl	0.1 M NaClO$_4$	0.101	6.70 ± 0.02	6.70 ± 0.05	67SBc
gl	0.68 M NaClO$_4$	0.704	6.38	6.37 ± 0.06	89BBa
emf	3.00 M NaClO$_4$	3.503	6.279 ± 0.015	6.21 ± 0.05	74HHb
gl	3.00 M NaClO$_4$	3.503	6.240 ± 0.008	6.17 ± 0.05	71PEb
gl, emf	3.00 M NaClO$_4$	3.503	6.270 ± 0.004	6.20 ± 0.05	69BSb
gl	0.15 M NaCl	0.151	6.638 ± 0.003	6.64 ± 0.06	81VSa
gl	1.00 M NaCl	1.021	6.36 ± 0.02	6.35 ± 0.06	83ISb
sp	1.00 M NaCl	1.021	6.34	6.33 ± 0.06	61BNa
gl	0.5 m NaCl	0.5	6.47 ± 0.01	6.47 ± 0.06	89HFa
gl	1.0 m NaCl	1.0	6.33 ± 0.01	6.33 ± 0.06	89HFa
gl	2.0 m NaCl	2.0	6.22 ± 0.02	6.22 ± 0.06	89HFa
gl	3.0 m NaCl	3.0	6.19 ± 0.04	6.19 ± 0.06	89HFa
gl	4.0 m NaCl	4.0	6.21 ± 0.03	6.21 ± 0.06	89HFa
gl	5.0 m NaCl	5.0	6.22 ± 0.01	6.22 ± 0.06	89HFa
gl	6.0 m NaCl	6.0	6.28 ± 0.01	6.28 ± 0.06	89HFa
gl	0.04 M NaCl	0.04	6.87	6.87 ± 0.06	91DDa
gl	0.16 M NaCl	0.161	6.65	6.65 ± 0.06	91DDa
gl	0.36 M NaCl	0.363	6.49	6.49 ± 0.06	91DDa
gl	0.64 M NaCl	0.649	6.38	6.37 ± 0.06	91DDa
gl	1.00 M NaCl	1.021	6.28	6.27 ± 0.06	91DDa
gl	0.20 M KCl	0.202	6.63 ± 0.01	6.63 ± 0.05	96AKa
gl	0.01 M KCl	0.010	7.042	7.04 ± 0.06	69MKa
gl	0.029 M KCl	0.029	6.921	6.92 ± 0.06	69MKa
gl	0.108 M KCl	0.109	6.742	6.74 ± 0.06	69MKa
gl	0.254 M KCl	0.257	6.620	6.62 ± 0.06	69MKa
gl	0.815 M KCl	0.837	6.443	6.43 ± 0.06	69MKa
gl	1.963 M KCl	2.090	6.460	6.43 ± 0.10	69MKa
gl	0.04 M KCl	0.040	6.88	6.88 ± 0.06	91DDa
gl	0.16 M KCl	0.161	6.69	6.69 ± 0.06	91DDa
gl	0.36 M KCl	0.365	6.56	6.56 ± 0.06	91DDa
gl	0.64 M KCl	0.654	6.44	6.43 ± 0.06	91DDa
gl	1.00 M KCl	1.033	6.30	6.29 ± 0.10	91DDa
gl	0.1 M NaNO$_3$	0.101	6.75 ± 0.01	6.75 ± 0.05	96SSa
gl	0.1 M NaNO$_3$	0.101	6.73 ± 0.01	6.73 ± 0.05	81BKb
gl	0.20 M NaNO$_3$	0.202	6.63 ± 0.01	6.63 ± 0.05	81BKb
gl	0.70 M NaNO$_3$	0.717	6.39 ± 0.01	6.38 ± 0.05	88MFa
gl	0.1 M KNO$_3$	0.101	6.79 ± 0.01	6.79 ± 0.05	81BKb
gl	0.70 M KNO$_3$	0.722	6.55 ± 0.04	6.55 ± 0.05	88MFa
gl	0.1 M (CH$_3$)$_4$NCl		6.76	6.76 ± 0.05	79DFa
gl	1.0 M (CH$_3$)$_4$NBr		6.61 ± 0.11	6.60 ± 0.11	61ICb

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Table A4-2 (*Continued*).

| Method | Ionic medium | | $Log_{10} K$ (reported) | $Log_{10} K$ (accepted) | Ref.[2] |
	Reported[1]	Molality/ mol kg^{-1}			
$H^+ + H_2PO_4^- \rightleftharpoons H_3PO_4$					
gl	0 corr[10]		2.141 ± 0.003	2.14 ± 0.05	78MAa
gl	0 corr[11]		2.145	2.14 ± 0.05	64SSd
con	0 corr		2.128	2.13 ± 0.05	62MLa
con	0 corr		2.15	2.15 ± 0.05	61EAa
gl	0 corr[12]		2.11	2.11 ± 0.05	60GLa
emf	0 corr[13]		2.148 ± 0.005	2.15 ± 0.02	51BAb
con	0 corr (H_3PO_4)		2.126	2.13 ± 0.05	49MCb
emf	0 corr[14]		2.124 ± 0.002	2.12 ± 0.02	34NIa
emf	0 corr		2.161	2.16 ± 0.02	29BUa
gl	0.10 M NaClO$_4$	0.101	1.90	1.90 ± 0.05	76TDa
gl	1.00 M NaClO$_4$	1.051	1.70 ± 0.02	1.69 ± 0.10	91MAb
sp	1.07 M NaClO$_4$	1.129	1.721 ± 0.002	1.71 ± 0.10	57THb
gl	3.00 M NaClO$_4$	3.503	1.83 ± 0.01	1.76 ± 0.05	74CIa
emf	3.00 M NaClO$_4$	3.503	1.88 ± 0.02	1.81 ± 0.05	74HHb
gl	3.00 M NaClO$_4$	3.503	1.88 ± 0.02	1.81 ± 0.05	73HSa
gl	3.00 M NaClO$_4$	3.503	1.83 ± 0.01	1.76 ± 0.05	71PEb
gl, emf	3.00 M NaClO$_4$	3.503	1.89 ± 0.01	1.82 ± 0.05	69BSb
gl	0.15 M NaCl	0.151	1.843 ± 0.003	1.84 ± 0.06	81VSa
emf	1.00 m NaCl	1.00	1.748 ± 0.016	1.75 ± 0.06	94VRa
gl	1.00 M NaCl	1.021	1.70 ± 0.02	1.69 ± 0.08	83ISb
emf	3.00 m NaCl	3.00	1.667 ± 0.019	1.67 ± 0.06	94VRa
gl	0.50 m NaCl	0.50	1.88 ± 0.01	1.88 ± 0.06	89HFa
gl	1.0 m NaCl	1.0	1.79 ± 0.02	1.79 ± 0.06	89HFa
gl	2.0 m NaCl	2.0	1.74 ± 0.03	1.74 ± 0.06	89HFa
gl	3.0 m NaCl	3.0	1.73 ± 0.07	1.73 ± 0.06	89HFa
gl	4.0 m NaCl	4.0	1.76 ± 0.04	1.76 ± 0.06	89HFa
gl	5.0 m NaCl	5.0	1.83 ± 0.06	1.83 ± 0.06	89HFa
gl	6.0 m NaCl	6.0	1.81 ± 0.01	1.81 ± 0.06	89HFa
gl	0.04 M NaCl	0.040	1.98	1.98 ± 0.06	91DDa
gl	0.16 M NaCl	0.161	1.87	1.87 ± 0.06	91DDa
gl	0.36 M NaCl	0.363	1.80	1.80 ± 0.06	91DDa
gl	0.20 M KCl	0.202	1.86 ± 0.01	1.86 ± 0.06	96AKa
gl	0.04 M KCl	0.040	1.99	1.99 ± 0.06	91DDa
gl	0.16 M KCl	0.161	1.90	1.90 ± 0.06	91DDa
gl	0.36 M KCl	0.365	1.84	1.84 ± 0.06	91DDa
gl	0.10 M NaNO$_3$	0.101	1.80 ± 0.04	1.80 ± 0.06	96SSa
gl	0.70 M NaNO$_3$	0.717	1.81 ± 0.03	1.80 ± 0.05	88MFa
gl	1.00 M NaNO$_3$	1.045	1.763 ± 0.003	1.75 ± 0.05	88KRb
gl	0.70 M KNO$_3$	0.722	1.94 ± 0.04	1.93 ± 0.05	88MFa

[1]Ionic medium for reported values. The symbol M indicates the molarity scale: amount concentration/mol dm^{-3}. The symbol m indicates the molality scale, units mol kg^{-1}.
[2]References for rejected data: [63GSb][j], [69SHa][j], [80GGa][j], [88JVa][j], [90TTa][j], [91DDa][j] (K_2), [58MAa][d], [56BAc][d], [61ICb][j], [86GTa][g], [65HSb][j], [85LLa][j], [92TSc][j], [90DNb][j], [61DKb][a].
[3]Medium: Na$_2$HPO$_4$ + NaOH.
[4]Medium: Na$_2$HPO$_4$ + Na$_3$PO$_4$.
[5]Medium: tpaH$_2$PO$_4$ + tpaOH + tpaBr.
[6]Medium: KH$_2$PO$_4$ + KNaHPO$_4$ + NaCl.

Table A4-2 (*Continued*).

[7]Medium: KH_2PO_4 + Na_2HPO_4 + NaCl.
[8]Medium: $Na(K)H_2PO_4$ + Na_2HPO_4 + NaCl.
[9]Medium: NaH_2PO_4 + Na_2HPO_4 + NaCl.
[10]Medium: HCl + KH_2PO_4.
[11]Medium: H_3PO_4 + NaOH + NaCl.
[12]Medium: H_3PO_4 + NaOH.
[13]Medium: HCl + KH_2PO_4 and HCOOH + KH_2PO_4 + KCl.

Table A4-3 Results of the weighted linear regression (SIT analysis) of the selected values for phosphate protonation in NaCl and KCl media. Values refer to 298.15 K, 1 bar, and I_m = 0 mol kg^{-1}. Parameter a_jB in eq. 1 variable.

Medium	NaCl	KCl
$Log_{10} K_1°$	12.338 ± 0.028	12.344 ± 0.032
$\Delta\varepsilon$ (kg mol^{-1})	–0.078 ± 0.019	–0.511 ± 0.240
a_jB	1.204 ± 0.090	1.024 ± 0.307
$Log_{10} K_2°$	7.200 ± 0.008	7.201 ± 0.008
$\Delta\varepsilon$ (kg mol^{-1})	–0.061 ± 0.016	–0.099 ± 0.089
a_jB	1.160 ± 0.083	1.239 ± 0.220
$Log_{10} K_3°$	2.141 ± 0.010	2.141 ± 0.010
$\Delta\varepsilon$ (kg mol^{-1})	–0.043 ± 0.017	–0.098 ± 0.872
a_jB	1.352 ± 0.235	1.349 ± 2.500

a

$\log_{10} K_1 + 2.044 \, I^{0.5}/(1 + 1.5 \, I^{0.5}) = 10.248 + 0.078 \, I$

$\log_{10} K_1^\circ = 10.248 \pm 0.002$
$\Delta \varepsilon = -0.078 \pm 0.001$

Ionic strength, I_m/mol kg^{-1}

b

$\log_{10} K_1 + 2.044 \, I^{0.5}/(1 + 1.117 \, I^{0.5}) = 10.336 + 0.116 \, I$

$\log_{10} K_1^\circ = 10.336 \pm 0.005$
$aB = 1.117 \pm 0.015$
$\Delta \varepsilon = -0.116 \pm 0.002$

Ionic strength, I_m/mol kg^{-1}
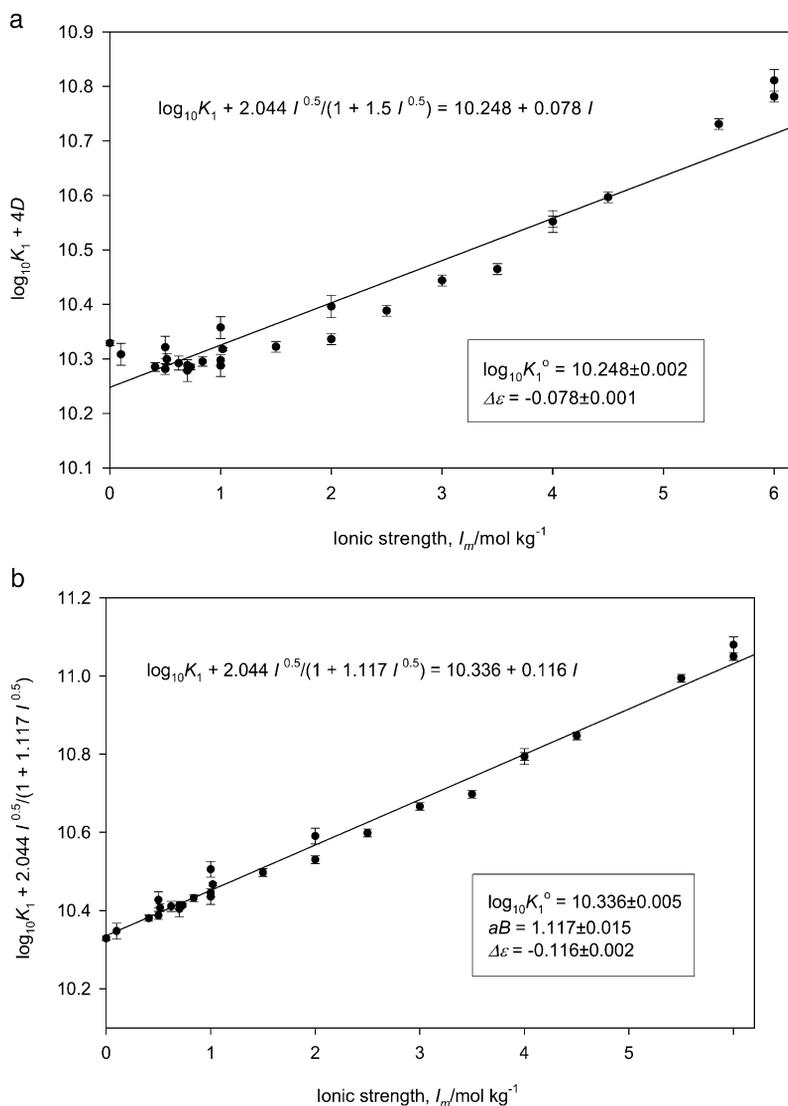
Fig. A4-1 Extrapolation to $I_m = 0$ mol kg^{-1} of $\log_{10} K_1 - \Delta(z^2)D$ for reaction 22, using the selected data for NaCl media, 25 °C (Table A4-1a). The regression uses eq. 3 with $a(H_2O)$ equal to unity. Figure (a) assumes $a_j B = 1.5$ kg$^{1/2}$ mol$^{-1/2}$. Figure (b) treats $a_j B$ in the term D (eq. 1) as an empirical parameter, which refines to 1.117 kg$^{1/2}$ mol$^{-1/2}$.

a

$$\log_{10}K_2 + 1.022\, I^{0.5}/(1 + 1.5\, I^{0.5}) = 6.317 + 0.072\, I$$

$\log_{10}K_2^{\circ}= 6.317 \pm 0.001$
$\Delta\varepsilon = -0.072 \pm 0.001$

b

$$\log_{10}K_2 + 1.022\, I^{0.5}/(1 + 1.136\, I^{0.5}) = 6.355 + 0.092\, I$$

$\log_{10}K_2^{\circ} = 6.355 \pm 0.003$
$aB = 1.136 \pm 0.022$
$\Delta\varepsilon = -0.092 \pm 0.002$
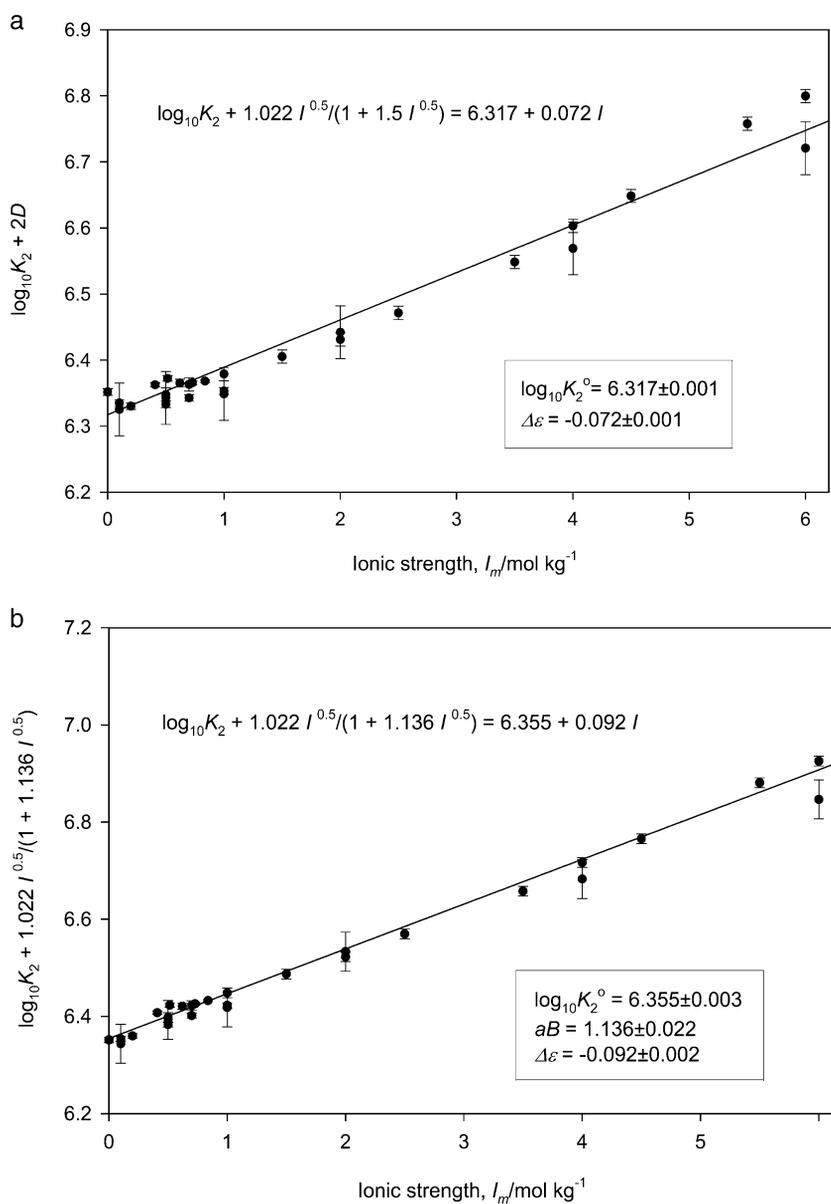
Fig. A4-2 Extrapolation to $I_m = 0$ mol kg^{-1} of $\log_{10} K_2 - \Delta(z^2)D$ for reaction 23, using the selected data for NaCl media, 25 °C (Table A4-1a). The regression uses eq. 3 with $a(H_2O)$ equal to unity. Figure (a) assumes $a_iB = 1.5$ kg$^{1/2}$ mol$^{-1/2}$. Figure (b) treats a_jB in the term D (eq. 1) as an empirical parameter, which refines to 1.136 kg$^{1/2}$ mol$^{-1/2}$.

a

$$\log_{10}K_1 + 3.066\, I^{0.5}/(1 + 1.5^{0.5}) = 12.277 + 0.029\, I$$

$\log_{10}K_1 + 6D$

$\log_{10}K_1^{\circ} = 12.277\pm0.019$
$\Delta\varepsilon = -0.029\pm0.008$

Ionic strength, I_m/mol kg^{-1}

b

$$\log_{10}K_1 + 3.066\, I^{0.5}/(1 + 1.204\, I^{0.5}) = 12.338 + 0.078\, I$$

$\log_{10}K_1 + 3.066\, I^{0.5}/(1 + 1.204\, I^{0.5})$

$\log_{10}K_1^{\circ} = 12.338\pm0.028$
$aB = 1.204\pm0.090$
$\Delta\varepsilon = -0.078\pm0.019$

Ionic strength, I_m/mol kg^{-1}
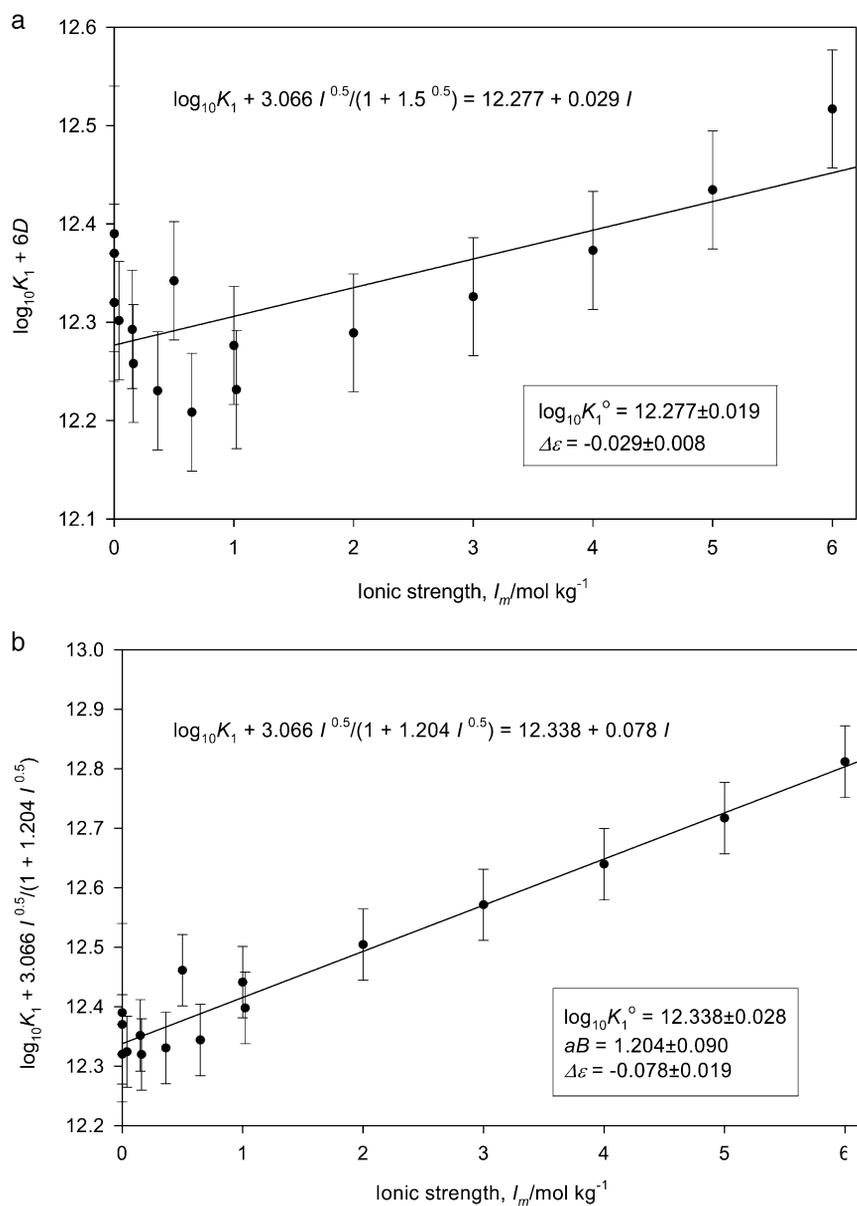
Fig. A4-3 Extrapolation to $I_m = 0$ mol kg^{-1} of $\log_{10} K_1 - \Delta(z^2)D$ for reaction 24, using the selected data for NaCl media, 25 °C (Table A4-2). The regression uses eq. 3 with $a(H_2O)$ equal to unity. Figure (a) assumes $a_jB = 1.5$ kg$^{1/2}$ mol$^{-1/2}$. Figure (b) treats a_jB in the term D (eq. 1) as an empirical parameter, which refines to 1.204 kg$^{1/2}$ mol$^{-1/2}$.
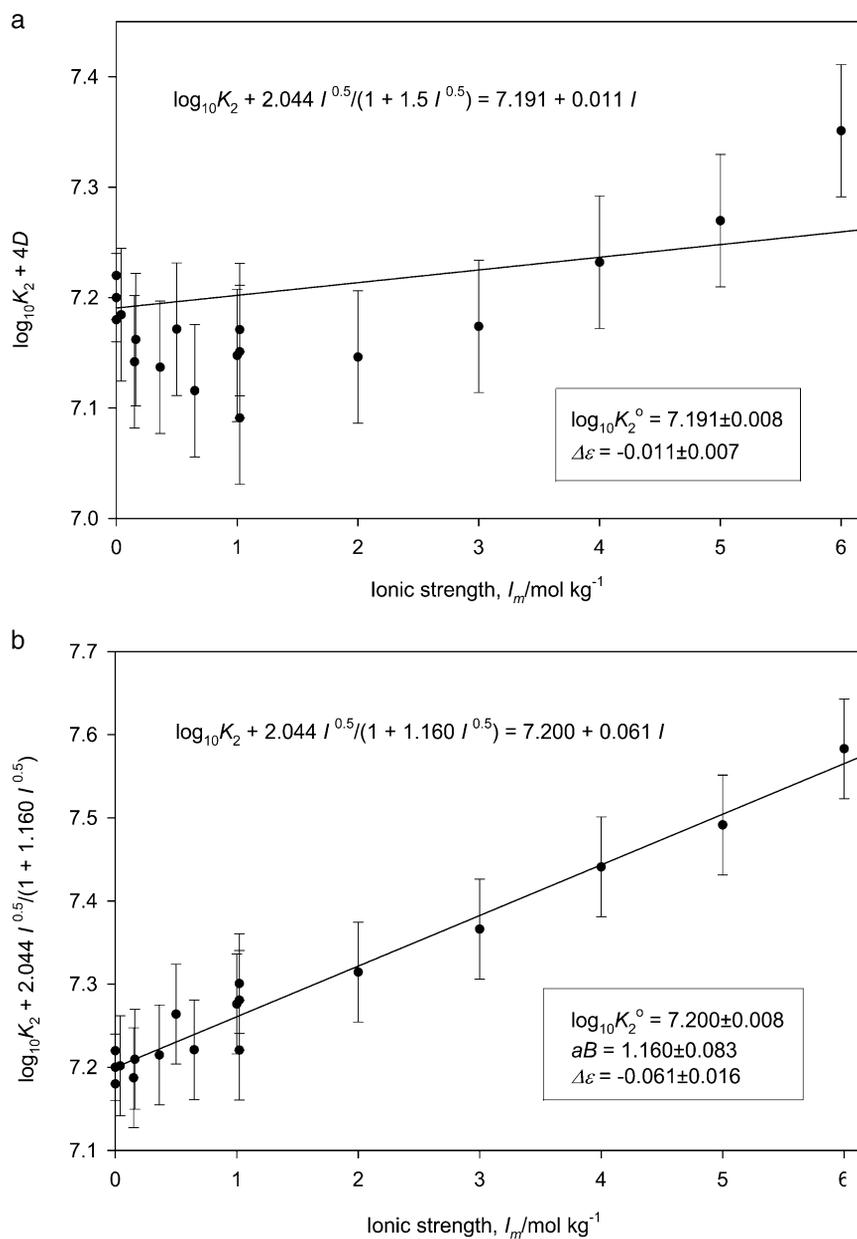
Fig. A4-4 Extrapolation to $I_m = 0$ mol kg^{-1} of $\log_{10} K_2 - \Delta(z^2)D$ for reaction 25, using the selected data for NaCl media, 25 °C (Table A4-2). The regression uses eq. 3 with $a(H_2O)$ equal to unity. Figure (a) assumes $a_jB = 1.5$ kg$^{1/2}$ mol$^{-1/2}$. Figure (b) treats a_jB in the term D (eq. 1) as an empirical parameter, which refines to 1.160 kg$^{1/2}$ mol$^{-1/2}$.
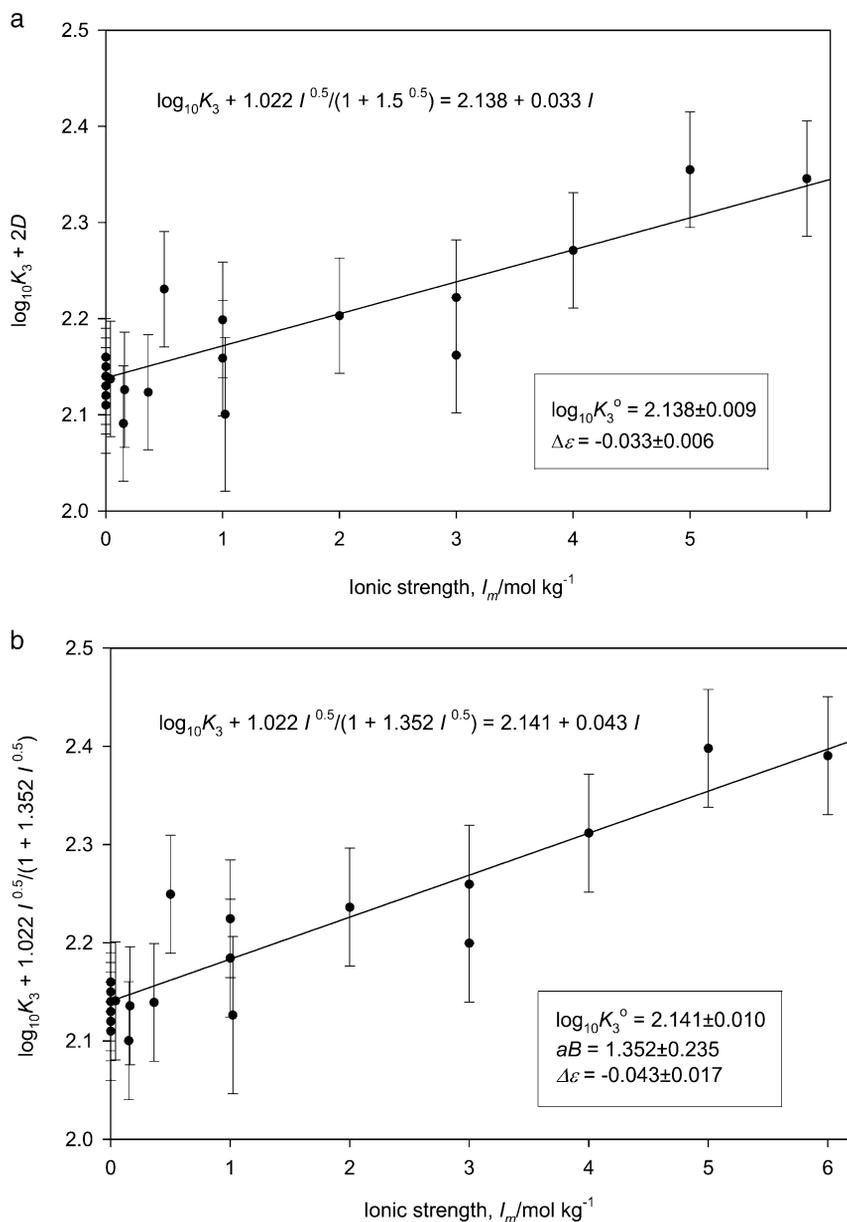
Fig. A4-5 Extrapolation to $I_m = 0$ mol kg^{-1} of $\log_{10} K_1$ for reaction (26) using the selected data for NaCl media, 25 °C (Table A4-2). The regression uses eq. 3 with $a(H_2O)$ equal to unity. Figure (a) assumes $a_jB = 1.5$ kg$^{1/2}$ mol$^{-1/2}$. Figure (b) treats a_jB in the term D (eq. 1) as an empirical parameter, which refines to 1.352 kg$^{1/2}$ mol$^{-1/2}$.