

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

ANALYTICAL CHEMISTRY DIVISION*

CHEMICAL SPECIATION OF ENVIRONMENTALLY SIGNIFICANT METALS WITH INORGANIC LIGANDS

PART 2: THE Cu^{2+} - OH^- , Cl^- , CO_3^{2-} , SO_4^{2-} , AND PO_4^{3-} SYSTEMS

(IUPAC Technical Report)

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

(IUPAC Technical Report)

Abstract: Complex formation between Cu^{II} and the common environmental ligands Cl^- , OH^- , CO_3^{2-} , SO_4^{2-} , and PO_4^{3-} can have a significant effect on Cu^{II} speciation in natural waters with low concentrations of organic matter. Copper(II) complexes are labile, so the Cu^{II} distribution amongst these inorganic ligands can be estimated by numerical modeling if reliable values for the relevant stability (formation) constants are available. This paper provides a critical review of such constants and related thermodynamic data. It recommends values of $\log_{10} \beta_{p,q,r}^\circ$ valid at $I_m = 0 \text{ mol kg}^{-1}$ and 25°C (298.15 K), along with the equations and specific ion interaction coefficients required to calculate $\log_{10} \beta_{p,q,r}$ values at higher ionic strengths. Some values for reaction enthalpies, $\Delta_r H_m$, are also reported where available.

In weakly acidic fresh water systems, in the absence of organic ligands, Cu^{II} speciation is dominated by the species $\text{Cu}^{2+}(\text{aq})$, with $\text{CuSO}_4(\text{aq})$ as a minor species. In seawater, it is dominated by $\text{CuCO}_3(\text{aq})$, with $\text{Cu}(\text{OH})^+$, $\text{Cu}^{2+}(\text{aq})$, CuCl^+ , $\text{Cu}(\text{CO}_3)\text{OH}^-$, $\text{Cu}(\text{OH})_2(\text{aq})$, and $\text{Cu}(\text{CO}_3)_2^{2-}$ as minor species. In weakly acidic saline systems, it is dominated by $\text{Cu}^{2+}(\text{aq})$ and CuCl^+ , with $\text{CuSO}_4(\text{aq})$ and $\text{CuCl}_2(\text{aq})$ as minor species.

Keywords: chemical speciation; copper; environmental; ligands; stability constants; IUPAC Analytical Chemistry Division.

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1. INTRODUCTION

This review is the second in a series relevant to the speciation of metal ions in environmental waters at low to moderate ionic strengths. It provides access to the best available stability constants for chemical speciation modeling of reactions of Cu^{2+} with the major environmental inorganic ligands: Cl^- , OH^- , CO_3^{2-} , SO_4^{2-} , and PO_4^{3-} . The first in this series was a review of Hg^{2+} complexation reactions with these ligands, and the protonation* reactions of CO_3^{2-} and PO_4^{3-} [2005PBa]. Future reviews will focus on equilibria involving the same ligands with Pb^{2+} , Cd^{2+} , and Zn^{2+} .

The first review [2005PBa] discussed the relevance of chemical speciation modeling to our understanding of the equilibrium reactions of labile species in aqueous systems. It noted the need for reliable

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

stability (formation) constants that are applicable at the ionic strength and temperature of the medium studied. The reader is referred to that document [2005PBA] for (i) the nomenclature used to express stability constants $\beta_{p,q,r}$, $^*\beta_{p,q,r}^\circ$, K_n , and *K_n (Appendix 1A); (ii) the criteria used to determine whether published data ($\beta_{p,q,r}$ and $\Delta_r H_m^\circ$) are “accepted” for inclusion in the critical evaluation or “rejected”; (iii) the principles of the specific ion interaction theory (SIT) [97GRE]; and (iv) the application of SIT functions [97GRE] to effect regression of “accepted” data at finite ionic strengths to obtain values at $I_m = 0 \text{ mol kg}^{-1}$ (infinite dilution). The primary source of data is the IUPAC Stability Constants Database, *SC-Database* [2005PET].

For each Cu^{2+} –ligand combination, the present review will

- identify the most reliable publications and stability constants;
- identify (and reject) unreliable stability constants;
- establish correlations among the accepted data on the basis of their ionic strength dependence, using the SIT functions;
- establish recommended values of $\beta_{p,q,r}^\circ$ and K_{s0}° at 25 °C (298.15 K) and $I_m = 0 \text{ mol kg}^{-1}$;
- identify the most reliable reaction enthalpy values $\Delta_r H_m^\circ$ for the equilibrium reactions;
- provide the user with the numerical relationships that can be used to calculate values of $\beta_{p,q,r}$ at $I_m > 0 \text{ mol kg}^{-1}$;
- provide examples of SIT plots for $\beta_{p,q,r}$ extrapolations;
- provide examples of distribution diagrams for binary and multicomponent systems; and
- provide values of $\beta_{p,q,r}$ applicable to calculations in fresh water and saline systems.

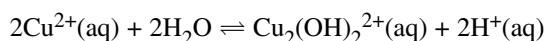
Literature values for stability constants [2005PET], or formation constants [97INC], of metal–ligand complexes are reported for ionic media of nominally fixed and (usually comparatively) high ionic strength. The high ionic strength is normally achieved by addition in large excess of a supposedly non-complexing 1:1 electrolyte such as NaClO_4 . The reported constants, designated by $\beta_{p,q,r}$ or K_n , are strictly valid only at the specified ionic strength in that medium. Most frequently, such constants are reported on the amount concentration (mol solute/dm^3 solution) scale as equilibrium concentration products (or quotients). These concentration products for a specified ionic strength, I_c , are related to the standard (state) equilibrium constants, $\beta_{p,q,r}^\circ$ and K_n° , the equilibrium activity products, by $\beta_{p,q,r} = \lim \beta_{p,q,r}(I_c \rightarrow 0)$ and $K_n = \lim K_n(I_c \rightarrow 0)$ [2005PBA].

The stability constants are as well defined thermodynamically as those referring to pure water (the equilibrium activity products) [97INC].

In this work, the “accepted” values for stability constants $\beta_{p,q,r}$ and K_n were initially converted to the molality (mol kg^{-1}) scale. The limiting values at $I_m = 0 \text{ mol kg}^{-1}$ ($\beta_{p,q,r}^\circ$ 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 amount concentration or molality scales) while the equilibrium activity products $\beta_{p,q,r}^\circ$ and K_n° are referred to as the standard (state) equilibrium constants; see [2005PBA] Appendix 1A.

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



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

2. SUMMARY OF RECOMMENDED VALUES

Tables 1 to 5 provide a summary of the standard equilibrium constants, reaction ion interaction coefficients, $\Delta\epsilon$, and reaction enthalpies (where available) for the formation of Cu^{2+} complexes with the selected inorganic anions. These were derived from a critical evaluation of the available literature data [2005PET], with a focus particularly on values for 25 °C and perchlorate media, and the application of SIT functions in regression analyses of the accepted data. The reader is referred to [2005PBa] for definition of the terms “Recommended” (R) and “Provisional” (P) used in these Tables. The $\log_{10} \beta_{p,q,r}^\circ$, $\log_{10} K_n^\circ$, and $\log_{10} {}^* \beta_{p,q,r}^\circ$ values are for 298.15 K, 1 bar (10^5 Pa), and infinite dilution ($I_m = 0$ mol kg^{-1}).

Table 1 Recommended values for the Cu^{2+} – OH^- system at 298.15 K, 1 bar, and $I = 0$ mol kg^{-1} .

R = Recommended; P = Provisional. $\Delta\epsilon$ values for NaClO_4 media. The uncertainties represent two standard deviations of the regression intercept ($\log_{10} K^\circ$) and of the slope ($\Delta\epsilon$).

Reaction	Constant	Evaluation
$\text{Cu}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{CuOH}^+ + \text{H}^+$	$\log_{10} {}^*K_1^\circ = -7.95 \pm 0.16$ $\Delta\epsilon = -(0.33 \pm 0.08)$ kg mol $^{-1}$	R
$\text{Cu}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Cu}(\text{OH})_2(\text{aq}) + 2\text{H}^+$	$\log_{10} {}^*\beta_2^\circ = -16.2 \pm 0.2$ $\Delta\epsilon = (0.14 \pm 0.36)$ kg mol $^{-1}$	R
$\text{Cu}^{2+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Cu}(\text{OH})_3^- + 3\text{H}^+$	$\log_{10} {}^*\beta_3^\circ = -26.60 \pm 0.09$ $\Delta\epsilon^1 = 0.50 \pm 0.06$ kg mol $^{-1}$	R
$\text{Cu}^{2+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Cu}(\text{OH})_4^{2-} + 4\text{H}^+$	$\log_{10} {}^*\beta_4^\circ = -39.74 \pm 0.18$ $\Delta\epsilon^1 = 0.43 \pm 0.05$ kg mol $^{-1}$	P
$2\text{Cu}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{Cu}_2\text{OH}^{3+} + \text{H}^+$	$\log_{10} {}^*\beta_{2,1}^\circ = -6.40 \pm 0.12$ $\Delta\epsilon = (0.04 \pm 0.04)$ kg mol $^{-1}$	P
$2\text{Cu}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Cu}_2(\text{OH})_2^{2+} + 2\text{H}^+$	$\log_{10} {}^*\beta_{2,2}^\circ = -10.43 \pm 0.07$ $\Delta\epsilon = -(0.09 \pm 0.04)$ kg mol $^{-1}$	R
$3\text{Cu}^{2+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Cu}_3(\text{OH})_4^{2+} + 4\text{H}^+$	$\log_{10} {}^*\beta_{3,4}^\circ = -21.1 \pm 0.2$	P
$\text{CuO}(\text{s}) + 2\text{H}^+ \rightleftharpoons \text{Cu}^{2+} + \text{H}_2\text{O}$	$\log_{10} {}^*K_{s0}^\circ = 7.64 \pm 0.06$ $\Delta\epsilon = (0.04 \pm 0.06)$ kg mol $^{-1}$	R
$\text{Cu}(\text{OH})_2(\text{s}) + 2\text{H}^+ \rightleftharpoons \text{Cu}^{2+} + 2\text{H}_2\text{O}$	$\log_{10} {}^*K_{s0}^\circ = 8.67 \pm 0.05$ $\Delta\epsilon^2 = (0.04 \pm 0.06)$ kg mol $^{-1}$	R
$\text{CuO}(\text{s}) + \text{H}_2\text{O} \rightleftharpoons \text{Cu}^{2+} + 2\text{OH}^-$	$\log_{10} K_{s0}^\circ = -20.36 \pm 0.06$	R
$\text{Cu}(\text{OH})_2(\text{s}) \rightleftharpoons \text{Cu}^{2+} + 2\text{OH}^-$	$\log_{10} K_{s0}^\circ = -19.33 \pm 0.05$	R

¹From [97PLY].

²Assumed value for $\Delta\epsilon$; see Section 7.1.

Table 2 Recommended values for the Cu^{2+} – Cl^- system at 298.15 K and $I_m = 0$ mol kg^{-1} .

R = Recommended, P = Provisional. $\Delta\epsilon$ values for ClO_4^- medium.

Reaction	Constant	Evaluation
$\text{Cu}^{2+} + \text{Cl}^- \rightleftharpoons \text{CuCl}^+$	$\log_{10} K_1^\circ = 0.83 \pm 0.09$ $\Delta\epsilon = -(0.05 \pm 0.02)$ kg mol $^{-1}$	R
$\text{Cu}^{2+} + 2\text{Cl}^- \rightleftharpoons \text{CuCl}_2(\text{aq})$	$\log_{10} \beta_2^\circ = 0.6 \pm 0.3$ $\Delta\epsilon = -(0.10 \pm 0.06)$ kg mol $^{-1}$	P

Table 3 Recommended values for the $\text{Cu}^{2+}\text{-H}^+\text{-CO}_3^{2-}$ system at 298.15 K, 1 bar, and $I_m = 0 \text{ mol kg}^{-1}$. R = Recommended, P = Provisional. $\Delta\epsilon$ values for ClO_4^- medium.

Reaction	Constant	Evaluation
$\text{Cu}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{CuCO}_3(\text{aq})$	$\log_{10} K_1^\circ = 6.75 \pm 0.03$ $\Delta\epsilon = -(0.18 \pm 0.04) \text{ kg mol}^{-1}$	R
$\text{Cu}^{2+} + 2\text{CO}_3^{2-} \rightleftharpoons \text{Cu}(\text{CO}_3)_2^{2-}$	$\log_{10} \beta_2^\circ = 10.3 \pm 0.1$ $\Delta\epsilon = (0.3 \pm 0.2) \text{ kg mol}^{-1}$	R
$\text{Cu}^{2+} + \text{HCO}_3^- \rightleftharpoons \text{CuHCO}_3^+$	$\log_{10} K^\circ = 1.84 \pm 0.10$ $\Delta\epsilon = (0.14 \pm 0.15) \text{ kg mol}^{-1}$	R
$\text{Cu}^{2+} + \text{HCO}_3^- \rightleftharpoons \text{CuCO}_3 + \text{H}^+$	$\log_{10} K^\circ = -3.56 \pm 0.03$ $\Delta\epsilon = -(0.19 \pm 0.04) \text{ kg mol}^{-1}$	R
$\text{Cu}^{2+} + 2\text{HCO}_3^- \rightleftharpoons \text{Cu}(\text{CO}_3)_2^{2-} + 2\text{H}^+$	$\log_{10} K^\circ = -10.3 \pm 0.1$ $\Delta\epsilon = (0.3 \pm 0.2) \text{ kg mol}^{-1}$	R
$\text{Cu}_2\text{CO}_3(\text{OH})_2(\text{s}) \rightleftharpoons 2\text{Cu}^{2+} + \text{CO}_3^{2-} + 2\text{OH}^-$	$\log_{10} K_{s0}^\circ = -33.16 \pm 0.08$	P
$\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2(\text{s}) \rightleftharpoons 3\text{Cu}^{2+} + 2\text{CO}_3^{2-} + 2\text{OH}^-$	$\log_{10} K_{s0}^\circ = -44.9 \pm 0.2$	P

Table 4 Recommended values for the $\text{Cu}^{2+}\text{-SO}_4^{2-}$ system at 298.15 K and $I_m = 0 \text{ mol kg}^{-1}$. R = Recommended, P = Provisional.

Reaction	Constant	Evaluation
$\text{Cu}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{CuSO}_4(\text{aq})$	$\log_{10} K_1^\circ = 2.35 \pm 0.05$	R
	$\Delta\epsilon = -(0.16 \pm 0.07) \text{ kg mol}^{-1}$	P ¹
	$\Delta\epsilon = -(0.05 \pm 0.02) \text{ kg mol}^{-1}$	P ²
	$\Delta_r H_m^\circ = 7.3 \pm 1.5 \text{ kJ mol}^{-1}$	R
	$\Delta_r S_m^\circ = 68.4 \pm 0.7 \text{ J K}^{-1} \text{ mol}^{-1}$	R

¹Calculated for NaClO_4 medium and $a_j B = 1.15$; see Section 6.4.1.

²Calculated for NaClO_4 medium, $a_j B = 1.50$ and $\log_{10} K_1^\circ$ fixed at 2.35 ± 0.05 ; see Section 6.4.1.

Table 5 Recommended values for the $\text{Cu}^{2+}\text{-H}^+\text{-PO}_4^{3-}$ system at 298.15 K and $I_m = 0.101 \text{ mol kg}^{-1} \text{ NaClO}_4$. R = Recommended, P = Provisional.

Reaction	Constant	Evaluation
$\text{Cu}^{2+} + \text{HPO}_4^{2-} \rightleftharpoons \text{CuHPO}_4(\text{aq})$	$\log_{10} K = 3.25 \pm 0.2$	R ¹
$\text{Cu}^{2+} + \text{H}^+ + \text{PO}_4^{3-} \rightleftharpoons \text{CuHPO}_4(\text{aq})$	$\log_{10} \beta = 14.93 \pm 0.2$	P ^{2,3}

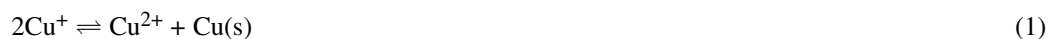
¹Provisional value calculated for $I = 0 \text{ mol kg}^{-1}$, $\log_{10} K^\circ = 4.15 \pm 0.3$.

²Provisional assignment, based on unavailability of phosphate protonation constant in $0.101 \text{ mol kg}^{-1} \text{ NaClO}_4$.

³Provisional value calculated for $I = 0 \text{ mol kg}^{-1}$ is $\log_{10} \beta^\circ = 16.49 \pm 0.3$.

3. Cu^{II} SOLUTION CHEMISTRY

In aqueous solution, copper has two common oxidation states, Cu^I and Cu^{II}. The disproportionation reaction 1,



has an equilibrium constant $\log_{10} K \approx 6$ [52LAA], and thus Cu^{II} is the predominant oxidation state in aqueous solution. However, in the presence of particular types of complexing agents, mostly those that

have “soft”, π -acceptor donor atoms [2005PET], Cu^{I} may become dominant. Other oxidation states of Cu are also known [88COT] but are not stable in aqueous solution.

The hydrolysis reactions of Cu^{2+} are less pronounced than those of Hg^{2+} (e.g., $\log_{10} {}^*K_1^\circ$ for Cu^{2+}) is -7.95 (cf. Hg^{2+} -3.40 [2005PBa]) and thus have a smaller influence on its aqueous speciation. Like Hg^{II} , Cu^{II} also shows a propensity to form polynuclear hydroxido complexes: $\text{Cu}_2(\text{OH})_2^{2+}$ and, to a lesser extent, $\text{Cu}_2(\text{OH})_3^{3+}$ and $\text{Cu}_3(\text{OH})_4^{2+}$. Due to the formation of these polynuclear species, the onset of Cu^{II} hydrolysis occurs at lower pH as $[\text{Cu}^{\text{II}}]_{\text{T}}$ increases (where here, and throughout this review, the subscript T denotes the total concentration). The Cu^{II} hydroxide precipitates that form at higher pH are weakly amphoteric and thus dissolve in strongly alkaline solution by formation of species such as $\text{Cu}(\text{OH})_3^-$ and $\text{Cu}(\text{OH})_4^{2-}$.

4. DATA SELECTION AND EVALUATION

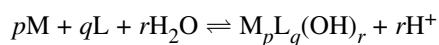
The data that meet our selection criteria for use in the SIT regression analyses for Cu^{2+} complexes are recorded in Tables A2-1 through A2-11 in Appendix 2. The criteria used for the acceptance of literature data as “reliable” (designated “reported” in the Tables, and included in the regression analysis) and those for the rejection of data (indicated by a reference superscript in the Table footnotes) are summarized in Appendix 1A. The abbreviations used in these Tables to describe the experimental methods are: **emf**: measurement of cell potentials (emf) using a redox electrode; **sol**: solubility determination; **gl**: pH measurement by glass electrode; **con**: conductivity; **cry**: cryoscopy; **dis**: distribution between partially miscible solvents; **ise**: measurement of the cell potentials using an ion selective electrode; **cal**: calorimetry; **refr**: refractometry; **vlt**: voltammetry (polarography); **sp**: (UV–vis) spectrometry; **K(T)**: variation of $\log_{10} K$ with temperature.

The column headed $\log_{10} K$ (reported) contains the “accepted” stability constant data, on the molality (mol kg^{-1}) or amount concentration (mol dm^{-3}) scales, as published. The column headed $\log_{10} K$ (accepted) contains the same data converted to the molality scale (to facilitate SIT analysis) and indicates our assigned uncertainty [2005PBa].

5. METHODS FOR NUMERICAL EXTRAPOLATION OF DATA TO $I_m = 0 \text{ mol kg}^{-1}$

An objective in this work was to obtain the most reliable values for $\beta_{p,q,r}$ at $I_m = 0 \text{ mol kg}^{-1}$. This was achieved by use of accepted data over a wide range of ionic strengths and by application of the Brønsted–Guggenheim–Scatchard model (named the specific ion interaction theory, or SIT). This model accounts for the ionic strength-dependent short-range, weak, non-electrostatic interactions between the reactant species and the electrolyte anions or cations. The associated regression analysis of $\log_{10} \beta_{p,q,r}$ against I_m yields $\log_{10} \beta_{p,q,r}^\circ$ (the standard equilibrium constant) as the intercept at $I_m = 0 \text{ mol kg}^{-1}$ and the specific ion interaction coefficient for the equilibrium, $-\Delta\epsilon(i,k)$, as the slope.

For the general reaction (omitting most charges for simplicity)



the stability constant $\beta_{p,q,r}$ determined for the $\text{M}_p\text{L}_q(\text{OH})_r$ species in an ionic medium (typically containing a 1:1 electrolyte NX of ionic strength I_m at concentrations well in excess of those of the interacting species) is related to the standard equilibrium constant $\beta_{p,q,r}^\circ$, by

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

where $\gamma_m(p,q,r)$ is the activity coefficient (on the molality scale, subscript m) of the species $\text{M}_p\text{L}_q(\text{OH})_r$ and $\gamma_m(i)$ is given by [97GRE]

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

$\varepsilon(i,k)$ is the aqueous species interaction coefficient for short-range interactions between ions i and k .

Substitution of eq. 3 into eq. 2, and for conditions such that $I_m \approx m_k$, gives

$$\log_{10} \beta_{p,q,r} - \Delta z^2 D - r \log_{10} a(\text{H}_2\text{O}) = \log_{10} \beta_{p,q,r}^\circ - \Delta \varepsilon I_m \quad (4)$$

where $\Delta z^2 = (pz_M + qz_L - r)^2 + r - p(z_M)^2 - q(z_L)^2$ and $\Delta \varepsilon = \varepsilon(\text{complex}, \text{N}^+ \text{ or } \text{X}^-) + r\varepsilon(\text{H}^+, \text{X}^-) - p\varepsilon(\text{M}^+, \text{X}^-) - q\varepsilon(\text{L}^-, \text{N}^+)$.

In this review, the term $a_j B$ is set at $1.5 \text{ kg}^{1/2} \text{ mol}^{-1/2}$, the value found by Scatchard to minimize the ionic strength dependence of derived $\varepsilon(i,k)$ values [76SCA]. For a 1:1 electrolyte, the term $\log_{10} a(\text{H}_2\text{O})$ can be calculated from the solution osmotic coefficient, φ_m [59ROB]. For NaClO_4 , the medium most frequently used in this review, the relationship $\log_{10} a(\text{H}_2\text{O}) = -(0.01378 \pm 0.00003)(I_m/\text{mol kg}^{-1})$ pertains at 25°C (298.15 K) and $I_m = 0$ to 3.5 mol kg^{-1} [2005PBa]. Values for other media can be calculated from data given in [59ROB].

The application of SIT to the selected literature values involves graphical extrapolation of $\log_{10} \beta_{p,q,r} - \Delta z^2 D - r \log_{10} a(\text{H}_2\text{O})$ to $m_k = 0$ (or $I_m = 0 \text{ mol kg}^{-1}$ for a system with a large excess of 1:1 electrolyte), using eq. 4. Regression analyses using SIT are represented graphically and are recorded in Appendix 3. For each datum, the assigned uncertainty (Tables A2-1 to A2-11) reflects our estimation of combined experimental, systematic, and numerical uncertainties (see Section 5.2 in [2005PBa]) and is used to weight each value in the SIT regression analysis. Where appropriate, an initial SIT analysis was used to identify outliers based on their deviation from the calculated confidence limits. For a more detailed description, see Section 5.2 in [2005PBa]. The reported uncertainties on $\log_{10} \beta_{p,q,r}$ ($\log_{10} K_n$) and $\Delta \varepsilon$ represent two standard deviations of the regression intercept and slope, respectively.

In view of the rather limited data sets available for some equilibrium reactions studied in NaClO_4 , data for other media have sometimes been included in the regression analyses, where necessary.

6. EVALUATION OF EQUILIBRIUM CONSTANTS (HOMOGENEOUS REACTIONS)

6.1 The Cu^{2+} - OH^- system

The speciation diagram for the Cu^{2+} - OH^- system, based on our recommended values recorded in Table 1 for stability constants at $I_m = 0 \text{ mol kg}^{-1}$, is shown in Fig. 1. Results outside the $-\log_{10} [\text{H}^+]$ range 2 to 12 should be viewed with caution as activity coefficients deviate significantly from 1.0.

The *SC-Database* [2005PET] contains 87 investigations that report data for the hydrolysis reactions of Cu^{2+} , but the values for the formation constants are strongly divergent. For example, at low ionic strengths the values reported for $\log_{10} {}^*K_1$ vary from -6.8 (30°C , 0.10 mol dm^{-3} KCl) [52CCa, 77VNa] to -8.0 (18°C) [43PEa], or even < -8 (25°C , 0.05 mol dm^{-3} KCl) [60PEc, 80PKb]. Proposed speciation schemes even do not agree about the number and stoichiometry of the mono- and/or polynuclear complexes formed. Indeed, the identification and quantification of the mononuclear $\text{Cu}(\text{OH})_n^{(2-n)+}$ complexes ($n = 1, 2$) is difficult due to the formation of di- and trinuclear complexes even at quite modest values of $[\text{Cu}^{\text{II}}]_{\text{T}}$. Furthermore, the formation of (possibly metastable) “ Cu^{II} -hydroxide” colloidal suspensions and/or precipitates in slightly hydrolyzed solutions adds complexity in terms of measurement accuracy and data interpretation.

The determination of stability constants for the mononuclear complexes $\text{Cu}(\text{OH})_3^-$ and $\text{Cu}(\text{OH})_4^{2-}$ is currently based on solubility measurements in alkaline solutions. On the other hand, the stabilities of CuOH^+ and $\text{Cu}(\text{OH})_2(\text{aq})$, as well as the composition and stabilities of the polynuclear species, have mostly been determined from potentiometric titrations utilizing a combination of glass and copper ion-selective electrode (ise) measurements.

Plyasunova et al. [97PLY] recently reported a critical evaluation of Cu^{II} hydrolysis equilibria. However, in their SIT analysis, no corrections were introduced for changes in the activity of water. Subsequent to this, De Robertis et al. [97RSb] published a comprehensive study of the Cu^{II} hydrolysis

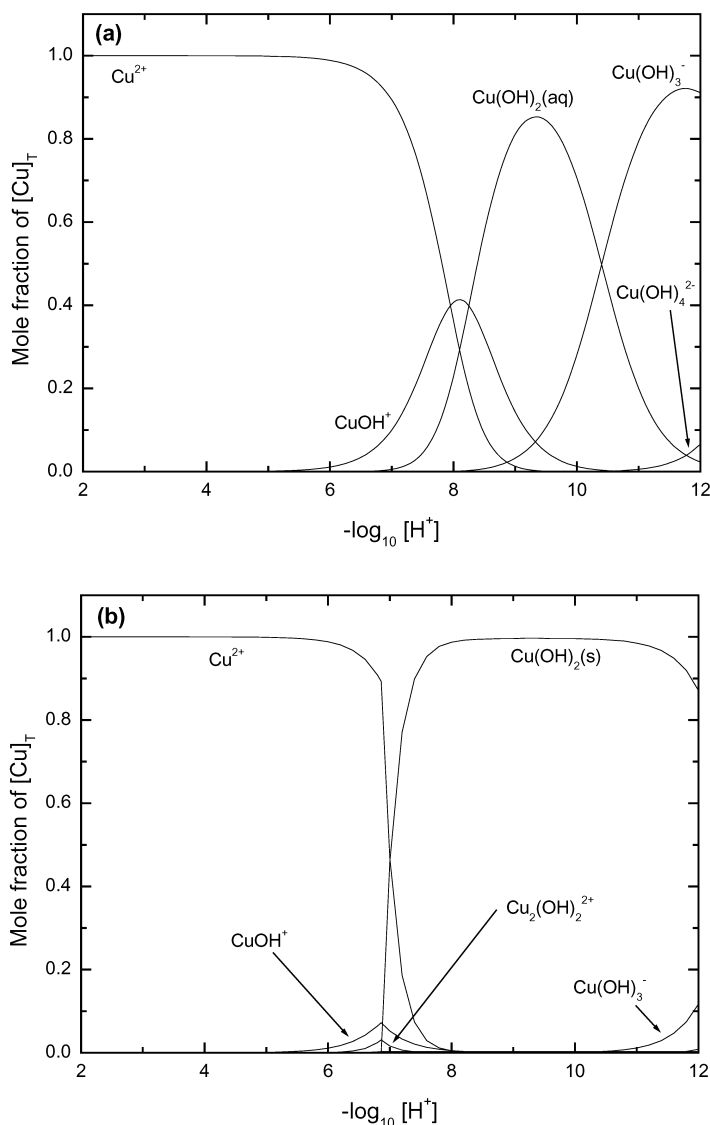


Fig. 1 Speciation diagram for the binary Cu^{2+} -hydroxide system at 25 °C as obtained from the Recommended stability constants at $I_m = 0 \text{ mol kg}^{-1}$ (Table 1). Results outside the $-\log [\text{H}^+]$ range of 2–12 should be viewed with caution as activity coefficients deviate from 1.0. No corrections were made for changes in formation constants at high pH ($I_m > 0 \text{ mol kg}^{-1}$). (a) $[\text{Cu}]_{\text{T}} = 10^{-9} \text{ mol dm}^{-3}$. If the total Cu^{II} concentration is less than ca. $10^{-8.35} \text{ mol dm}^{-3}$, $\text{CuO}(\text{s})$ will not form. The corresponding value with respect to $\text{Cu}(\text{OH})_2(\text{s})$ is $10^{-7.31} \text{ mol dm}^{-3}$. (b) $[\text{Cu}]_{\text{T}} = 10^{-5} \text{ mol dm}^{-3}$.

reactions in homogeneous solution at $I_c = 0.10\text{--}1.0 \text{ mol dm}^{-3} \text{ NaClO}_4$. These data, which were not cited by [97PLY], have contributed significantly to the present analysis.

6.1.1 Formation of CuOH^+

Formation of the first monomeric hydrolysis species can be described by eq. 5,



This reaction is dominant only when $[\text{Cu}^{\text{II}}]_{\text{T}}$ is in or below the $\mu\text{mol dm}^{-3}$ concentration range. This follows from the value $\log_{10} K^{\circ}(6) = 5.46$ (Section 6.1.4) for the dimerization reaction 6



The accepted data for equilibrium 5 are listed in Table A2-1, along with the relevant references and our assigned uncertainties. The data used for the SIT analysis, to determine the standard equilibrium constant, $\log_{10} {}^*K_1^{\circ}$ (eq. 5), and the reaction interaction coefficient, $\Delta\epsilon(5)$, were limited to NaClO_4 media and 25 °C. The study by Paulson and Kester [80PKb] is regarded as the most reliable with respect to the stability of the species CuOH^+ . They studied Cu^{II} hydrolysis in 0.05 and 0.70 mol kg^{-1} NaClO_4 media using a copper ise and low $[\text{Cu}^{\text{II}}]_{\text{T}}$: (1, 2, and 4 $\mu\text{mol kg}^{-1}$) to minimize the formation of polynuclear complexes. Furthermore, effects due to the adsorption of Cu^{II} onto the vessel walls were accounted for. In addition, the data of Burkov et al. [82BBb] for 3.0 mol dm^{-3} NaClO_4 were also included in the SIT analysis.

The weighted regression (Fig. A3-1) used the expression

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

derived from eqs. 4 and 5 with $\Delta z^2 = -2$. The intercept yields the Recommended standard constant

$$\log_{10} {}^*K_1^{\circ}(\text{eq. 5, 298.15 K}) = -7.95 \pm 0.16$$

and the slope yields the value for $\Delta\epsilon(5) = -(0.33 \pm 0.08) \text{ kg mol}^{-1}$, where the uncertainties represent two standard deviations of the regression intercept and slope, respectively. This value of $\log_{10} {}^*K_1^{\circ}$ is in excellent agreement with the result of -7.97 ± 0.09 given by Plyasunova et al. [97PLY] from their critical evaluation of Cu^{II} hydrolysis data. On the other hand, the present Recommended value of $\log_{10} {}^*K_1^{\circ}$ disagrees significantly from the earlier estimates derived from potentiometric measurements at low ionic strength and 25 °C (-7.6 [67MSb]; -7.34 [64ACa, 58ACa]; -7.53 [38OGa]). As these latter measurements were performed at relatively high $[\text{Cu}^{\text{II}}]_{\text{T}}$ and as higher (i.e., less negative) values of $\log_{10} {}^*K_1^{\circ}$ are consistent with the presence of (undetected) $\text{Cu}^{\text{II}}/\text{OH}^-$ polynuclear complexes and/or colloidal suspensions, these values are rejected.

The values for $\epsilon(\text{Cu}^{2+}, \text{ClO}_4^-) = (0.32 \pm 0.02) \text{ kg mol}^{-1}$ and $\epsilon(\text{H}^+, \text{ClO}_4^-) = (0.14 \pm 0.02) \text{ kg mol}^{-1}$ [97GRE] lead to $\epsilon(\text{CuOH}^+, \text{ClO}_4^-) = -(0.15 \pm 0.08) \text{ kg mol}^{-1}$. These estimates are in good agreement with those given by Plyasunova et al.: [97PLY] $\Delta\epsilon(5) = -(0.35 \pm 0.06) \text{ kg mol}^{-1}$ and $\epsilon(\text{CuOH}^+, \text{ClO}_4^-) = -(0.13 \pm 0.10) \text{ kg mol}^{-1}$. From $\log_{10} {}^*K_1^{\circ} = -7.95 \pm 0.16$, we derive $\log_{10} K_1^{\circ} = 6.05 \pm 0.16$ at 25 °C.

6.1.2 Formation of $\text{Cu}(\text{OH})_2(\text{aq})$

The formation of the aqueous $\text{Cu}(\text{OH})_2$ species can be defined by reaction 7:



To avoid the formation of colloidal Cu^{II} -hydroxide particles, studies have been performed at $\mu\text{mol dm}^{-3}$ concentrations of total copper. Reliable results appear to have been obtained [84GLb, 80PKb] by use of a copper ise, in combination with a glass electrode to measure pH. A SIT analysis (Fig. A3-2) on data presented in Table A2-2 gave the result

$$\log_{10} {}^*\beta_2^{\circ}(\text{eq. 7, 298.15 K}) = -16.2 \pm 0.2$$

This value is in excellent agreement with that given by Plyasunova et al. [97LY] ($\log_{10} {}^*\beta_2^{\circ} = -16.23 \pm 0.15$). The value for $\Delta\epsilon(7)$ is $(0.1 \pm 0.3) \text{ kg mol}^{-1}$. The values for $\epsilon(\text{Cu}^{2+}, \text{ClO}_4^-) = (0.32 \pm 0.02) \text{ kg mol}^{-1}$ and $\epsilon(\text{H}^+, \text{ClO}_4^-) = (0.14 \pm 0.02) \text{ kg mol}^{-1}$ [97GRE] lead to $\epsilon(\text{Cu}(\text{OH})_2, \text{Na}^+, \text{ClO}_4^-) = (0.14 \pm 0.36) \text{ kg mol}^{-1}$. This value is high for an uncharged complex but has a very large uncertainty that includes zero within its range.

The present critical evaluation indicates that $\log_{10} {}^*K_1^{\circ} = -7.95$ ($\log_{10} K_1^{\circ} = 6.05$) and $\log_{10} {}^*K_2^{\circ} = -8.2_5$ ($\log_{10} K_2^{\circ} = 5.7_5$), which is the normal sequence for metal ion hydrolysis reactions

and Cu^{2+} complex formation constants. In contrast, [67MSb] and [68SMd] reported $\log_{10} K_2 > \log_{10} K_1$, i.e., $-\log_{10} {}^*K_1 > -\log_{10} {}^*K_2$. This unexpected relationship suggests a change in coordination number at the second hydrolysis step, which seems unlikely for Cu^{II} . Higher values of $\log_{10} K_2$ may result from the presence of a Cu^{II} -hydroxy colloid at $\text{pH} > 7$ [80PKb] and/or polynuclear species. The values of [67MSb] and [68SMd] are therefore rejected.

6.1.3 Formation of $\text{Cu}(\text{OH})_3^-$ and $\text{Cu}(\text{OH})_4^{2-}$

$\text{Cu}(\text{OH})_3^-$ and $\text{Cu}(\text{OH})_4^{2-}$ form in alkaline solutions, with the former predominating above $\text{pH} = 10$ and $\text{Cu}(\text{OH})_4^{2-}$ being the main hydrolysis product above $\text{pH} = 13$. McDowell and Johnston [36MJa] determined the stability of these species from studies on the solubility of crystalline $\text{CuO}(\text{s})$ in strongly alkaline solutions (0.04 to 8 mol dm^{-3} KOH). Reactions 8 and 9 were considered:



These solubility data have been re-evaluated [97PLY] using the SIT approach. The reported regression provided a good fit to the experimental data and resulted in the solubility constants: $\log_{10} K_{s3}^\circ = -4.96 \pm 0.05$ and $\log_{10} K_{s4}^\circ = -4.10 \pm 0.15$ for reactions 8 and 9, respectively. The derived ion interaction coefficients were $\varepsilon(\text{K}^+, \text{Cu}(\text{OH})_3^-) = 0.40 \pm 0.02$ and $\varepsilon(\text{K}^+, \text{Cu}(\text{OH})_4^{2-}) = 0.29 \pm 0.05$. Solubility studies in 2.2–4.2 mol kg^{-1} NaOH solutions [36MJa], also processed using SIT [97PLY], gave $\log_{10} K_{s4}^\circ = -4.07 \pm 0.18$ with $\varepsilon(\text{Na}^+, \text{Cu}(\text{OH})_4^{2-}) = 0.19 \pm 0.05$. The weighted mean of these two values is $\log_{10} K_{s4}^\circ = -4.10 \pm 0.16$.

From these data, we calculate $\log_{10} K_4^\circ(\text{eq. 10, 298.15 K}) = \log_{10} K_{s4}^\circ - \log_{10} K_{s3}^\circ = 0.86 \pm 0.16$.



The value calculated using the above SIT parameters is 0.92 at $I_m = 1.05$ mol kg^{-1} (1.0 mol dm^{-3} NaClO_4), which is in good agreement with that reported by [70GHb] for 1.0 mol dm^{-3} NaClO_4 ($\log_{10} K_4 = 1.1$) and that reported by [96FSa] for 1.0 mol dm^{-3} KNO_3 ($\log_{10} K_4 = 0.90$). Other values reported are: $\log_{10} K_4 = 0.9$ ($I_c = 0.5$ mol dm^{-3} NaClO_4) [75LRa] and 0.90 ($I_m = 0$ mol kg^{-1}) [36MJa]. Thus, there is consistency in the literature with respect to the stepwise stability constant for $\text{Cu}(\text{OH})_4^{2-}$.

Ziemniak et al. [92ZJb] studied the dissolution of $\text{CuO}(\text{s})$ in alkaline phosphate solutions at 290 to 530 K. From their equilibrium constants for the reactions $\text{CuO}(\text{s}) + 2\text{H}_2\text{O} \rightleftharpoons \text{Cu}(\text{OH})_3^- + \text{H}^+$, and $\text{Cu}(\text{OH})_3^- + \text{H}_2\text{O} \rightleftharpoons \text{Cu}(\text{OH})_4^{2-} + \text{H}^+$ and $\text{p}K_w = 14.00$, we calculate for 25 °C, $\log_{10} K_{s3}^\circ = -4.04 \pm 0.17$ and $\log_{10} K_4^\circ = 0.38 \pm 1.1$ for reactions 8 and 10, respectively. These values differ significantly from those discussed above and therefore are rejected.

For reaction 11



the Recommended equilibrium constant (Section 7.1) is $\log_{10} K_{s0}^\circ(\text{eq. 11, 298.15 K}) = -20.36 \pm 0.06$. Combining reactions 8 and 11 gives the Recommended value for reaction 12



$\log_{10} \beta_3^\circ(\text{eq. 12, 298.15 K}) = -4.96 + 20.36 = 15.40 \pm 0.08$. Assuming that $\log_{10} K_4^\circ = 0.86 \pm 0.16$ (as above), one obtains the Recommended value for reaction 13



$\log_{10} \beta_4^\circ(\text{eq. 13, 298.15 K}) = 16.26 \pm 0.24$.

To summarize, at $I_m = 0$ mol kg^{-1} and 25 °C, the stability of the mononuclear hydrolytic complexes, $\text{Cu}(\text{OH})_n^{(2-n)+}$ expressed in terms of hydrolysis constants have the following Recommended values: $\log_{10} {}^*\beta_1^\circ = -7.95 \pm 0.16$; $\log_{10} {}^*\beta_2^\circ = -16.2 \pm 0.2$; $\log_{10} {}^*\beta_3^\circ = -26.60 \pm 0.09$ ($= \log_{10} \beta_3^\circ -$

$3 \text{ p}K_w$); and $\log_{10} {}^*\beta_4^\circ = -39.74 \pm 0.18$ ($= \log_{10} \beta_4^\circ - 4 \text{ p}K_w$). The corresponding $\log_{10} \beta_n^\circ$ values are: 6.05; 11.8, 15.40, and 16.26.

Although these values are Recommended, they exhibit some worrying features. In particular, although the present stepwise constants ($\log_{10} K_n^\circ$) show a more or less normal sequence of declining values with increasing coordination number [88COT], the difference $\log_{10} K_2^\circ - \log_{10} K_1^\circ$ ($= -0.27$) is small and close to the statistical value of -0.38 for six-coordinated Cu^{II} – complexes (despite the significant difference in the donor strengths of H_2O and OH^-). In contrast, there are the expected large differences between $\log_{10} K_2^\circ = 5.78$, $\log_{10} K_3^\circ = 3.57$, and $\log_{10} K_4^\circ = 0.86$.

6.1.4 Formation of $\text{Cu}_2\text{OH}^{3+}$, $\text{Cu}_2(\text{OH})_2^{2+}$, and $\text{Cu}_3(\text{OH})_4^{2+}$

Several intensive studies indicate that $\text{Cu}_2(\text{OH})_2^{2+}$ is the predominant polynuclear species in slightly acidic solutions at moderate $[\text{Cu}^{\text{II}}]_{\text{T}}$. Its formation, first reported by Hasigawa [39HAA], has since been confirmed in many studies employing $[\text{Cu}^{\text{II}}]_{\text{T}}$ in the millimol dm^{-3} range [43PEa, 56BEa, 64ACa, 70KAb, 72OKa, 76ACb, 79SDb, 82BBb, 97RSb].

In contrast, $\text{Cu}_2\text{OH}^{3+}$ has been claimed to form only at high $[\text{Cu}^{\text{II}}]_{\text{T}}$ (0.3 to 0.9 mol dm^{-3}) at $\text{pH} \leq 3.5$ and then to less than 1 % [84NEa]. Its existence has also been postulated by others [72OKa, 82BBb, 97RSb]. In addition to these dimeric species, a trinuclear complex $\text{Cu}_3(\text{OH})_4^{2+}$ has been suggested [60PEc, 76ACb, 79SDb]. This appears to form in measurable amounts only in solutions supersaturated with respect to $\text{CuO}(\text{s})$ and $\text{Cu}(\text{OH})_2(\text{s})$.

$\text{Cu}_2\text{OH}^{3+}$

The formation of this species can be represented by reaction 14



It forms only in concentrated, acidic Cu^{II} solutions. A detailed study of the ionic strength dependence for this reaction, as well as for reaction 15 below, has been reported by De Robertis et al. [97RSb] in NaClO_4 media at 25 °C. Data selected for the SIT analysis are listed in Table A2-3, along with references and our assigned uncertainties. References to (and reasons for) data rejected from this analysis are shown in footnote 2. The Recommended stability constant at zero ionic strength, derived from the weighted regression (Fig. A3-3), is

$$\log_{10} {}^*\beta_{2,1}^\circ(\text{eq. 14, 298.15 K}) = -6.40 \pm 0.12$$

The reaction ion interaction coefficient, $\Delta\epsilon(14)$, is $(0.04 \pm 0.04) \text{ kg mol}^{-1}$. The values for $\epsilon(\text{Cu}^{2+}, \text{ClO}_4^-) = (0.32 \pm 0.02) \text{ kg mol}^{-1}$ and $\epsilon(\text{H}^+, \text{ClO}_4^-) = (0.14 \pm 0.02) \text{ kg mol}^{-1}$ [97GRE] lead to $\epsilon(\text{Cu}_2\text{OH}^{3+}, \text{ClO}_4^-) = (0.54 \pm 0.05) \text{ kg mol}^{-1}$.

Close inspection of the $\log_{10} {}^*\beta_{2,1}$ vs. I_m data (Fig. A3-3) indicates that they are *not* well described by a simple SIT analysis. At high I_m , where experimental accuracy should be greatest, large discrepancies exist among the reported values (Table A2-3). Perhaps more importantly, the trend in the data at low I_m , all from a single source [97RSb], does not correspond to that imposed by the SIT analysis. The latter problem can be treated by allowing the SIT parameter $a_i\beta$ to vary from the Scatchard value of $1.5 \text{ kg}^{1/2} \text{ mol}^{-1/2}$ [76SCA], as was done previously for the protonation equilibria of carbonate and phosphate [2005PBA]. However, the uncertainties associated with the detection of small concentrations of polynuclear complexes at low ionic strengths do not warrant such action at present. Accordingly, the above value of $\log_{10} {}^*\beta_{2,1}^\circ(\text{eq. 14}) = -6.40 \pm 0.12$ is downgraded to Provisional and the stated uncertainty must be regarded as indicative only.

$\text{Cu}_2(\text{OH})_2^{2+}$

The formation of the dimeric species $\text{Cu}_2(\text{OH})_2^{2+}$ can be represented by reaction 15

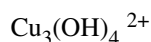


Data for NaClO₄ media selected for the SIT analysis are listed in Table A2-3, with our assigned uncertainties. References (and reasons) for data rejected from this analysis are shown in footnote 2. The Recommended stability constant at zero ionic strength, derived from the weighted regression (Fig. A3-4), is

$$\log_{10} {}^*\beta_{2,2}^{\circ}(\text{eq. 15, 298.15 K}) = -10.43 \pm 0.07$$

The reaction ion interaction coefficient, $\Delta\epsilon(15)$, is $-(0.07 \pm 0.04) \text{ kg mol}^{-1}$. The values for $\epsilon(\text{Cu}^{2+}, \text{ClO}_4^-) = (0.32 \pm 0.02) \text{ kg mol}^{-1}$ and $\epsilon(\text{H}^+, \text{ClO}_4^-) = (0.14 \pm 0.02) \text{ kg mol}^{-1}$ [97GRE] lead to $\epsilon(\text{Cu}_2(\text{OH})_2^{2+}, \text{ClO}_4^-) = (0.29 \pm 0.12) \text{ kg mol}^{-1}$.

From the values for $\log_{10} {}^*\beta_{2,2}^{\circ}$ and $\log_{10} {}^*K_1^{\circ}$, we derive the value for the dimerization reaction at 25 °C, $\log_{10} K^{\circ}(6) = 5.46 \pm 0.23$.



The formation of the trimeric species can be represented by reaction 16. It has been claimed that this species is observed at high $[\text{Cu}^{\text{II}}]_{\text{T}}$ and pH \approx 6:



A SIT analysis for this reaction is not possible because of the limited data available. Sylva and Davidson [79SDB] reported a value for $\log_{10} {}^*\beta_{3,4}$ ($I_c = 0.1 \text{ mol dm}^{-3} \text{ KNO}_3$) which is in reasonable agreement with that reported by [76ACb] ($I_c = 0.1 \text{ mol dm}^{-3} \text{ NaClO}_4$) (Table A2-3). The average of these two values gives $\log_{10} {}^*\beta_{3,4}$ ($I_c = 0.1 \text{ mol dm}^{-3}$) = -21.5 ± 0.2 at 25 °C. An extrapolation to $I_m = 0 \text{ mol kg}^{-1}$, assuming the ionic strength dependence to be the same as for the formation of the dimer, $\text{Cu}_2(\text{OH})_2^{2+}$ [$\Delta\epsilon = -(0.07 \pm 0.04) \text{ kg mol}^{-1}$], gives the Provisional value

$$\log_{10} {}^*\beta_{3,4}^{\circ}(\text{eq. 16, 298.15 K}) = -21.1 \pm 0.2$$

6.2 The Cu²⁺–Cl[–] system

Cu^{II} is generally thought (but see below) to form four consecutive chlorido- complexes in aqueous solution (reactions 17 to 20).



These complexes are claimed to have different electronic absorption bands, and their formation has therefore been investigated mostly by UV–vis spectrometry. Unfortunately, the bands are strongly overlapping and require simultaneous determination of the constants and the absorptivities, leading to correlation problems in the data. Furthermore, the complexes CuCl⁺ and CuCl₂(aq) are weak, while the higher-order complexes are extremely weak and only form at very high chloride concentrations. Reliable stability constants can therefore only be obtained from measurements in solutions containing background electrolyte at high concentration. However, use of high ionic strength media does not *a priori* guarantee constant activity coefficients when the replacement of the background anion (usually perchlorate) by chloride is significant. Several authors have discussed these problems and presented possible solutions, e.g., [77BSa, 83BWA, 83RFa, 87BJE, 89IPa, 97WZb]. No evidence has been reported for the existence of polynuclear species.

Most of the following discussion refers to the better-characterized lower-order complexes (reactions 17 and 18). The Recommended values for stability constants at $I_m = 0 \text{ mol kg}^{-1}$ are shown in Table 2. As the chloride concentrations required for the formation of these complexes is well above

those in environmental systems at low ionic strength, they will not contribute significantly to Cu speciation in nonsaline systems, and a speciation diagram is not presented.

6.2.1 Formation of CuCl^+

Values selected for the SIT analysis, to determine the stability constant at zero ionic strength (the standard equilibrium constant) and the ion interaction coefficient $\Delta\epsilon$ for reaction 17, are listed in Table A2-4, along with our assigned uncertainties according to the estimated overall precision of the data. The selected data all refer to NaClO_4 media and 25 °C. Other ionic media have not been considered. Some studies [76KF a, 74BR a, 74BR b] are rejected because higher complexes were not taken into account although the chloride concentrations used would suggest their presence. A re-evaluation [76KSc] of data reported in [73SCc] is also rejected because the calculated absorptivities and formation constants contradict those reported in most other investigations. A re-evaluation [86RAa] of the experiments in [83RF a] is accepted in spite of the apparent absence of acid to prevent Cu^{II} hydrolysis, an effect that is assumed to be covered by the error assigned to the constant.

The SIT analysis reveals surprising consistency among the data. The anion replacement (perchlorate by chloride) during the experiments seems to have only a minor effect on the activity coefficients. The weighted linear regression (Fig. A3-5) results in the Recommended standard constant

$$\log_{10} K_1^\circ(\text{eq. 17, 298.15 K}) = 0.83 \pm 0.09$$

The reaction ion interaction coefficient based on this regression is $\Delta\epsilon(17) = -(0.05 \pm 0.02) \text{ kg mol}^{-1}$. From $\Delta\epsilon(17)$, and the reported values $\epsilon(\text{Cu}^{2+}, \text{ClO}_4^-) = (0.32 \pm 0.02) \text{ kg mol}^{-1}$ and $\epsilon(\text{Cl}^-, \text{Na}^+) = (0.03 \pm 0.01) \text{ kg mol}^{-1}$ [97GRE], we calculate $\epsilon(\text{CuCl}^+, \text{ClO}_4^-) = (0.30 \pm 0.05) \text{ kg mol}^{-1}$, a value consistent with ion interaction coefficients for other species of the same charge type [97GRE].

6.2.2 Formation of $\text{CuCl}_2(\text{aq})$

The complex $\text{CuCl}_2(\text{aq})$ is less stable than CuCl^+ . Reliable data in NaClO_4 media are available only at ionic strengths of 3 mol dm^{-3} and higher. An extrapolation to $I_m = 0 \text{ mol kg}^{-1}$ is not feasible without lower ionic strength data. If the constant reported at $I_m = 1 \text{ mol kg}^{-1}$ in HClO_4 [50MDa] is accepted, then the SIT analysis shown in Fig. A3-6 is obtained. Although the value at $I_m = 1 \text{ mol kg}^{-1}$ refers to HClO_4 , it can be used with some confidence because the same authors' value for $\log_{10} K_1$ (0.11 ± 0.01) in this medium [50MDa] is consistent with our accepted values in $1 \text{ mol dm}^{-3} \text{ NaClO}_4$ (Table A2-4). We assign a larger error to this constant to cover any medium effect. The values used for the SIT analysis are listed in Table A2-4. The weighted linear regression (Fig. A3-6) shows that there is reasonable consistency between the data; it results in the Provisional standard constant

$$\log_{10} \beta_2^\circ(\text{eq. 18, 298.15 K}) = 0.6 \pm 0.3$$

The resulting ion interaction coefficient is $\Delta\epsilon(18) = -(0.10 \pm 0.06) \text{ kg mol}^{-1}$. From this, we derive the new value $\epsilon(\text{CuCl}_2, \text{Na}^+, \text{ClO}_4^-) = (0.28 \pm 0.07) \text{ kg mol}^{-1}$. Note that $\log_{10} \beta_2^\circ < \log_{10} K_1^\circ$, indicating that the value of the stepwise formation constant for the second complex is less than 1.0 ($\log_{10} K_2^\circ = -0.2$).

6.2.3 Formation of CuCl_3^- and CuCl_4^{2-}

Publications on the higher complexes are of limited number, refer to very high ionic strengths, and the reported constants differ considerably [62MSc, 73SCc, 77BSa, 81AHa, 82WLa, 83BWA, 83RFa, 86RAa, 89IPa]. These values cannot be used in a statistical treatment, and we cannot recommend any constants for the formation of CuCl_3^- and CuCl_4^{2-} even though such complexes have been characterized at very high chloride concentrations.

6.3 The Cu^{2+} - CO_3^{2-} system

Figure 2 shows a speciation diagram for the Cu^{2+} - H^+ - CO_3^{2-} system, based on the Recommended and Provisional stability constants for mononuclear species recorded in Tables 1 and 3. The results shown in Fig. 2, for which $I_m = 0 \text{ mol kg}^{-1}$, $t = 25 \text{ }^\circ\text{C}$ and $f(\text{CO}_2) = 10^{-3.5} \text{ bar}$ (1 bar = 10^5 Pa), indicate that carbonato- complexes dominate hydroxido- complexes over a wide range of solution conditions unless $f(\text{CO}_2)$ is significantly lower than atmospheric levels. This contrasts with the situation for Hg^{II} where hydroxido- complexes dominate up to pH 10.5 [2005PBA]. Figure 2 shows that for $f(\text{CO}_2) = 10^{-3.5} \text{ bar}$, $\text{CuCO}_3(\text{aq})$ is the dominant species of Cu^{II} in weakly alkaline solutions ($7.4 < \text{pH} < 9.0$) and $\text{Cu}(\text{CO}_3)_2^{2-}$ becomes dominant above $\text{pH} = 9.0$.

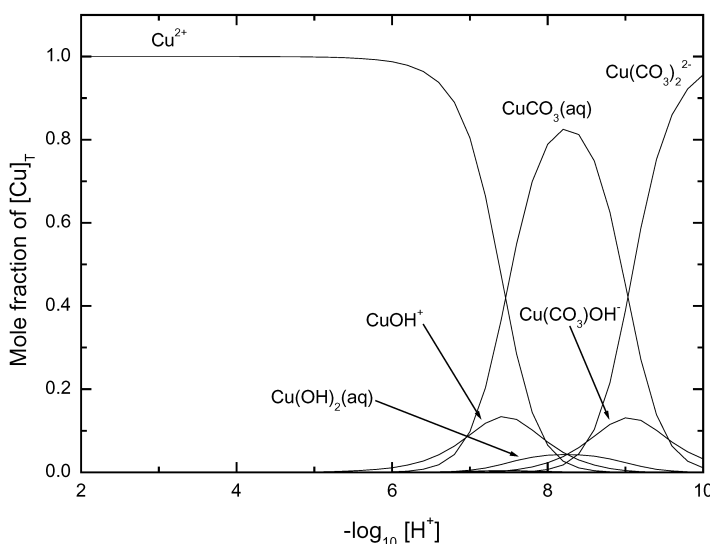


Fig. 2 Speciation diagram for the ternary Cu^{2+} - H^+ -carbonate system at $25 \text{ }^\circ\text{C}$ as obtained from the Recommended and Provisional stability constants at $I_m = 0 \text{ mol kg}^{-1}$ (Tables 1 and 3) and calculated for $[\text{Cu}]_T = 10^{-9} \text{ mol dm}^{-3}$ and $f(\text{CO}_2) = 10^{-3.5} \text{ bar}$ (1 bar = 10^5 Pa). The upper limit of $-\log_{10} [\text{H}^+]$ is set at 10 to limit the equilibrium carbonate concentration determined by $f(\text{CO}_2)$.

6.3.1 Formation of $\text{CuCO}_3(\text{aq})$

Selected formation constants for the equilibrium



are shown in Table A2-5. Figure A3-7 shows that these data, appropriate to NaClO_4 media at $25 \text{ }^\circ\text{C}$, are well represented by the equation

$$\log_{10} K_1(\text{eq. 21}, 298.15 \text{ K}) = (6.75 \pm 0.03) - 8D + (0.18 \pm 0.04)I_m$$

i.e., $\log_{10} K_1^\circ = 6.75 \pm 0.03$. Since CO_3^{2-} forms ion pairs to a significant extent with Na^+ , Mg^{2+} , and Ca^{2+} in natural waters, it is useful to express $\text{CuCO}_3(\text{aq})$ formation in terms of bicarbonate, which is typically very weakly ion paired to the stated cations. Selected formation constants for the equilibrium



are shown in Table A2-6. These constants were derived from the data in Table A2-5 plus the equilibrium constants for the reaction $\text{CO}_3^{2-} + \text{H}^+ \rightleftharpoons \text{HCO}_3^-$ that were used in the original publications (ref-

erenced in Table A2-5) to determine $\log_{10} K_1(21)$. Figure A3-8 shows that $\text{CuCO}_3(\text{aq})$ formation constants expressed in terms of HCO_3^- concentrations are well represented by the equation

$$\log_{10} K(\text{eq. 22, 298.15 K}) = -(3.56 \pm 0.03) - 4D + (0.19 \pm 0.04)I_m$$

i.e., $\log_{10} K^\circ(22) = -3.56 \pm 0.03$. From the value $\Delta\epsilon(22) = -(0.19 \pm 0.04) \text{ kg mol}^{-1}$ and the values for $\epsilon(\text{Cu}^{2+}, \text{ClO}_4^-) = (0.32 \pm 0.02) \text{ kg mol}^{-1}$, $\epsilon(\text{H}^+, \text{ClO}_4^-) = (0.14 \pm 0.02) \text{ kg mol}^{-1}$, and $\epsilon(\text{Na}^+, \text{HCO}_3^-) = (0.00 \pm 0.02) \text{ kg mol}^{-1}$ [97GRE], we derive $\epsilon(\text{CuCO}_3(\text{aq}), \text{Na}^+, \text{ClO}_4^-) = -(0.01 \pm 0.10) \text{ kg mol}^{-1}$.

6.3.2 Formation of $\text{Cu}(\text{CO}_3)_2^{2-}$

Selected formation constants for the equilibrium



are shown in Table A2-5. Figure A3-9 shows that all selected data, applicable to NaClO_4 media at 25 °C, are adequately represented by the equation

$$\log_{10} \beta_2(\text{eq. 23, 298.15 K}) = (10.3 \pm 0.1) - 8D - (0.3 \pm 0.2)I_m$$

within the assigned uncertainties of the equilibrium data. The equilibrium constants obtained for formation of $\text{CuCO}_3(\text{aq})$ and $\text{Cu}(\text{CO}_3)_2^{2-}$ from Cu^{2+} indicate that the stepwise equilibrium constant for the reaction



at zero ionic strength is

$$\log_{10} K_2^\circ(\text{eq. 24, 298.15 K}) = 3.55 \pm 0.13$$

Since this stepwise equilibrium constant describes an isocoulombic reaction, the boundary between domains of predominance for $\text{CuCO}_3(\text{aq})$ and $\text{Cu}(\text{CO}_3)_2^{2-}$ occurs at a free carbonate ion concentration near $2.8 \times 10^{-4} \text{ mol kg}^{-1}$ over a wide range of ionic strength.

Selected formation constants for the equilibrium



are shown in Table A2-6. Figure A3-10 shows that the selected data are adequately described by the equation

$$\log_{10} K(\text{eq. 25, 298.15 K}) = -(10.3 \pm 0.1) - (0.3 \pm 0.2)I_m$$

It is useful to note that the formation constants appropriate to equilibria 22 and 25 are dimensionless; they are thus weakly dependent on ionic strength relative to equilibria 21 and 23. Most importantly, equilibrium calculations formulated in terms of HCO_3^- concentrations are weakly influenced by ion pairing with major cations relative to calculations expressed in terms of CO_3^{2-} concentrations.

6.3.3 Formation of CuHCO_3^+

Selected formation constants for the equilibrium



are shown in Table A2-5. The weighted regression of these data (shown in Fig. A3-11) indicates that CuHCO_3^+ formation at 25 °C is well represented by the equation

$$\log_{10} K^\circ(\text{eq. 26, 298.15 K}) = (1.8 \pm 0.1) - 4D - (0.14 \pm 0.15)I_m$$

CuHCO_3^+ formation constants are sufficiently small that CuHCO_3^+ is unlikely to be a significant environmental species. It can, however, become a significant species in experiments conducted at high levels of bicarbonate. In determinations of $\log_{10} K_1$ and $\log_{10} \beta_2$, high levels of bicarbonate are generally

desirable in order to obtain significant complexation by CO_3^{2-} at a pH sufficiently low to limit the formation of CuOH^+ , $\text{Cu}(\text{OH})_2(\text{aq})$, and $\text{Cu}(\text{OH})\text{CO}_3^-$.

6.3.4 Formation of $\text{Cu}(\text{CO}_3)\text{OH}^-$

The single stability constant, $\log_{10} K [\text{CuCO}_3(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{Cu}(\text{CO}_3)\text{OH}^- + \text{H}^+] = -9.27$, is calculated from results for the formation of $\text{CuCO}_3(\text{aq})$ and $\text{Cu}(\text{CO}_3)\text{OH}^-$ at 25 °C and $I_m = 0.72 \text{ mol kg}^{-1}$ (NaClO_4) [85SKc]. This calculation involves a correction (-0.046) for conversion of the published data from an apparent H^+ activity scale to a free H^+ concentration scale. This value is considered to be indicative only, but can be used to ascertain the possible relevance of carbonato-hydroxido- complex formation in environmental systems. It can be combined with the hydrolysis constant of water at 25 °C and $I_m = 0.72 \text{ mol kg}^{-1}$ ($\log_{10} K_w = -13.73$ [86BAE]), to calculate the formation constant $\log_{10} K(\text{eq. 27}, 298.15 \text{ K}) = 4.46 \pm 0.30$ for reaction 27, which directly relates $\text{CuCO}_3(\text{aq})$ and $\text{Cu}(\text{CO}_3)\text{OH}^-$ concentrations.



Since this formation constant describes an isocoulombic reaction, it can be expected to have a minimal dependence on ionic strength ($\Delta z^2 = 0$ and $\Delta \epsilon \approx 0$). Combining the above result with the SIT description of $\text{CuCO}_3(\text{aq})$ formation leads to the following description for formation of $\text{Cu}(\text{CO}_3)\text{OH}^-$ from Cu^{2+}



$$\log_{10} K(\text{eq. 28}, 298.15 \text{ K}) = (11.21 \pm 0.3) - 8D + (0.18 \pm 0.04)I_m$$

In this relationship, $\Delta \epsilon$ is assumed to have the same value as that obtained for formation of $\text{CuCO}_3(\text{aq})$ from Cu^{2+} and CO_3^{2-} . As indicated by the inclusion of $\text{Cu}(\text{CO}_3)\text{OH}^-$ in the speciation calculation for Fig. 2, its numerical value, although indicative only, suffices to establish that $\text{Cu}(\text{CO}_3)\text{OH}^-$ will be only a minor species in terrestrial waters at $\text{pH} < 7.5$, but it could be significant in marine and alkaline systems. The value for $\log_{10} K^\circ$ (28), that is statistically predicted from $\log_{10} \beta_2^\circ = 10.3$, $\log_{10} {}^*\beta_2^\circ = -16.22$ and $\log_{10} K_w = -14.00$, is $\log_{10} K^\circ(28) = 11.3_6 \pm 0.17$. The agreement between the two values is well within the estimated uncertainties.

6.4 The Cu^{2+} - SO_4^{2-} system

The speciation diagram for the Cu^{2+} - H^+ - SO_4^{2-} system at $I_m \approx 0 \text{ mol kg}^{-1}$, based on our Recommended values in Tables 1 and 4, is shown in Fig. 3. Because of the rapid decrease in K_1 with increasing I_m , the calculations are truncated at $[\text{SO}_4^{2-}] = 10 \text{ mM}$. However, even at this low I_m there is a significant activity coefficient effect [$\log_{10} K_1 = 1.64$ at $I_m = 0.04 \text{ mol kg}^{-1}$, Table A2-7(b)] and the calculations should be viewed with caution. At $\text{pH} 6.5$ and $[\text{Cu}^{2+}]_T = 10^{-9} \text{ mol dm}^{-3}$, the percentage of copper present as $\text{CuSO}_4(\text{aq})$ is 46 % at $-\log_{10} [\text{SO}_4^{2-}] = 2.4$ and 18 % at $-\log_{10} [\text{SO}_4^{2-}] = 3.0$.

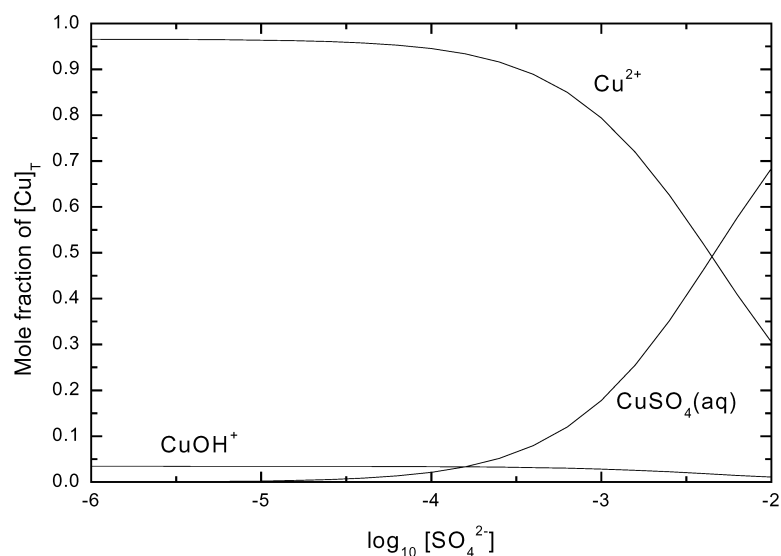


Fig. 3 Speciation diagram for the ternary Cu^{2+} - H^+ -sulfate system at 25 °C as obtained from the Recommended and Provisional stability constants at $I_m = 0 \text{ mol kg}^{-1}$ (Tables 1 and 4). Figure plotted for $-\log_{10} [\text{H}^+] = 6.5$, $[\text{Cu}]_T = 10^{-9} \text{ mol dm}^{-3}$, and $[\text{SO}_4^{2-}] = 10^{-6}$ to $10^{-2} \text{ mol dm}^{-3}$.

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

In purely thermodynamic terms, i.e., ignoring the formation of species with differing levels of hydration (see Appendix 1B), there is only one significant association equilibrium in the Cu^{2+} - SO_4^{2-} system, reaction 29



At least 70 papers report stability constant or related thermodynamic data for this reaction. Selected values of $\log_{10} K_1$ and their uncertainties are listed in Tables A2-7(a) and (b) along with brief details of rejected data.

Including recalculations, 17 values for $\log_{10} K_1$ based on high-quality conductivity measurements have been reported, following the first “modern” study [38OGa]. Older studies [04KOH, 12NFa, 27DAb] are only of historical interest but agree well with more recent data. Consideration of the “accepted” values in Table A2-7(a) gives $\log_{10} K_1^\circ = 2.356 \pm 0.052$ ($N = 10$). Pending further developments in the theory of electrolyte solutions (Appendix 1B), the “best estimate” for the formation of $\text{CuSO}_4(\text{aq})$ is $\log_{10} K_1^\circ = 2.35 \pm 0.05$. This value is Recommended. It agrees, within the precision adopted for Recommended data, with the values obtained from UV-vis spectrometry (but this may be fortuitous, see below) and thermodynamic measurements. The comparatively large uncertainty reflects the difficulties in quantifying this apparently simple system, which is often taken as a paradigm for the study of ion association [50FRa, 55BPb, 62DAV, 66NAN, 59ROB].

The common spectroscopic methods, such as NMR, IR, Raman, and UV-vis, generally probe only those species in which the ions are in direct contact (Appendix 1B). Therefore, the obtained stability constants may be lower than the true values if (undetected) solvent-separated complexes are present [2006HEF]. Both dielectric [65POa, 92BAR, 06AHR] and ultrasonic [68HPd, 70FIT, 70BEC, 70FRI] relaxation studies indicate significant formation of solvent-separated Cu^{2+} - SO_4^{2-} species. Thus, estimates of $K_1^\circ \approx 0$ [64HPb] or ≈ 10 [2006HEF] obtained by Raman spectroscopy, which typically detects only contact species [2003RUD, 2004BUC], are rejected.

The situation with respect to UV–vis spectroscopy is less clear-cut. The $d-d$ transition for $\text{Cu}^{2+}(\text{aq})$ at ca. 820 nm is unchanged upon addition of SO_4^{2-} , suggesting little formation of contact species. However, a new band appears at ca. 260 nm [2006HEF], and this is used for the quantitative evaluation of K_1 . The location and intensity of this band suggests that it arises from a ligand-to-metal charge transfer. Whilst such a transition may be sensitive to solvent-shared (SIP) and contact (CIP) ion pair species, it is improbable that double solvent separated ion pairs (2SIPs) would be detected. Thus, spectrometrically determined stability constants for $\text{CuSO}_4(\text{aq})$ must be viewed with caution.

Many K_1° values have been obtained by UV–vis spectrometry; but, for the reasons just given, all accepted values in Table A2-7(b) have been assigned a relatively high uncertainty (± 0.2 in $\log_{10} K_1$). Some of these investigations have included extensive consideration of activity coefficients and other computational problems (Appendix 1B). The average of the 11 estimates for $I_m = 0$ is $\log_{10} K_1^\circ = 2.274 \pm 0.066$ or 2.300 ± 0.042 if the two outliers [49NAb, 85LYa] are excluded ($N = 9$; with the outliers $>3\sigma$ from the mean). Although neither value differs substantially from the conductivity result, because of the inherent uncertainty in the accuracy of the spectrometric data, the conductivity mean is considered the more reliable estimate of K_1° .

The few studies of this system employing thermodynamic measurements, Table A2-7(b), have either been made at relatively low I , incorporating activity coefficient corrections to $I_m = 0$, or at a single ionic strength. Calculations based on cryoscopic, activity coefficient, and heat of dilution data [55BPb, 56KEb, 72PIa, 90WAA] give $\log_{10} K_1^\circ = 2.43 \pm 0.02$, if the one outlier [90WAA] is excluded. To date, no high-quality potentiometric investigation as a function of I has been reported.

At higher values of I , most of the K_1 values have been obtained by UV–vis spectrometry [Table A2-7(b)]. SIT regression analyses of the accepted data for LiClO_4 and NaClO_4 media are shown in Figs. A3-12 and A3-13, respectively. For LiClO_4 media, the derived value is $\log_{10} K_1^\circ = 2.30 \pm 0.10$ [with $\Delta\varepsilon = -(0.08 \pm 0.04) \text{ kg mol}^{-1}$], which is in close agreement with the Recommended value. In comparison, the SIT analysis of the NaClO_4 data (Fig. A3-13), gives $\log_{10} K_1^\circ = 2.19 \pm 0.07$ [with $\Delta\varepsilon = -(0.10 \pm 0.03) \text{ kg mol}^{-1}$], which is in only modest agreement with the Recommended value based on conductivity measurements.

The apparent discrepancy between the Recommended value at $I_m = 0$ based on conductivity measurements and the value obtained from regression of the NaClO_4 data creates a dilemma in terms of how to calculate values of $\log_{10} K_1$ for media that contain a significant concentration of sodium ions. Furthermore, the analysis of conductivity data that leads to the Recommended value of $\log_{10} K_1^\circ$ does not yield a value for $\Delta\varepsilon$. Inspection of the NaClO_4 regression plot (Fig. A3-13) indicates, apart from the inherent uncertainties in the spectrometric values (Appendix 1B), a significant degree of curvature for the data at lower ionic strength. This suggests that for this reaction and medium, in which there is the possibility of relatively strong $\text{Na}^+ - \text{SO}_4^{2-}$ interactions, the SIT relationship with $a_j B = 1.5$ underestimates the strength of short range forces and their effect on the calculated stability constant. A similar phenomenon was reported for $\log_{10} K_1$ for the $\text{H}^+ - \text{CO}_3^{2-}$ and $\text{H}^+ - \text{PO}_4^{3-}$ systems in NaCl media [2005PBA]; an analysis of the large data sets for these systems indicated values of $a_j B = 1.047$ and 1.152 , respectively, which provided a much improved SIT regression. The availability of large data sets covering a wide range of I_m for the $\text{Cu}^{2+} - \text{SO}_4^{2-}$ reaction in both NaClO_4 and LiClO_4 media allows similar analyses.

The SIT regression based on the accepted data for NaClO_4 [Table A2-7(b)], and using $a_j B$ as a fitting parameter, gave $\log_{10} K_1^\circ = 2.36 \pm 0.07$ and $a_j B = 1.15$ [with $\Delta\varepsilon(29) = -(0.16 \pm 0.07) \text{ kg mol}^{-1}$], Fig. A3-14. A similar analysis for the accepted data for LiClO_4 medium (not shown) gave $\log_{10} K_1^\circ = 2.34 \pm 0.09$ and $a_j B = 1.40$ [with $\Delta\varepsilon(29) = -(0.09 \pm 0.04) \text{ kg mol}^{-1}$]. Both values of $\log_{10} K_1^\circ$ are in excellent agreement with that obtained from conductivity measurements at $I_m \approx 0 \text{ mol kg}^{-1}$. It is not meaningful to calculate values of $\varepsilon(\text{CuSO}_4, \text{Na}^+, \text{ClO}_4^-)$ from these reaction ion interaction coefficients, $\Delta\varepsilon(29)$, because the available contributing single ion interaction coefficients are calculated for $a_j B = 1.50$ [97GRE]. If $\log_{10} K_1^\circ$ is fixed at 2.35 ± 0.05 and $a_j B$ is fixed at 1.50 for the NaClO_4 data, regres-

sion provides the calculated reaction ion interaction coefficient $\Delta\epsilon(29) = -(0.05 \pm 0.02) \text{ kg mol}^{-1}$. The two values of $\Delta\epsilon$ for NaClO_4 media, are each conditional on the applicable value of $a_j B$; these values are noted in Table 4 as Provisional.

One objective of this review is to provide the user with access to the best possible values of $\log_{10} K$ that will be applicable in the medium of choice. Clearly, in the CuSO_4 system, there is a higher level of uncertainty in the ionic strength dependence of $\log_{10} K_1$ than is the case for those equilibria studied by potentiometric methods. The data presented in Tables 4 and 6 (see Section 9) provide the best interpretation that is possible at this time (Appendix 1B). The application of these data in speciation calculations for systems at $I_m > 0 \text{ mol kg}^{-1}$ is discussed in Section 9.

6.4.2 Higher-order Cu^{2+} - SO_4^{2-} complexes

A number of earlier papers [48FRa, 56KEb, 51NLb] and interpretations [72PIa] reported the existence of higher order $\text{Cu}(\text{SO}_4)_n^{2(1-n)+}$ species ($n = 2, 3$) using various techniques. Close inspection of the data suggests that the observed effects might instead be due to changes in activity coefficients, as significant replacement of the medium anion (usually ClO_4^-) by SO_4^{2-} occurs at nominally constant I . Consequently, such constants are considered unreliable and are rejected. Nevertheless, by analogy with similar systems (cf. Cl^- and CO_3^{2-} in this review), it is possible that a comparatively weak complex, $\text{Cu}(\text{SO}_4)_2^{2-}$, is formed.

6.5 The Cu^{2+} - PO_4^{3-} system

The number of data for the Cu^{2+} - H^+ - PO_4^{3-} system is limited. In general, the agreement between published values is poor. The selected data are recorded in Table A2-8.

Difficulties in studying M^{2+} - H^+ - PO_4^{3-} systems, and in quantifying the speciation and stability constants, relate in general to

- The relatively low stability of phosphato complexes. Consequently, the measured pH changes in potentiometric studies are small for typical reactant concentrations ($0.001 \text{ M} \leq c_M, c_L \leq 0.01 \text{ M}$). This can be overcome by use of a large excess of metal ion or ligand. However, the stoichiometry of complexes formed in significant amount is constrained by the use of excess component, while the pH change upon complex formation becomes negligible in the case of excess phosphate.
- The formation of dimeric protonated ligand species $(\text{H}_x(\text{PO}_4)_2)^{(6-x)-}$, with $2 \leq x \leq 6$, at higher $[\text{PO}_4^{3-}]_T$; see [2005PBa].
- The formation of ion pairs between phosphate anions and alkali metal (medium) cations; see [2005PBa].
- The sparing solubility of many metal-phosphate solid phases.
- The competing effects of metal ion hydrolysis reactions.

In acidic solutions ($2 \leq \text{pH} \leq 5$), rather weak $\text{Cu}(\text{H}_2\text{PO}_4)_x^{(2-x)+}$ species are formed, reactions 30 and 31



Although the accepted values for $\log_{10} K$ in Table A2-8 are mutually consistent, there are insufficient data to assign Recommended or Provisional values to reactions 30 and 31.

The majority of studies were performed in the range ($5 \leq \text{pH} \leq 6$), where the formation of $\text{Cu}(\text{HPO}_4)_x^{(2-2x)+}$ complexes was also detected, reactions 32 and 33



The data in Table A2-8 show good agreement between published stability constants for reaction 32 in 0.10 mol dm⁻³ NaClO₄ and NaNO₃. Based on these results, we assign the Recommended value at 25 °C:

$$\log_{10} K(\text{eq. 32}; I_c = 0.10 \text{ mol dm}^{-3}) = 3.25 \pm 0.20$$

From this $\log_{10} K$ value and the protonation constant for PO₄³⁻ at $I_c = 0.10 \text{ M NaNO}_3$ ($\log_{10} K_1 = 11.68 \pm 0.05$ [2005PBA]), we derive the Provisional value

$$\log_{10} \beta(\text{eq. 34}; I_c = 0.10 \text{ mol dm}^{-3}) = 14.93 \pm 0.20$$

for reaction 34



Application of the SIT function to reaction 32, assuming $\epsilon(\text{CuHPO}_4, \text{NaClO}_4) = 0$ (for an uncharged species), and taking $\epsilon(\text{Na}_2\text{HPO}_4^{2-}) = -0.15 \pm 0.06$ and $\epsilon(\text{Cu}^{2+}, \text{ClO}_4^-) = 0.32 \pm 0.02$ [97GRE], yields $\log_{10} K^\circ(32) = 4.11 \pm 0.3$, from which $\log_{10} K^\circ(34) = 16.45 \pm 0.3$. These latter values can be taken as Provisional. Childs [70CHc] studied the Cu²⁺-H⁺-PO₄³⁻ system at 37 °C and $I_c = 0.15 \text{ M KNO}_3$. His value $\log_{10} K(32) = 3.25 \pm 0.15$ is in reasonable agreement with the Recommended constant for $I_c = 0.10 \text{ mol dm}^{-3}$ (no value is available for $\Delta_r H_m$).

Speciation calculations based on the equilibrium constants for Cu²⁺ hydrolysis (Table 1, or calculated for $I = 0.10 \text{ mol dm}^{-3}$) and the above value of $\log_{10} K(34) = 14.93$ ($I_c = 0.10 \text{ mol dm}^{-3}$) or $\log_{10} K^\circ(34) = 16.49$ ($I = 0.0 \text{ mol dm}^{-3}$), establish that the formation of copper-phosphate complexes is not significant (<1 %) at typical environmental concentrations of $[\text{Cu}^{\text{II}}]_{\text{T}} = [\text{PO}_4^{3-}]_{\text{T}} = 10^{-6} \text{ mol dm}^{-3}$. At both ionic strengths, the maximum concentration of CuHPO₄(aq) occurs at ca. pH 7.4; it reaches ca. 13 % (45 %) of $[\text{Cu}^{\text{II}}]_{\text{T}}$ when $[\text{PO}_4^{3-}]_{\text{T}} = 10^{-3.9}$ and ca. 55 % (87 %) of $[\text{Cu}^{\text{II}}]_{\text{T}}$ when $[\text{PO}_4^{3-}]_{\text{T}} = 10^{-3.0} \text{ mol dm}^{-3}$ for $I_c = 0.10 \text{ mol dm}^{-3}$ ($I_c = 0.0 \text{ mol dm}^{-3}$).

PO₄³⁻ is the most basic H_nPO₄⁽³⁻ⁿ⁾⁻ species, and is therefore expected to be the strongest phosphate ligand. However, formation of Cu(PO₄)_x^{(2-3x)+} complexes at higher pH is prevented (or possibly accompanied) by metal ion hydrolysis. In their studies on the hydrolysis reactions of Cu²⁺, based on the dissolution of CuO(s) in alkaline phosphate solutions, Ziemniak et al. [92ZJb] postulated the formation of the complexes Cu(OH)₂HPO₄²⁻, Cu(OH)₃H₂PO₄²⁻, and Cu(OH)₂PO₄³⁻; for example, reaction 35



for which $\log_{10} K^\circ(35) = -4.64$. However, their values for hydroxido-phosphato complexes are considered to be doubtful, as were the hydrolysis constants reported by these authors.

7. EVALUATION OF EQUILIBRIUM CONSTANTS (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.

7.1 The Cu²⁺-OH⁻ system: Solubility of CuO (tenorite) and Cu(OH)₂

Of the two solid phases commonly reported to form from Cu^{II}/OH⁻ solutions, CuO(s) and Cu(OH)₂(s), CuO (tenorite) is the more stable (less soluble) at near-ambient conditions. The solid commonly referred to as “Cu(OH)₂(s)” represents a less well defined, metastable species. Solubility constants *K_{s0}(CuO) and *K_{s0}[Cu(OH)₂] can be defined according to the reactions





A limited number of studies have been performed in NaClO_4 media. The selected values of $\log_{10} {}^*K_{s0}[\text{CuO}(\text{s})]$ and $\log_{10} {}^*K_{s0}[\text{Cu(OH)}_2(\text{s})]$ are listed in Table A2-9. References and reasons for the many data rejected from this analysis are shown in the footnotes. The studies by Feitknecht and Schindler [63FSa] and Schindler et al. [65SAc] are regarded as the most reliable. The restricted range of ionic strengths used in these studies does not allow a SIT regression analysis. Instead, values at zero ionic strength were calculated by using the values from [65SAc] and the reaction ion interaction coefficient, $\Delta\epsilon(36 \text{ or } 37) = 0.04$, derived from the values $\epsilon(\text{Cu}^{2+}, \text{ClO}_4^-) = (0.32 \pm 0.02) \text{ kg mol}^{-1}$ and $\epsilon(\text{H}^+, \text{ClO}_4^-) = (0.14 \pm 0.02) \text{ kg mol}^{-1}$ [97GRE] and assuming that $\epsilon(\text{solid phase}, \text{Na}^+, \text{ClO}_4^-) = 0$. The following Recommended values were obtained (Table 1)

$$\log_{10} {}^*K_{s0}^\circ(\text{eq. 36}, 298.15 \text{ K}) = 7.64 \pm 0.06$$

$$\log_{10} {}^*K_{s0}^\circ(\text{eq. 37}, 298.15 \text{ K}) = 8.67 \pm 0.05$$

The following values for the dissolution of the solid phases in water, calculated using $\text{p}K_w = 14.00$, are also Recommended (Table 1): $\log_{10} K_{s0}^\circ(\text{CuO}) = -20.36 \pm 0.06$ (reaction 38) and $\log_{10} K_{s0}^\circ[\text{Cu(OH)}_2] = -19.33 \pm 0.05$ (reaction 39).



These values are in exact agreement with the Tentative values (-20.35 and -19.32) reported in the IUPAC Solubility Data Series [86DIR].

[86VAa] reported $\log_{10} K_{s2}^\circ = -8.6$ for the equilibrium $\text{CuO}(\text{s}) + \text{H}_2\text{O} \rightleftharpoons \text{Cu(OH)}_2(\text{aq})$. From this, by using $\log_{10} {}^*\beta_2^\circ = -16.17$, the value $\log_{10} {}^*K_{s0}^\circ = 7.62$ can be derived for reaction 36, in excellent agreement with that above. The Tentative value of $\log_{10} K_{s0}^\circ(\text{CuO}) = -20.35$ [86DIR] corresponds to $\log_{10} {}^*K_{s0}^\circ = 7.65$, again in quantitative agreement with the present Recommended value.

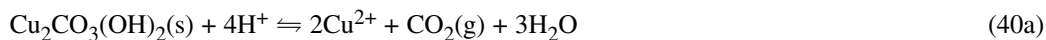
7.2 The Cu^{2+} - CO_3^{2-} - OH^- system

7.2.1 The solubility of $\text{Cu}_2\text{CO}_3(\text{OH})_2(\text{s})$ (malachite)

Solubility constants for malachite can be defined according to reaction 40



Selected values from the limited number of studies in NaClO_4 at 25°C are shown in Table A2-10. References and reasons for rejected data are shown in the footnotes. A SIT regression analysis is not possible. The result of [68SRe] for $I_m = 0.202 \text{ mol kg}^{-1}$ is considered to be the more reliable. From this, the authors calculated ($\log_{10} K_{s0}^\circ = -33.16 \pm 0.08$ at $I_m = 0 \text{ mol kg}^{-1}$). The solubility of malachite in $\text{HClO}_4/\text{NaClO}_4$, reaction 40a,



has been measured by [2002PRE] as a function of ionic strength ($I_m = 1.0$ to 3.0 mol kg^{-1}) and of temperature at $I_m = 1.0 \text{ mol kg}^{-1}$ using the pH variation method at constant partial pressure of $\text{CO}_2(\text{g})$. The solubility constants were corrected to $I = 0$ using SIT. From the derived standard molar Gibbs energy of formation, $\Delta_f G_m^\circ[\text{Cu}_2\text{CO}_3(\text{OH})_2(\text{s})]$, the solubility constant (reaction 40) is calculated as $\log_{10} K_{s0}^\circ(40) = -33.49 \pm 0.22$ at $I_m = 0 \text{ mol kg}^{-1}$, a value in agreement with that calculated from [68RSe]. The value $\log_{10} K_{s0}^\circ = -33.16 \pm 0.08$ is accepted as Provisional. From this value, and using the reaction interaction coefficient $\Delta\epsilon(40) = 0.64$, derived from the values $\epsilon(\text{Cu}^{2+}, \text{ClO}_4^-) = (0.32 \pm 0.02) \text{ kg mol}^{-1}$, $\epsilon(\text{OH}^-, \text{Na}^+) = (0.04 \pm 0.01) \text{ kg mol}^{-1}$, and $\epsilon(\text{CO}_3^{2-}, \text{Na}^+) = -(0.08 \pm 0.03) \text{ kg mol}^{-1}$ [97GRE] and assuming that $\epsilon(\text{solid phase}, \text{Na}^+, \text{ClO}_4^-) = 0$, we derive $\log_{10} K_{s0}^\circ = -31.9 \pm 0.1$ at $I_m =$

0.72 mol kg⁻¹. This value is in reasonable agreement with that of [84SKb] ($\log_{10} K_{s0} = -31.2 \pm 0.1$ at $I_m = 0.72$ mol kg⁻¹; including corrections for (a) NaCO₃⁻ formation and (b) the activity coefficient of OH⁻).

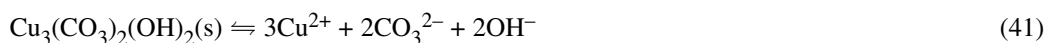
Conversely, the solubility constant for reaction 40 ($\log_{10} K_{s0}^{\circ} = -33.16 \pm 0.08$) can be combined with relationships between CO₃²⁻ protonation constants, CO₂ fugacity $f(\text{CO}_2)$, and the Henry's law constant for CO₂ (i.e., $[\text{CO}_3^{2-}] = K_{\text{H}} K_1^{-1} K_2^{-1} f(\text{CO}_2) [\text{H}^+]^{-2} = 10^{-18.16} f(\text{CO}_2) [\text{H}^+]^{-2}$, where $\log_{10} K_{\text{H}} = -1.47$ and $\log_{10} K_1 K_2 = 16.691$ at $I_m = 0$ mol kg⁻¹) and $K_w = 10^{-14.00}$ to produce

$$\log_{10} K^{\circ}(\text{eq. 40a, 298.15 K}) = \log_{10} ([\text{Cu}^{2+}]^2 f(\text{CO}_2) [\text{H}^+]^{-4}) = 13.00 \pm 0.09$$

This value is in fair agreement with that of Preis and Gamsjäger [2002PRE], $\log_{10} K^{\circ}(40a) = 12.68 \pm 0.20$.

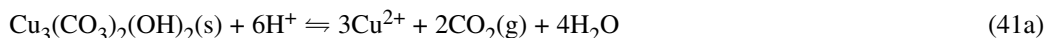
7.2.2 The solubility of Cu₃(CO₃)₂(OH)₂ (azurite)

The one reliable value for the dissolution reaction of azurite, reaction 41, is given in Table A2-10.



From this value, the authors and the reviewers [assuming $\Delta\epsilon(41) = 0.88$, based on the above assumptions for malachite] estimate the value $\log_{10} K_{s0}^{\circ} = -44.9 \pm 0.2$ at $I_m = 0$ mol kg⁻¹.

The solubility of azurite in HClO₄/NaClO₄, reaction 41a



has also been measured [2002PRE]. From the derived standard molar Gibbs energy of formation, $\Delta_f G_m^{\circ}[\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2(\text{s})]$, the solubility constant (reaction 41) is calculated as $\log_{10} K_{s0}^{\circ} = -45.42 \pm 0.35$ at $I_m = 0$ mol kg⁻¹, a value in reasonable agreement with that calculated from [68RSe]. The value $\log_{10} K_{s0}^{\circ} = -44.9 \pm 0.2$ at $I_m = 0$ mol kg⁻¹ is accepted as Provisional. Conversely, from this value of $\log_{10} K_{s0}^{\circ}$ we derive

$$\log_{10} K^{\circ}(\text{eq. 41a, 298.15 K}) = \log_{10} \{[\text{Cu}^{2+}]^3 [f(\text{CO}_2)]^2 [\text{H}^+]^{-6}\} = 19.42 \pm 0.2$$

This value is in reasonable agreement with that of [2002PRE], $\log_{10} K^{\circ}(41a) = 18.90 \pm 0.30$.

The equations $\log_{10} K^{\circ}(40a) = \log_{10} \{[\text{Cu}^{2+}]^2 f(\text{CO}_2) [\text{H}^+]^{-4}\}$ and $\log_{10} K^{\circ}(41a) = \log_{10} \{[\text{Cu}^{2+}]^3 [f(\text{CO}_2)]^2 [\text{H}^+]^{-6}\}$ can be combined to calculate the boundary for azurite vs. malachite stability at $I_m = 0$ mol kg⁻¹ and 25 °C. The calculated boundary occurs near $\log_{10} f(\text{CO}_2) = -0.16$ bar (1 bar = 10⁵Pa). Thus, at $\log_{10} f(\text{CO}_2) \leq -0.16$ bar malachite is the more stable carbonate phase, but is replaced by tenorite [$\log_{10} K_{s0}^{\circ}(\text{CuO}) = 7.64$] at $\log_{10} f(\text{CO}_2) \leq -2.28$ bar; thus, neither phase is more stable than tenorite under atmospheric conditions [$\log_{10} f(\text{CO}_2) = -3.5$].

7.3 The Cu²⁺-SO₄²⁻ system

Under most conditions encountered in the environment, the equilibrium form of solid copper(II) sulfate is the blue pentahydrate, CuSO₄·5H₂O(s). This salt has a high solubility (>2 mol dm⁻³ at 25 °C in water which increases rapidly with temperature [58LS]); thus, it will not have a significant influence on Cu^{II} equilibria in natural waters. On the other hand, there are a number of "basic" sulfates such as antlerite, Cu₃(OH)₄SO₄(s), and brochantite, Cu₄(OH)₆SO₄(s), that are sparingly soluble in basic media and thus may become important under certain conditions. However, these equilibria have not been considered in this review. Their solubilities can be obtained from standard sources including the IUPAC Stability Constant Database [2005PET].

7.4 The $\text{Cu}^{2+}\text{-PO}_4^{3-}$ system

Only one value has been reported for the solubility product of $\text{Cu}_3(\text{PO}_4)_2$, corresponding to the equilibrium



From the solubility at 20 °C and at low but varying ionic strength, a value of $\log_{10} K_{s0} = -36.9 \pm 0.4$ was derived [61CAa]. The reported constant is noted, but not accepted as reliable as no account was taken of the complex formation between Cu^{2+} and HPO_4^{2-} .

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

When enthalpy data are available for an appropriate electrolyte and cover an adequate range of ionic strengths, an extrapolation to $I_m = 0 \text{ mol kg}^{-1}$ is possible by use of the SIT procedure for enthalpy data [97GRE]. The relevant equation is

$$\Delta_r H_m - 0.75\Delta z^2 A_L \sqrt{I_m} (1 + 1.5\sqrt{I_m})^{-1} - rL_1 = \Delta_r H_m^\circ - RT^2 \Delta \varepsilon_L I_m \quad (43)$$

A linear regression of $(\Delta_r H_m - \Psi(I_m) - rL_1)$ against I_m yields $\Delta_r H_m^\circ$ as the intercept and $(-RT^2 \Delta \varepsilon_L)$ as the slope. A more detailed discussion and definition of terms is given in [2005PBA].

8.1 The $\text{Cu}^{2+}\text{-OH}^-$ system

There are few reported studies of the reaction enthalpies for the hydrolysis of Cu^{2+} or the dissolution of Cu^{II} -oxide/hydroxide solids.

From enthalpy titrations in $3 \text{ mol dm}^{-3} \text{ NaClO}_4$ at 25 °C, Arnek and Patel [68APa] reported $\Delta_r H_m(*\beta_{2,2}) = 66.0 \pm 0.8 \text{ kJ mol}^{-1}$ for the formation of $\text{Cu}_2(\text{OH})_2^{2+}$ (reaction 15). They found it impossible to determine the corresponding value for the formation of CuOH^+ . However, from calorimetric measurements in $0.1 \text{ mol dm}^{-3} \text{ NaClO}_4$ at 25 °C, Arena et al. [76ACb] reported $\Delta_r H_m(*K_1) = 35.6 \pm 2.9 \text{ kJ mol}^{-1}$ for the formation of CuOH^+ (reaction 5), $\Delta_r H_m(*\beta_{2,2}) = 77.0 \pm 1.7 \text{ kJ mol}^{-1}$ for $\text{Cu}_2(\text{OH})_2^{2+}$ (reaction 15) and $\Delta_r H_m(*\beta_{3,4}) = 109 \pm 4 \text{ kJ mol}^{-1}$ for $\text{Cu}_3(\text{OH})_4^{2+}$ (reaction 16). Using $K(T)$ data based upon potentiometric titrations within the temperature interval 10–45 °C ($0.10 \text{ mol dm}^{-3} \text{ NaClO}_4$) [97RSb] reported: $\Delta_r H_m(*\beta_{2,1}) = 46.1 \pm 2.9 \text{ kJ mol}^{-1}$ and $\Delta_r H_m(*\beta_{2,2}) = 68.1 \pm 1.7 \text{ kJ mol}^{-1}$. Similar measurements by [60PEc] within the interval 15–42 °C resulted in $\Delta_r H_m^\circ(*\beta_{2,2}) = 73.2 \pm 8.4 \text{ kJ mol}^{-1}$.

Due to the limited data set with respect to variation in I , and the assumption of different speciation schemes in the different studies, no SIT analysis was performed. No Recommended enthalpy values for the different soluble species are given. Calorimetric studies by [53SLa] provide a single value for the dissolution of $\text{Cu}(\text{OH})_2(\text{s})$ in $2.0 \text{ mol dm}^{-3} \text{ HClO}_4$ (reaction 37), $\Delta_r H_m[*K_{s0} (37)] = -55.9 \text{ kJ mol}^{-1}$.

8.2 The $\text{Cu}^{2+}\text{-Cl}^-$ system

The enthalpy changes accompanying the formation of the weak Cu^{II} -chlorido complexes are small. Enthalpy change values for reaction 17 have been obtained from calorimetric measurements [66KLb, 74BRa, 74BRb, 77KFb, 82APa] and from the temperature dependence of $\log_{10} K_1$ [50MDa, 60LRa]. Ashton et al. [85ABb] also reported $\log_{10} K_1(T)$ values from 15 to 90 °C, but concluded that the total inaccuracies were too large to allow an evaluation of $\Delta_r H$. Other papers [66KLb, 74BRa, 74BRb] are rejected due to the neglect of higher complexes under conditions where they should be taken into ac-

count. The results of the remaining studies show poor agreement (they range from +2.5 to +17 kJ mol⁻¹), and it is not considered possible to select any of these data.

8.3 The Cu²⁺–SO₄²⁻ system

The enthalpy change associated with formation of CuSO₄(aq) has been extensively studied (Table A2-11). Almost the full panoply of thermochemical techniques has been used, including titration calorimetry, both with [73HPa, 73POa] and without [69IEe] independent determination of K_1 , heats of dilution [70LAe, 72PIa], and the variation of the stability constant with temperature (using spectrometric [77ASH, 82DKb, 2005MBa] or conductometric [2005BES] data).

The published values for $\Delta_r H^\circ$ show a significant spread for an apparently simple reaction. However, because of the relative weakness of complexation, there is a strong correlation between the chosen activity coefficient model and the derived values of $\log_{10} K_1$ ($\Delta_r G$) and $\Delta_r H$. A number of investigators [72CAB, 73POa, 73HPa] have shown that the popular “entropy titration” technique [69IEe] in which K and $\Delta_r H$ are determined simultaneously from the observed reaction heats can be unreliable for M^{m+}/SO_4^{2-} systems. It is preferable to determine K separately by an appropriate independent method and then to use them to determine $\Delta_r H$ by calorimetry with fixed K values.

Heats of dilution are an attractive alternative method to obtain $\Delta_r H^\circ$ for ion association in solutions of symmetrical electrolytes such as CuSO₄ because accurate data can in principle be measured down to very low concentrations [81WAC]. However, this technique is restricted to a single $[M^{2+}]/[\text{SO}_4^{2-}]$ ratio and is particularly sensitive to the choice of activity coefficient model [72PIa]. It is also not readily adaptable for estimation of $\Delta_r H$ at $I > 0$.

Averaging of the accepted enthalpy data at $I = 0$ (Table A2-11) gives $\Delta_r H_m^\circ = 7.3 \pm 1.5$ kJ mol⁻¹ and $\Delta_r S_m^\circ = 68.4 \pm 0.7$ J K⁻¹ mol⁻¹. The uncertainties, although large, fit the criteria for Recommended quantities. As discussed in Appendix 1B, they reflect the real difficulties in *accurately* quantifying association in M^{m+}/SO_4^{2-} systems. From the thermodynamic relationship $\Delta_r G^\circ = -RT \ln K^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$, we obtain $\Delta_r G^\circ = 13.09 \pm 1.3$ kJ mol⁻¹; thus, $\log_{10} K_1^\circ = 2.29 \pm 0.23$ at 25 °C, a value consistent with the present “best estimate” of $\log_{10} K_1^\circ = 2.35 \pm 0.05$.

No comprehensive systematic study of $\Delta_r H$ has been reported at finite I in any one medium, and the available data are insufficient to justify a SIT analysis at this stage. If required, interpolation of the available data (Table A2-11) provides the best estimates of $\Delta_r H$ and $\Delta_r S$ at the present time. Fortunately, neither $\Delta_r H$ nor $\Delta_r S$ is large, and so the effect of temperature on K is relatively small.

On the other hand, $\Delta_r C_p$ for the formation of CuSO₄(aq) is significant and should not be neglected. Pitzer [72PIa] derived $\Delta_r C_p^\circ = 272$ J K⁻¹ mol⁻¹ from limited thermodynamic data. More recently, Mendez De Leo et al. [2005MBa] obtained $\Delta_r C_p^\circ = 327 \pm 41$ J K⁻¹ mol⁻¹ by using UV–vis spectrometry over the temperature range 25–200 °C. Although neither of these values may be reliable, their average ($\Delta_r C_p^\circ = 300$ J K⁻¹ mol⁻¹, with a probable uncertainty of ± 50 J K⁻¹ mol⁻¹) is useful for estimating K at temperatures far removed from 25 °C. No studies have been reported for $\Delta_r C_p$ at finite I .

9. SPECIATION IN MULTICOMPONENT SYSTEMS: Cu²⁺–H⁺–Cl⁻–CO₃²⁻–PO₄³⁻–SO₄²⁻

As an aid to the user, this section presents results from speciation calculations for model aquatic systems. The required stability constants were calculated from the standard equilibrium constants in Tables 1 to 5, or from the published critical evaluation for the protonation reactions of the ligands [2005PBa]. These standard equilibrium constants were corrected, as required, for ionic strength effects and water activity, $a(\text{H}_2\text{O})$, according to eq. 4 and as described in Section 5:

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

The calculation of $\log_{10} \beta_{p,q,r}$ at the required ionic strength (molality scale) and its correction to the amount concentration (molar) scale are conveniently achieved by using the program SIT, which is included in *SC-Database* [2005PET], in the *Sol-Eq* tutorials [98PET], and is also available in the suite of programs *Aq_Solutions* from <www.iupac.org/publications/epub/index_060228.html>. In the calculations presented here, the changes in I and therefore in $\log_{10} \beta_{p,q,r}$ are minimal within the prescribed pH range.

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

Typical total concentrations of inorganic anions in an average fresh water are: $[\text{Cl}^-]_{\text{T}} = 0.23 \text{ mmol dm}^{-3}$, $[\text{SO}_4^{2-}]_{\text{T}} = 0.42 \text{ mmol dm}^{-3}$, and $[\text{HPO}_4^{2-}]_{\text{T}} = 0.7 \text{ } \mu\text{mol dm}^{-3}$ [93MOR]. The total concentration of Cu^{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 $10^{-3.5}$ bar. Furthermore, $-\log_{10} [\text{H}^+]$ was allowed to vary between 3.91 and 8.91 (ca. pH 4.0–9.0); in this range, the ionic strength is approximately constant, ca. $I_c = 0.0015 \text{ mol dm}^{-3}$ up to $-\log_{10} [\text{H}^+] = 7$, but then increases due to the increase in $[\text{HCO}_3^-]$ and $[\text{CO}_3^{2-}]$ at constant $f(\text{CO}_2)$.

The result of this calculation is visualized as a distribution diagram in Fig. 4. The speciation is not significantly different from that for the $\text{Cu}^{2+}\text{-H}^+\text{-CO}_3^{2-}$ system, except for the formation of a small amount of $\text{CuSO}_4(\text{aq})$ at $-\log_{10} [\text{H}^+] < 8$. This indicates that SO_4^{2-} plays a minor role, and Cl^- and PO_4^{3-} a negligible role, in Cu^{II} speciation with inorganic ligands in weakly acidic or near-neutral fresh waters in equilibrium with CO_2 . None of the possible Cu^{II} -containing solid phases forms under the specified conditions. At pH ($-\log_{10} [\text{H}^+]$) 6.4 the dominant species is $\text{Cu}^{2+}(\text{aq})$ (90.8 % of $[\text{Cu}^{2+}]_{\text{T}}$): the minor species are $\text{CuSO}_4(\text{aq})$ (6.0 %), CuOH^+ (2.3 %), $\text{CuCO}_3(\text{aq})$ (0.7 %), and CuCl^+ (0.1 %).

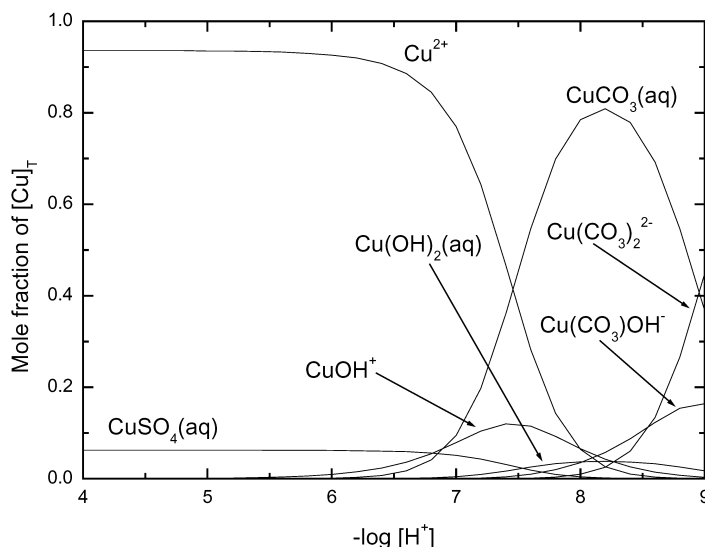


Fig. 4 Speciation diagram for the $\text{Cu}^{2+}\text{-H}^+\text{-Cl}^-\text{-CO}_2\text{-HPO}_4^{2-}\text{-SO}_4^{2-}$ system at $25 \text{ }^\circ\text{C}$ with total concentrations $[\text{Cl}^-]_{\text{T}} = 0.23 \text{ mmol dm}^{-3}$, $[\text{SO}_4^{2-}]_{\text{T}} = 0.42 \text{ mmol dm}^{-3}$ and $[\text{HPO}_4^{2-}]_{\text{T}} = 0.7 \text{ } \mu\text{mol dm}^{-3}$. The total concentration of Cu^{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 $10^{-3.5}$ bar (1 bar = 10^5 Pa). $\text{Log } K_{10}[\text{CO}_2(\text{g}) = \text{CO}_2(\text{aq})] = -1.5$ [93MOR]. All other formation constants are according to Table 6 ($I_c = 0.0015 \text{ mol dm}^{-3}$).

The stability constants applicable at $I = 0.0015 \text{ mol dm}^{-3}$ for the critical species are shown in Table 6. These constants are shown for the equilibrium reactions as defined in this review and also in the format used in the speciation calculations, i.e., in terms of the component species H_2CO_3 .

Table 6 Stability constants for species critical to the speciation of Cu^{II} in fresh water and seawater at $25 \text{ }^\circ\text{C}$ ¹.

Reaction	Medium ionic strength $I_c/\text{mol dm}^{-3}$		
	$\text{Log}_{10} K^\circ$ ($I = 0$)	$\text{Log}_{10} K$ ($I = 0.0015$)	$\text{Log}_{10} K$ ($I = 0.70$)
$\text{Cu}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{CuOH}^+ + \text{H}^+$	-7.95 ± 0.16	-7.99 ± 0.16	-8.10 ± 0.22
$\text{Cu}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Cu}(\text{OH})_2(\text{aq}) + 2\text{H}^+$	-16.20 ± 0.2	-16.24 ± 0.2	-16.65 ± 0.4
$\text{Cu}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{CuCO}_3(\text{aq})$	6.75 ± 0.03	6.60 ± 0.03	5.37 ± 0.06
$\text{Cu}^{2+} + \text{H}_2\text{CO}_3 \rightleftharpoons \text{CuCO}_3(\text{aq}) + 2\text{H}^+$	-9.94 ± 0.03	-9.98 ± 0.03	-10.15 ± 0.06
$\text{Cu}^{2+} + 2\text{CO}_3^{2-} \rightleftharpoons \text{Cu}(\text{CO}_3)_2^{2-}$	10.30 ± 0.10	10.15 ± 0.10	8.58 ± 0.24
$\text{Cu}^{2+} + 2\text{H}_2\text{CO}_3 \rightleftharpoons \text{Cu}(\text{CO}_3)_2^{2-} + 4\text{H}^+$	-23.08 ± 0.10	-23.01 ± 0.10	-22.46 ± 0.24
$\text{Cu}^{2+} + \text{H}_2\text{O} + \text{CO}_3^{2-} \rightleftharpoons \text{Cu}(\text{CO}_3)\text{OH}^- + \text{H}^+$	-2.79 ± 0.30^2	-2.90 ± 0.30^2	-3.87 ± 0.35^2
$\text{Cu}^{2+} + \text{H}_2\text{CO}_3 \rightleftharpoons \text{Cu}(\text{CO}_3)\text{OH}^- + 3\text{H}^+$	-19.48 ± 0.30^2	-19.48 ± 0.30^2	-19.19 ± 0.35^2
$\text{Cu}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{CuSO}_4(\text{aq})$	2.35 ± 0.05	2.20 ± 0.05^3	0.73 ± 0.10^3
$\text{Cu}^{2+} + \text{Cl}^- \rightleftharpoons \text{CuCl}^+$	0.83 ± 0.09	0.76 ± 0.09	0.11 ± 0.10
$\text{Cu}^{2+} + 2\text{Cl}^- \rightleftharpoons \text{CuCl}_2(\text{aq})$	0.6 ± 0.30	0.49 ± 0.30	-0.46 ± 0.35
$\text{H}_2\text{CO}_3 \rightleftharpoons \text{HCO}_3^- + \text{H}^+$	-6.355 ± 0.003	-6.317 ± 0.003	-5.983 ± 0.003
$\text{H}_2\text{CO}_3 \rightleftharpoons \text{CO}_3^{2-} + 2\text{H}^+$	-16.691 ± 0.008	-16.58 ± 0.003	-15.52 ± 0.003
$\text{Mg}^{2+} + \text{H}_2\text{CO}_3 \rightleftharpoons \text{MgHCO}_3^+ + \text{H}^+$	-5.67		-6.21
$\text{Mg}^{2+} + \text{H}_2\text{CO}_3 \rightleftharpoons \text{MgCO}_3(\text{aq}) + 2\text{H}^+$	-13.81		-14.15
$\text{Mg}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{MgCO}_3(\text{aq})$	2.88		1.37
$\text{Mg}^{2+} + \text{CO}_3^{2-} + \text{H}^+ \rightleftharpoons \text{MgHCO}_3^+$	11.02		9.31
$\text{Mg}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{MgSO}_4(\text{aq})$	2.23		0.87
$\text{Ca}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{CaSO}_4(\text{aq})$	2.31		0.91
$\text{Ca}^{2+} + \text{H}_2\text{CO}_3 \rightleftharpoons \text{CaHCO}_3^+ + \text{H}^+$	-5.36		-5.94
$\text{Ca}^{2+} + \text{H}_2\text{CO}_3 \rightleftharpoons \text{CaCO}_3(\text{aq}) + 2\text{H}^+$	-13.54		-13.92
$\text{Ca}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{CaCO}_3(\text{aq})$	3.15		1.60
$\text{Ca}^{2+} + \text{CO}_3^{2-} + \text{H}^+ \rightleftharpoons \text{CaHCO}_3^+$	11.65		9.58

¹ $\text{Log}_{10} K_1^\circ$ values for Mg^{2+} and Ca^{2+} complexes taken from [2005PET].

²Values for $\text{Cu}(\text{CO}_3)\text{OH}^-$ are indicative only; see Section 6.3.4

³Calculated from $\text{log}_{10} K_1^\circ$ and assuming $\Delta\epsilon = -(0.16 \pm 0.07) \text{ kg mol}^{-1}$ and $a_B = 1.15$; see Section 6.4.1.

The $\Delta\epsilon$ values given in this review generally apply to NaClO_4 media. For calculations in fresh water media of low ionic strength, (i) the use of $\Delta\epsilon$ (NaClO_4) values has minimal effect, and (ii) the activity of water can be set equal to one.

9.2 Seawater and saline systems

Distinctive features of saline systems are the higher pH, the much higher concentrations of Cl^- , HCO_3^- , CO_3^{2-} , and SO_4^{2-} , and the significant concentrations of Mg^{2+} and Ca^{2+} both of which form moderately stable complexes with CO_3^{2-} and SO_4^{2-} [2005PET]. Although the pH of seawater is in a narrow band ($-\text{log}_{10} [\text{H}^+]$ ca. 8.2 ± 0.2 for an open system at $25 \text{ }^\circ\text{C}$), it is informative to effect a calculation for a more generic saline system over a range of pH but approximating to seawater composition. The calculations presented here included all of the inorganic components of seawater with the exception of trace metals, fluoride, bromide, silicate, and borate. It is noted that for this medium an approximation is involved in using SIT parameters, $\Delta\epsilon$, that were derived for NaClO_4 media; however, the overall uncertainty is small because of the relative importance of the terms $\Delta z^2 D$ and $\Delta\epsilon I_m$ in eq. 4.

For these calculations, $\log_{10} K_1$ for $\text{CuSO}_4(\text{aq})$ was calculated from $\log_{10} K_1^\circ$ by using the values $\Delta\epsilon(29) = -(0.16 \pm 0.07) \text{ kg mol}^{-1}$ and $a_j B = 1.15$ (Table 6). The calculations were performed (a) with, and (b) without inclusion of the competing reactions involving Ca^{2+} and Mg^{2+} , respectively. Weaker interactions, such as those between Na^+ and CO_3^{2-} and SO_4^{2-} , are considered as an intrinsic aspect of the SIT theory when applied to measurements in NaClO_4 medium and so do not require inclusion as ion pairing interactions in the speciation calculations. The speciation diagram for case (a) (Fig. 5a) indicates that at $-\log_{10} [\text{H}^+] < 6$, the composition is ca. 52.5 % $\text{Cu}^{2+}(\text{aq})$, 36.2 % CuCl^+ , 5.2 %

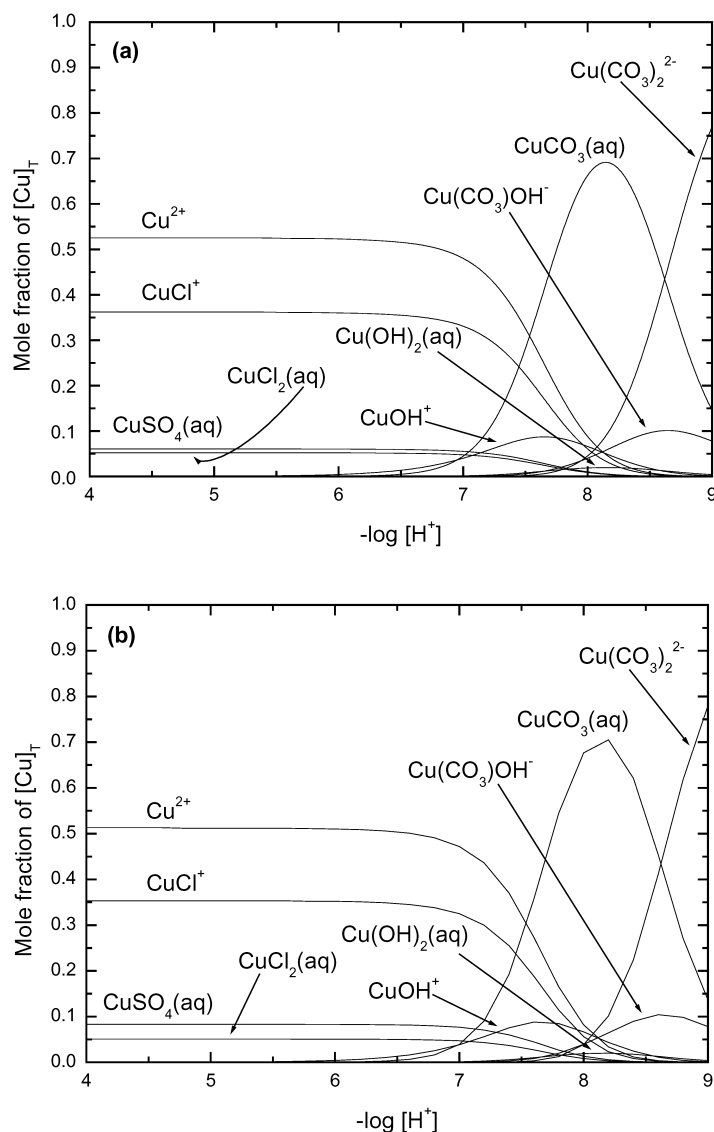


Fig. 5 Speciation diagram for the $\text{Cu}^{2+}\text{-H}^+\text{-Cl}^-\text{-CO}_2\text{-HPO}_4^{2-}\text{-SO}_4^{2-}$ system at 25 °C in a simulated seawater medium, $I_c = 0.70 \text{ mol dm}^{-3}$. The total concentration of Cu^{II} was set to 1 nmol dm^{-3} , and it was assumed that the system was in equilibrium with air having a CO_2 fugacity of $10^{-3.5} \text{ bar}$ (1 bar = 10^5 Pa). $\log K_{10}[\text{CO}_2(\text{g}) = \text{CO}_2(\text{aq})] = -1.5$ [93MOR]. All other formation constants are according to Table 6 ($I_c = 0.70 \text{ mol dm}^{-3}$) or Section 9.2. (a): including carbonato- and sulfato-complexes of Mg^{2+} and Ca^{2+} ; (b): excluding carbonato- and sulfato-complexes of Mg^{2+} and Ca^{2+} .

$\text{CuCl}_2(\text{aq})$, 6.1 % $\text{CuSO}_4(\text{aq})$. In contrast, at $-\log_{10} [\text{H}^+] = 8.2$, the strongly basic carbonate ion dominates complex formation and the composition is ca. 70.6 % $\text{CuCO}_3(\text{aq})$, 10.2 % $\text{Cu}(\text{CO}_3)_2^{2-}$, 4.4 % CuOH^+ , 3.4 % $\text{Cu}^{2+}(\text{aq})$, 2.3 % CuCl^+ , 6.4 % $\text{Cu}(\text{CO}_3)\text{OH}^-$, 2.0 % $\text{Cu}(\text{OH})_2(\text{aq})$, 0.3 % $\text{CuCl}_2(\text{aq})$, and 0.4 % $\text{CuSO}_4(\text{aq})$.

For case (b) the exclusion of carbonate complexes of Ca^{2+} and Mg^{2+} from the model did not affect the concentrations of Cu^{II} -hydroxido or -carbonato species because at a given pH the concentration of free CO_3^{2-} is constant in an open system in equilibrium with CO_2 . The exclusion of sulfato complexes of Ca^{2+} ($\log_{10} K_1^\circ = 2.31$) and Mg^{2+} ($\log_{10} K_1^\circ = 2.23$) from the model had a small effect on the concentration of $\text{CuSO}_4(\text{aq})$ at pH 8.2 (increased to 0.6 %). Therefore, these competing reactions have no significant impact on the species distribution of Cu^{II} in seawater, even though 15.5 % of Ca^{2+} and 14.5 % of Mg^{2+} is present as sulfato complexes. In contrast, at $\text{pH} < 6.5$, the effects, although still minor, are more significant. The calculated percentage $\text{CuSO}_4(\text{aq})$ increases from 6.1 to 8.3 %; there are corresponding small decreases in the percentages of $\text{Cu}^{2+}(\text{aq})$ (to 51.2 %), CuCl^+ (to 35.3 %), and $\text{CuCl}_2(\text{aq})$ (to 5.1 %).

The percentage increase in ionic strength in the range $-\log_{10} [\text{H}^+] = 7$ to 9 due to the increase in $[\text{HCO}_3^-]$ and $[\text{CO}_3^{2-}]$ at constant $f(\text{CO}_2)$ was negligible in this medium and therefore had minimal effect on the stability constants. The stability constants calculated by WinSGW applicable at $I_c = 0.70 \text{ mol dm}^{-3}$ for the critical species are shown in Table 6.

9.3 SUMMARY

The speciation calculations indicate that, except at high salinities, the ion $\text{Cu}^{2+}(\text{aq})$ is the dominant Cu^{II} species at $-\log_{10} [\text{H}^+] < 7.5$ in the absence of organic ligands. In non-humic fresh waters, a small percentage of Cu^{II} will be present as the species $\text{CuSO}_4(\text{aq})$. In weakly alkaline saline solutions, $7.5 < -\log_{10} [\text{H}^+] < 8.5$, in the absence of organic ligands, the speciation is dominated by the uncharged species $\text{CuCO}_3(\text{aq})$, with moderate contributions from $\text{Cu}^{2+}(\text{aq})$, CuCl^+ , and CuOH^+ and minor contributions from $\text{CuSO}_4(\text{aq})$, $\text{Cu}(\text{CO}_3)\text{OH}^-$, and $\text{Cu}(\text{CO}_3)_2^{2-}$.

These results indicate that for reliable speciation calculations of Cu^{II} in environmental systems the accuracy of the equilibrium data for formation of $\text{CuCO}_3(\text{aq})$ (reaction 21), CuOH^+ (reaction 5), $\text{CuSO}_4(\text{aq})$ (reaction 29), $\text{Cu}(\text{CO}_3)\text{OH}^-$ (reaction 28), $\text{Cu}(\text{CO}_3)_2^{2-}$ (reaction 23), CuCl^+ (reaction 17), and $\text{CuCl}_2(\text{aq})$ (reaction 18) is crucial. This document provides critically evaluated, IUPAC-Recommended (or Provisional) standard equilibrium constant values for the formation of each of these species. Table 6 also provides the user with values for their stability constants in media at $I_c = 0.0015 \text{ mol dm}^{-3}$ (simulating fresh water) and $I_c = 0.70 \text{ mol dm}^{-3}$ (simulating seawater).

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

10.1 Quantities, symbols, and units

Name	Symbol	Definition	SI Unit
amount of substance	n	(SI base unit)	mol
molar mass	M	$M_A = m_A/n_A$ (= mass/amount)	kg mol ⁻¹
molality	m, b	$m_B = n_B/M_A(n - \sum_B n_B)$	mol kg ⁻¹
amount concentration	$c,$ [species], M	$c_B = [\text{species B}] = n_B/V$	mol m ⁻³ a(mol dm ⁻³)
ionic strength, molality basis	I_m	$I_m = \frac{1}{2} \sum m_B z_B^2$	mol kg ⁻¹
ionic strength, amount concentration basis	I_c	$I_c = \frac{1}{2} \sum c_B z_B^2$	mol m ⁻³ a(mol dm ⁻³)
stepwise formation constant (equilibrium concentration product) ^b	K_n	$K_n = [\text{ML}_n]/[\text{ML}_{n-1}][\text{L}]$ for the reaction: $\text{ML}_{n-1} + \text{L} \rightleftharpoons \text{ML}_n$	m ³ mol ⁻¹ a(dm ³ mol ⁻¹)
cumulative (overall) formation constant ^b	β_n	$\beta_n = [\text{ML}_n]/[\text{M}][\text{L}]^n$ for the reaction: $\text{M} + n\text{L} \rightleftharpoons \text{ML}_n$	(m ³ mol ⁻¹) ⁿ a(dm ³ mol ⁻¹) ⁿ
stepwise (metal ion) hydrolysis constant ^b	* K_n	* $K_n = [\text{M}(\text{H}_2\text{O})_{6-n}(\text{OH})_n][\text{H}^+]/[\text{M}(\text{H}_2\text{O})_{6-n+1}(\text{OH})_{n-1}]$ for the reaction: $\text{M}(\text{H}_2\text{O})_{6-n+1}(\text{OH})_{n-1} + \text{H}_2\text{O} \rightleftharpoons \text{M}(\text{H}_2\text{O})_{6-n}(\text{OH})_n + \text{H}^+$ or: $\text{M}(\text{OH})_{n-1} + \text{H}_2\text{O} \rightleftharpoons \text{M}(\text{OH})_n + \text{H}^+$	mol m ⁻³ a(mol dm ⁻³)
cumulative (metal ion) hydrolysis constant ^b	* β_n	* $\beta_n = [\text{M}(\text{H}_2\text{O})_{6-n}(\text{OH})_n][\text{H}^+]^n/[\text{M}(\text{H}_2\text{O})_6]$ for: $\text{M}(\text{H}_2\text{O})_6 + n\text{H}_2\text{O} \rightleftharpoons \text{M}(\text{H}_2\text{O})_{6-n}(\text{OH})_n + n\text{H}^+$	(mol m ⁻³) ⁿ a(mol dm ⁻³) ⁿ
	* $\beta_{m,n}$	* $\beta_{m,n} = [\text{M}_m(\text{OH})_n][\text{H}^+]^n/[\text{M}(\text{H}_2\text{O})_6]^m$ for: $m\text{M}(\text{H}_2\text{O})_6 + n\text{H}_2\text{O} \rightleftharpoons \text{M}_m(\text{OH})_n + n\text{H}^+$	(mol m ⁻³) ^{n-m+1} a(mol dm ⁻³) ^{n-m+1}
solubility constant ^b	K_{s0}	$K_{s0} = [\text{M}][\text{X}]^p$ for the reaction: $\text{MX}_p(\text{s}) \rightleftharpoons \text{M} + p\text{X}$	(mol m ⁻³) ^{p+1} a(mol dm ⁻³) ^{p+1}
solubility constant ^b	K_{sn}	$K_{sn} = [\text{MX}_{p+q}]/[\text{X}]^q$ (where $n = p + q$) for the reaction: $\text{MX}_p(\text{s}) + q\text{X} \rightleftharpoons \text{MX}_{p+q}$	(m ³ mol ⁻¹) ^{q-1} a(dm ³ mol ⁻¹) ^{q-1}

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(Continued).

Name	Symbol	Definition	SI Unit
solubility constant ^b	$*K_{s0}$	$*K_{s0} = [M]/[H^+]^p$ for the reaction: $M(OH)_p(s) + pH^+ \rightleftharpoons M + pH_2O$	$(m^3 \text{ mol}^{-1})^{p-1}$ ^a $(\text{dm}^3 \text{ mol}^{-1})^{p-1}$
cumulative (overall) equilibrium concentration product ^b	$\beta_{p,q,r}$	$\beta_{p,q,r} = [M_p L_q(OH)_r]/[H^+]^r/[M]^p/[L]^q$ for the reaction: $pM + qL + rH_2O \rightleftharpoons M_p L_q(OH)_r + rH^+$	$(\text{mol m}^{-3})^{r-p-q+1}$ ^a $(\text{mol dm}^{-3})^{r-p-q+1}$
(molar) enthalpy	H_m	H/n	J mol^{-1}
(molar) reaction enthalpy	$\Delta_r H_m$	$\Delta_r H_m = \Sigma(H_m(\text{products})) - \Sigma(H_m(\text{reactants}))$	J mol^{-1}
activity coefficient, molality basis	γ_m	$RT \ln(\gamma_{m,B} m_B/m^\ominus) = \mu_B - \mu_B^\ominus = \lim_{m_B \rightarrow 0} [\mu_B - RT \ln(m_B/m^\ominus)]$	1
osmotic coefficient, molality basis	φ_m	$\varphi_{m,A} = (\mu_A^* - \mu_A)/RTM_A \Sigma m_B$	1
temperature (Celsius)	θ, t	$\theta/^\circ\text{C} = T/\text{K} - 273.15$	$^\circ\text{C}$
temperature, thermodynamic	T	(SI base unit)	K

^aCommon units used in this report.^bEach amount concentration should be considered as [species]/ c^\ominus , where $c^\ominus = 1 \text{ mol dm}^{-3}$ is the standard amount concentration, thus making the argument in each $\log_{10} K_n$ ($\log_{10} \beta_{p,q,r}$) dimensionless.

10.2 Subscripts and superscripts

10.2.1 Subscripts

A, B general constituent

m molal = mol kg^{-1}

c amount concentration

10.2.2 Superscripts

o standard state ($I \rightarrow 0$)

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APPENDIX 1A

Data evaluation criteria

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

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

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

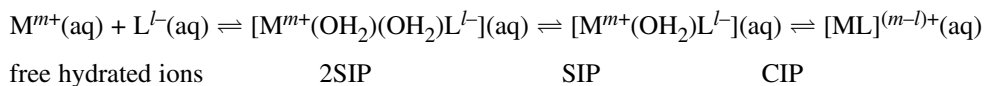
- (a) data for temperature(s) other than 25 °C, cannot be corrected to 25 °C, or the temperature is not defined;
- (b) data for a different medium and are not readily comparable with other data;
- (c) ionic strength has not been held constant, or the medium composition has changed excessively, or inadequate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

APPENDIX 1B**Complex formation by polyvalent anions (SO₄²⁻, CO₃²⁻, PO₄³⁻)**

Some comments on the difficulties of quantifying complex formation between polyvalent ions were made in the previous article in this series [2005PBA]. Nevertheless, the unusually detailed studies that have been made on the Cu²⁺/SO₄²⁻ system justify further discussion of these problems. It is emphasized, as previously [2005PBA], that although the comments focus on the sulfate ion, similar considerations apply to all strongly hydrated anions including carbonate and phosphate.

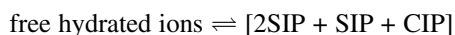
Problems associated with ion pair formation

Association of strongly hydrated ions occurs via the well-known Eigen mechanism [62EIG]:



where 2SIP, SIP, and CIP refer respectively to double solvent-separated, solvent-shared, and contact ion pairs.

From a purely thermodynamic point of view, the mechanism of association is unimportant because thermodynamic (and conductivity) measurements do not distinguish between the various ion pair types, i.e., they measure only the overall amount of association



However, as discussed in detail elsewhere [2003RUD, 2004BCa, 2006HEF], the presence of solvent-separated species (2SIPs and SIPs) creates difficulties for the common spectroscopic methods (UV-vis, NMR, IR, and Raman) because in general they detect only CIPs. In the presence of significant amounts of solvent-separated IPs, the association constants obtained from such spectroscopic measurements may be seriously in error [2006HEF]. The magnitude of the error depends on the system and the technique. Such effects need to be considered when critically evaluating stability constant data and great care needs to be exercised before equating spectroscopically-derived constants with those measured by thermodynamic (or conductivity) methods. In general, it is unwise to use spectroscopic constants for speciation calculations whenever significant amounts of solvent-separated IPs are likely to be present [2003RUD, 2004BCa, 2006HEF].

A similar caveat applies to the so-called inner- and outer-sphere association constants that have been derived from various essentially arbitrary assumptions about the species present. Such constants are again unsuitable for speciation calculations and therefore are ignored in this compilation. In contrast, techniques such as ultrasonic absorption or dielectric spectroscopy, which (respectively) detect all of the equilibria or all of the ion pair species present, produce constants that are in quantitative agreement with the thermodynamic data.

Problems associated with activity coefficients: The determination of K°

Because of the availability of numerous high quality conductivity and, to a lesser extent, activity (osmotic) coefficient data, a detailed consideration has been given by a number of authors [55BPb, 65MAe, 71HPa, 72PIa] to the interplay between calculated ion association constants and activity coefficient models adopted for the CuSO₄(aq) system. Unfortunately, the insights produced by these comprehensive and sophisticated investigations have been largely ignored in subsequent publications reporting stability constant or related data. It is inappropriate here to go into the details of the investigations by Pitzer [72PIa], Prue et al. [55BPb, 71HPa], and others on this topic, but a summary of

the key findings is necessary because of their implications for the critical evaluation of the literature values of K and for the determination of K° via the SIT.

The problem may be stated as follows. The association between Cu^{2+} and SO_4^{2-} in aqueous solution is relatively weak ($\log_{10} K_1^\circ \approx 2$) and, because of the high charges on the ions, it is strongly dependent on ionic strength (e.g., $\log_{10} K_1 \approx 1$ at $I_c \approx 1 \text{ mol dm}^{-3}$). For such systems, there is at present *no theoretically rigorous method* for disentangling weak complexation and activity coefficient effects. In extended Debye–Hückel treatments (of which SIT is a relatively simple example) this problem typically evidences itself in the form of a strong correlation between the calculated value of K° and the so-called “distance of closest approach” parameter $\overset{\circ}{a}$ (or d) assumed in the activity coefficient expression. Although the more sophisticated “chemical” models for the calculation of activity coefficients [98BAR] permit sensible definitions of d , and hence calculation of K° , they still involve somewhat arbitrary assumptions. Pending further theoretical developments, this means that all estimates of K° , however good the accuracy of the data on which they are based and however precise the fit obtained, contain a degree of arbitrariness. To put it another way, the true uncertainty in such K° values is *far* greater than their apparent precision.

Perceptive investigators have long recognized this. For example, Pitzer [72PIa], using an extended Debye–Hückel model, derived K° and related thermodynamic quantities from a combination of high-quality potentiometric, osmotic coefficient, and calorimetric (heat of dilution) data from the literature. After a detailed analysis, he noted that, “variations in theoretical treatment may substantially change [K° , and that] it may become desirable to adopt reasonable but *arbitrary conventions* [present authors’ italics] which would make K values unambiguous” [but, note, not more accurate]. Similarly, Prue et al. [71HPa] and others [81YYa, 2005BES], analyzing reliable high-accuracy conductivity data, have shown that K° is significantly dependent both on the activity coefficient expression *and* the conductivity expression adopted. These studies have shown in detail why it is not possible to unambiguously fix the value of K° with the sort of accuracy which would normally be expected from high-quality data for such an apparently uncomplicated system.

It is difficult to define the uncertainty created by these theoretical inadequacies, but at present it would appear that it is not possible to define $\log_{10} K^\circ$ for weak complexes or ion pairs to better than ca. ± 0.1 , regardless of the quality of the data. It should also be noted that some modern theories of activity coefficients, such as that of Pitzer [91PIT], do not invoke *any* complexation in divalent metal sulfate solutions [97MAL]. Instead, the observed variations (in osmotic coefficients, heats of dilution, etc.) with concentration are accounted for (subsumed by) a set of empirical “interaction parameters”. This has led some authors [97MAL] to suggest that complexation in divalent metal sulfate solutions is “fictitious”. However, as discussed in detail elsewhere [2003RUD, 2004BCa, 2006HEF], the independent evidence from a variety of techniques for the existence of complexes in these solutions is extensive. Until activity coefficient models can properly take into account the actual species present, without resort to arbitrary assumptions or empirical parameters, it seems that little improvement on this situation will occur.

K° and SIT

As developed by Brønsted, Scatchard, and Guggenheim, SIT is a relatively simple extension of the Debye–Hückel theory that does not address the issues discussed above [97GRE]. Because it is not theoretically rigorous, SIT, however useful, cannot produce a more reliable estimate of K° than those obtained from more sophisticated analyses, especially when applied to reliable measurements at low I . On the other hand, most speciation calculations do not refer to $I = 0$ and SIT can still be utilized as a convenient tool to correlate values of K at finite I .

APPENDIX 2

Selected equilibrium constants

Table A2-1 Selected stability constants for the reaction: $\text{Cu}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{CuOH}^+ + \text{H}^+$ at 25 °C.

Method	Ionic medium		<i>t</i> /°C	Log ₁₀ * <i>K</i> ₁ (reported)	Log ₁₀ * <i>K</i> ₁ (accepted) ²	Ref. ³
	Amount ¹ concn./mol dm ⁻³	Molality/ mol kg ⁻¹				
ise	0.05 NaClO ₄ ⁴	0.050	25	-8.12 ± 0.1	-8.12 ± 0.20	80PKb
ise	0.70 NaClO ₄ ⁴	0.70	25	-8.09 ± 0.1	-8.09 ± 0.20	80PKb
gl	3.0 NaClO ₄	3.503	25	-7.4 ± 0.1	-7.33 ± 0.20	82BBb

¹Conventional terminology for "amount concentration".

²Constant corrected from molar to molal units and including our assigned errors. Many reported uncertainties reflect analytical and numerical precision but not systematic errors; log₁₀ *K_n* (reported). Some values have much stronger experimental bases than others, some result from a few, others from a large number of datum points; experimental methods may also differ. We assign an additional uncertainty to each value that reflects our estimation of accuracy and reliability of the experimental methods, log₁₀ *K_n* (accepted), according to [92GRE, Appendix C].

³References for rejected data: [2000MSa]^j, [99PPa]^{a,b}, [99PGa]^j, [95STa]^a, [92OMa]^{e,j}, [91CSa]^a, [85RDb]^a, [84GLb]^j, [80NAd]^{a,d}, [79SUN]^j, [79SDB]^j, [77VNa]^{b,j}, [76ACb]^j, [72OKa]^b, [70KAb]^b, [70CHc]^a, [64ACa]^c, [58ACa]^j, [52CCa]^{a,j}, [43PEa]^a, [38OGa]^c, [37CBa]^a, [37QUa]^{e,j}, [35BJa]^{a,j}, [13KUa]^a, [09ALa]^a

⁴Reported on the molality (mol kg⁻¹) scale.

Table A2-2 Selected stability constants for the reaction: $\text{Cu}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Cu}(\text{OH})_2(\text{aq})$ at 25 °C.

Method	Ionic medium		<i>t</i> /°C	Log ₁₀ * <i>β</i> ₂ (reported)	Log ₁₀ * <i>β</i> ₂ (accepted) ¹	Ref. ²
	Molality/ mol kg ⁻¹					
ise	0 corr		25	-16.22	-16.22 ± 0.30	79SUN
ise	0.05 NaClO ₄		25	-16.40 ± 0.10	-16.40 ± 0.20	80PKb
ise	0.70 NaClO ₄		25	-16.68 ± 0.10	-16.68 ± 0.20	80PKb

¹Constant including our assigned errors.

²References for rejected data: [99PPa]^{a,b}, [94NVa]^{a,b}, [92OMa]^{e,i}, [91CSa]^a, [85RDb]^a, [84GLb]^j, [80NAd]^{a,d}, [68SMd]^{c,j}, [67MSb]^{a,c}, [37QUa]^j.

Table A2-3 Selected stability constants for the formation of $\text{Cu}_2\text{OH}^{3+}$, $\text{Cu}_2(\text{OH})_2^{2+}$, and $\text{Cu}_3(\text{OH})_4^{2+}$.

Method	Ionic medium		<i>t</i> /°C	$\text{Log}_{10} \text{*}\beta_{\text{m,n}}$ (reported)	$\text{Log}_{10} \text{*}\beta_{\text{m,n}}$ (accepted) ¹	Ref. ²
	Amount concn./mol dm ⁻³	Molality/ mol kg ⁻¹				
$2\text{Cu}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{Cu}_2\text{OH}^{3+} + \text{H}^+ (\text{*}\beta_{2,1})$						
gl	0.10 NaClO ₄	0.101	25	-6.08 ± 0.14	-6.08 ± 0.30	97RSb
gl	0.25 NaClO ₄	0.254	25	-6.06 ± 0.11	-6.06 ± 0.30	97RSb
gl	0.50 NaClO ₄	0.513	25	-6.07 ± 0.07	-6.07 ± 0.20	97RSb
gl	0.75 NaClO ₄	0.779	25	-6.09 ± 0.06	-6.09 ± 0.20	97RSb
gl	1.00 NaClO ₄	1.051	25	-6.11 ± 0.09	-6.11 ± 0.20	97RSb
gl	3.0 NaClO ₄	3.503	25	-5.75 ± 0.10	-5.75 ± 0.20	84NEa
gl	3.0 NaClO ₄	3.503	25	-6.02 ± 0.02	-6.02 ± 0.10	82BBb
$2\text{Cu}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Cu}_2(\text{OH})_2^{2+} + 2\text{H}^+ (\text{*}\beta_{2,2})$						
gl	0.10 NaClO ₄	0.101	25	-10.75 ± 0.01	-10.75 ± 0.20	76ACb
gl	0.10 NaClO ₄	0.101	25	-10.72 ± 0.05	-10.72 ± 0.20	97RSb
gl	0.25 NaClO ₄	0.254	25	-10.76 ± 0.04	-10.75 ± 0.20	97RSb
gl	0.50 NaClO ₄	0.513	25	-10.77 ± 0.03	-10.76 ± 0.10	97RSb
gl	0.75 NaClO ₄	0.779	25	-10.77 ± 0.02	-10.75 ± 0.10	97RSb
gl	1.00 NaClO ₄	1.051	25	-10.78 ± 0.04	-10.76 ± 0.10	97RSb
gl	3.0 NaClO ₄	3.503	25	-10.6 ± 0.1	-10.53 ± 0.20	56BEa
gl	3.0 NaClO ₄	3.503	25	-10.93 ± 0.02	-10.86 ± 0.10	82BBb
$3\text{Cu}^{2+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Cu}_3(\text{OH})_4^{2+} + 4\text{H}^+ (\text{*}\beta_{3,4})$						
gl	0.10 NaClO ₄	0.101	25	-21.37 ± 0.04	-21.37 ± 0.20	76ACb
gl	0.10 KNO ₃	0.101	25	-21.62 ± 0.03	-21.62 ± 0.20	79SDb

¹Constant corrected from molar to molal units and including our assigned errors.²References for rejected data: [92OMa]^{e,i}, [85RDb]^a, [79SDb]^b, [78WNB]^b, [77VNa]^{b,e,j}, [72OKa]^b, [70KAb]^b, [70Chc]^a, [70ARb]^{e,j}, [67MSb]^{a,c}, [64WEB]^a, [64ACa]^c, [60PEc]^a, [57LHa]^b, [43PEa]^a, [39HAa]^d.**Table A2-4** Selected stability constants for the formation of CuCl^+ and $\text{CuCl}_2(\text{aq})$ at 25 °C.

Method	Ionic medium		<i>t</i> /°C	$\text{Log}_{10} K$ (reported)	$\text{Log}_{10} K$ (accepted) ¹	Ref. ^{2,6}
	Amount concn./mol dm ⁻³	Molality/ mol kg ⁻¹				
$\text{Cu}^{2+} + \text{Cl}^- \rightleftharpoons \text{CuCl}^+ (K_1)$						
sp	1.0 NaClO ₄	1.051	25	0.07 ± 0.03	0.05 ± 0.10	85ABb
kin	1.0 NaClO ₄	1.051	25	0.15 ± 0.09	0.13 ± 0.30	73HHB
sp	2.0 NaClO ₄	2.212	25	0.086	0.04 ± 0.10	60LRa
sp	3.0 NaClO ₄	3.503	25	-0.004 ± 0.066	-0.07 ± 0.10	77Sjd
sp	5.0 NaClO ₄	6.584	25	0.18	0.06 ± 0.20	77BSa
sp	5.0 NaClO ₄	6.584	25	0.16 ± 0.03	0.04 ± 0.10	81AHa
sol	5.0 NaClO ₄	6.584	25	0.37 ± 0.01 ³	0.25 ± 0.20	86RAa
sol	6.0 NaClO ₄	6.0	25	0.057 ± 0.015	0.06 ± 0.20	89IPa

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Table A2-4 (Continued).

Method	Ionic medium		<i>t</i> /°C	Log ₁₀ <i>K</i> (reported)	Log ₁₀ <i>K</i> (accepted) ¹	Ref. ^{2,6}
	Amount concn./mol dm ⁻³	Molality/ mol kg ⁻¹				
Cu²⁺ + 2Cl⁻ ⇌ CuCl₂(aq) (β₂)						
sp	1.0 HClO ₄	1.051	25	-0.52 ± 0.28 ⁵	-0.56 ± 0.40	50MDa
sp	3.0 NaClO ₄	3.503	25	-0.40 ± 0.09	-0.54 ± 0.20	77SJd
sp	5.0 NaClO ₄	6.584	25	-0.20	-0.44 ± 0.30	77BSa
sp	5.0 NaClO ₄	6.584	25	-0.24 ± 0.03	-0.48 ± 0.20	81AHa
sol	5.0 NaClO ₄	6.584	25	0.17 ± 0.06 ³	-0.07 ± 0.30	86RAa
sol	6.0 NaClO ₄ ⁴	6.0	25	-0.26 ± 0.04	-0.26 ± 0.30	89IPa

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

²References for rejected data: [76KFb]^c, [73SCc]ⁱ, [74BRa]^e, [74BRb]^e.

³This is a reanalysis of the experiment reported in [83RFa].

⁴Reported on the molality (mol kg⁻¹) scale.

⁵The constant from this study was used here, although it refers to HClO₄ medium (see text).

⁶Reference for rejected data: [73SCc]ⁱ.

Table A2-5 Selected stability constants for the system Cu²⁺-H⁺-CO₃²⁻ at 25 °C and 10⁵ Pa (1 bar).

Method	Ionic medium		<i>t</i> /°C	Log ₁₀ <i>K</i> (reported)	Log ₁₀ <i>K</i> (accepted) ¹	Ref.
	Amount concn./mol dm ⁻³	Molality/ mol kg ⁻¹				
Cu²⁺ + CO₃²⁻ ⇌ CuCO₃(aq) (K₁)²						
sol	0 corr	0 corr	25	6.77 ± 0.08	6.77 ± 0.1	58SIa
ise	0 corr	0 corr	25	6.74	6.74 ± 0.05	79SUN
ise	0.022 NaHCO ₃	0.022	25	6.25 ± 0.02	6.25 ± 0.04	85BMb
ise	0.70 NaClO ₄	0.725	25	5.38 ± 0.01	5.36 ± 0.04	85BMb
ise	0.72 NaClO ₄	0.746	25	5.38 ± 0.02	5.36 ± 0.05	85BMb
ise	1.00 NaClO ₄	1.051	25	5.30 ± 0.01	5.28 ± 0.04	85BMb
Cu²⁺ + 2CO₃²⁻ ⇌ Cu(CO₃)₂²⁻ (β₂)³						
ise	0 corr	0 corr	25	10.24	10.24 ± 0.2	79SUN
ise	0.022 NaClO ₄	0.022	25	9.98 ± 0.07	9.98 ± 0.2	85BMb
ise	0.70 NaClO ₄	0.725	25	8.54 ± 0.01	8.51 ± 0.2	85BMb
ise	0.72 NaClO ₄	0.746	25	8.61 ± 0.06	8.58 ± 0.2	85BMb
ise	1.00 NaClO ₄	1.051	25	8.49 ± 0.05	8.45 ± 0.2	85BMb
Cu²⁺ + HCO₃⁻ ⇌ CuHCO₃⁺ + 4						
ise	0.022 NaClO ₄	0.022	25	1.60 ± 0.03	1.60 ± 0.1	85BMb
ise	0.70 NaClO ₄	0.725	25	0.95 ± 0.14	0.93 ± 0.15	85BMb
ise	0.72 NaClO ₄	0.746	25	0.96 ± 0.04	0.94 ± 0.15	85BMb
ise	1.00 NaClO ₄	1.051	25	0.94 ± 0.11	0.92 ± 0.15	85BMb

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

²References for rejected data: [89SBc]^b, [85SKc]ⁱ, [83ZKa]^{g,h}, [79SGf]^{a,b,h}, [79BKb]^{d,e}, [75EAa]^{b,c,e}, [71STd]^e, [68SRe]^h, [57SCa]^{e,e}.

³References for rejected data: [79SGf]^{a,b,h}, [75EAa]^{b,c,e}, [69FFa]^{a,b}, [68SRe]^h, [59FBa]^{a,b,e}, [58SIa]^e

⁴References for rejected data: [85SKc]ⁱ, [83ZKa]^{g,j,k}, [71STd]^e.

Table A2-6 Selected stability constants for the system $\text{Cu}^{2+}\text{-HCO}_3^-$ at 25 °C and 10^5 Pa (1 bar).

Method	Ionic medium		<i>t</i> /°C	$\text{Log}_{10} K$ (reported) ¹	$\text{Log}_{10} K$ (accepted) ²	Ref.
	Amount concn./mol dm ⁻³	Molality/ mol kg ⁻¹				
$\text{Cu}^{2+} + \text{HCO}_3^- \rightleftharpoons \text{CuCO}_3(\text{aq}) + \text{H}^+ (K)^3$						
sol	0 corr	0 corr	25	-3.55 ± 0.08	-3.55 ± 0.1	58SIa
ise	0 corr	0 corr	25	-3.59	-3.59 ± 0.05	79SUN
ise	0.022 NaHCO ₃	0.022	25	-3.80 ± 0.02	-3.80 ± 0.04	85BMb
ise	0.70 NaClO ₄	0.725	25	-4.17 ± 0.01	-4.17 ± 0.04	85BMb
ise	0.72 NaClO ₄	0.746	25	-4.17 ± 0.02	-4.17 ± 0.05	85BMb
ise	1.0 NaClO ₄	1.051	25	-4.20 ± 0.01	-4.20 ± 0.04	85BMb
$\text{Cu}^{2+} + 2\text{HCO}_3^- \rightleftharpoons \text{Cu}(\text{CO}_3)_2^{2-} + 2\text{H}^+ (K)^4$						
ise	0 corr	0 corr	25	-10.42	-10.42 ± 0.2	79SUN
ise	0.022 NaClO ₄	0.022	25	-10.12 ± 0.07	-10.12 ± 0.2	85BMb
ise	0.70 NaClO ₄	0.725	25	-10.56 ± 0.06	-10.56 ± 0.2	85BMb
ise	0.72 NaClO ₄	0.746	25	-10.49 ± 0.01	-10.49 ± 0.2	85BMb
ise	1.00 NaClO ₄	1.051	25	-10.51 ± 0.05	-10.51 ± 0.2	85BMb

¹Constants calculated using CO_3^{2-} protonation constants assumed in each referenced work.

²Constant corrected from molar to molal units and including our assigned errors.

³References for rejected data: [89SBc]^b, [85SKc]ⁱ, [83ZKa]^{g,h}, [79SGf]^{a,b,h}, [79BKb]^{d,e}, [75EAa]^{b,c,e}, [71STd]^e, [68SRe]^h, [57SCa]^{c,e}.

⁴References for rejected data: [79SGf]^{a,b,h}, [75EAa]^{b,c,e}, [69FFa]^{a,b}, [68SRe]^h, [59FBa]^{a,b,e}, [58SIa]^e.

Table A2-7(a) Selected stability constants for the reaction $\text{Cu}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{CuSO}_4(\text{aq})$ for $I = 0 \text{ mol kg}^{-1}$, as determined by conductivity (and other techniques).

Method	Ionic medium		$t/^\circ\text{C}$	$\text{Log}_{10} K_1^\circ$ (reported) ¹	$\text{Log}_{10} K_1^\circ$ (accepted) ²	Ref. ³
	Molality/ mol kg^{-1}					
cry	0 corr	~0	25	2.33 ± 0.15	2.45 ± 0.20^4	55BPb
cry	0 corr	~0	25	2.33	2.45 ± 0.20^4	56KEb
con	0 corr	25	25	2.37	2.37 ± 0.05	38OGa
recalc(con)	0 corr	25	25	2.36 ± 0.05	2.36 ± 0.05	38OGa, 57DOa
recalc(con)	0 corr	25	25	2.28	2.28 ± 0.10	38OGa, 62AYa
oth ⁵	0 corr	25	25	2.32	2.32 ± 0.10	62AYa, 68YMa
recalc(con)	0 corr	25	25	2.40	2.40 ± 0.05	38OGa, 71HPa
recalc (act, $\Delta_{\text{dil}}H$)	0 corr	25	25	2.40	2.40 ± 0.10	72PIa
con	0 corr	25 ⁶	25	2.42	2.42 ± 0.20^7	83ADc
con	0 corr	25	25	2.31 ± 0.01	2.31 ± 0.05	85SGd
con	0 corr	25	25	2.35 ± 0.09	2.35 ± 0.20	89MBb
con	0 corr	25	25	2.274 ± 0.001	2.27 ± 0.05	94NHa
con	0 corr	25	25	2.43	2.43 ± 0.10	2000TMa
con	0 corr	25 ⁶	25	2.37 ± 0.03	2.37 ± 0.05	2005BES

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

²Constant with errors assigned by reviewer (see text).

³References for rejected data: [27DAb]^l, [38DAa]^l, [52BPa, 61PFa]^{d,h}, [65YKa]^{d,g}, [69SMd]^j, [75TAa]^{h,j}, [77STd]^{h,j}.

⁴Recalculated value to 25 °C assuming $\Delta_r H = 7.3 \text{ kJ mol}^{-1}$ (Table A2-11).

⁵High field conductivity

⁶Data also reported at other temperatures.

⁷Higher uncertainty applied because data at other T reported in the same paper show negative $\Delta_r H$ (cf. Table A2-11).

Table A2-7(b) Selected stability constants for the reaction $\text{Cu}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{CuSO}_4(\text{aq})$ as determined by UV-vis spectrometry in NaClO_4 and LiClO_4 media.

Method	Ionic medium		$t/^\circ\text{C}$	$\text{Log}_{10} K_1$ (reported) ¹	$\text{Log}_{10} K_1$ (accepted) ²	Ref. ³
	Amount concn./ mol dm^{-3}	Molality/ mol kg^{-1}				
sp	→0	→0	25	2.15	2.15 ± 0.20	49NAa, 49NAb
sp	0 corr	0 corr	25	2.33 ± 0.03	2.33 ± 0.20	56BDa
sp	0 corr	0 corr	25	2.28 ± 0.18	2.28 ± 0.20	57DOa
sp	0 corr	0 corr	25	2.32 ± 0.09	2.32 ± 0.20	65MAe
sp	0 corr	0 corr	25	2.35	2.35 ± 0.20	68HPd
sp	→0	→0	25	2.26	2.26 ± 0.20	71KV a
sp	0 corr	0 corr	25 ⁴	2.32 ± 0.02	2.32 ± 0.20	82DKb
sp	→0	→0	25	2.17	2.17 ± 0.20	85LYa
sp	0 corr	0 corr	25	2.24 ± 0.07	2.24 ± 0.20	90GLa
recalc (act, sp)	0 corr	0 corr	25	2.19	2.19 ± 0.20	90WAa
sp	0 corr	0 corr	25 ^{4,5}	2.35 ± 0.05	2.35 ± 0.20	2005MBa
sp	0.041 NaClO_4	0.041 NaClO_4	25	1.64	1.64 ± 0.20	65MAe
sp	0.091 NaClO_4	0.091 NaClO_4	25	1.38	1.38 ± 0.20	65MAe

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Table A2-7(b) (Continued).

Method	Ionic medium		<i>t</i> /°C	Log ₁₀ <i>K</i> ₁ (reported) ¹	Log ₁₀ <i>K</i> ₁ (accepted) ²	Ref. ³
	Amount concn./mol dm ⁻³	Molality/ mol kg ⁻¹				
sp	0.2 LiClO ₄	0.202 LiClO ₄	25	1.21 ⁵	1.20 ± 0.20	85LYa
sp	0.2 NaClO ₄	0.202 NaClO ₄	25	1.02 ⁵	1.01 ± 0.20	85LYa
sp	0.5 LiClO ₄	0.513 LiClO ₄	25	0.84 ⁵	0.83 ± 0.20	49NAa
sp	0.5 LiClO ₄	0.513 LiClO ₄	25	0.96 ⁵	0.95 ± 0.20	85LYa
sp	0.5 NaClO ₄	0.513 NaClO ₄	25	0.80 ⁵	0.79 ± 0.20	49NAb
sp	0.5 NaClO ₄	0.513 NaClO ₄	25	0.77 ⁵	0.76 ± 0.20	85LYa
sp	0.5 NaClO ₄	0.513 NaClO ₄	25	0.90	0.89 ± 0.20	90GLa
sp	1 LiClO ₄	1.050 LiClO ₄	25	0.72 ⁵	0.70 ± 0.20	49NAa
sp	1 LiClO ₄	1.050 LiClO ₄	25	0.75 ⁵	0.73 ± 0.20	85LYa
sp	1 LiClO ₄	1.050 LiClO ₄	25	0.81	0.79 ± 0.20	71KVa
sp	1 NaClO ₄	1.051 NaClO ₄	20	0.64	0.64 ± 0.20 ⁴	48FRa, 70SWa
qh	1 NaClO ₄	1.051 NaClO ₄	20	0.97	0.95 ± 0.05 ⁴	50FRa
sp	1 NaClO ₄	1.051 NaClO ₄	25	0.66 ⁵	0.64 ± 0.20	49NAb
sp	1 NaClO ₄	1.051 NaClO ₄	25	0.58	0.56 ± 0.20	77ASH, 77AHa
sp	1 NaClO ₄	1.051 NaClO ₄	25	0.62 ⁵	0.60 ± 0.20	85LYa
sp	1 NaClO ₄	1.051 NaClO ₄	25	0.74	0.72 ± 0.20	90GLa
sp	2 LiClO ₄	2.204 LiClO ₄	25	0.73 ⁵	0.69 ± 0.20	49NAa
sp	2 LiClO ₄	2.204 LiClO ₄	25	0.60 ± 0.02	0.56 ± 0.20	77KFa
sp	2 LiClO ₄	2.204 LiClO ₄	25	0.62 ⁵	0.58 ± 0.20	85LYa
sp	2 NaClO ₄	2.212 NaClO ₄	25	0.61 ⁵	0.57 ± 0.20	49NAb
cal	2 NaClO ₄	2.212 NaClO ₄	25	0.53 ± 0.03	0.49 ± 0.10	69BGa
sp	2 NaClO ₄	2.212 NaClO ₄	25	0.54 ⁵	0.50 ± 0.20	85LYa
sp	2 NaClO ₄	2.212 NaClO ₄	25	0.63	0.59 ± 0.20	90GLa
sp	3 LiClO ₄	3.482 LiClO ₄	25	0.83 ⁶	0.67 ± 0.20	49NAa
sp	3 LiClO ₄	3.482 LiClO ₄	25	0.38 ± 0.04	0.31 ± 0.20	53NAb
sp	3 LiClO ₄	3.482 LiClO ₄	25	0.70 ⁵	0.63 ± 0.20	68MMf, 70MMj, 71KVa
cal	3 LiClO ₄	3.482 LiClO ₄	25	0.66	0.59 ± 0.20	70MMj, 74BRa
sp	3 LiClO ₄	3.482 LiClO ₄	25	0.68 ⁵	0.61 ± 0.20	85LYa
sp	3 NaClO ₄	3.503 NaClO ₄	25	0.66 ⁵	0.59 ± 0.20	49NAb
sp	3 NaClO ₄	3.503 NaClO ₄	25	0.73	0.66 ± 0.20	71KVa
sp	3 NaClO ₄	3.503 NaClO ₄	25	0.63 ⁵	0.56 ± 0.20	85LYa
sp	3 NaClO ₄	3.503 NaClO ₄	25	0.45	0.38 ± 0.20	77ASH, 77AHa
sp	3 NaClO ₄	3.503 NaClO ₄	25	0.69	0.62 ± 0.20	90GLa
sp	4 LiClO ₄	4.906 LiClO ₄	25	0.52 ± 0.04	0.43 ± 0.20	77KFa
sp	4 NaClO ₄	4.950 NaClO ₄	25	0.77 ⁵	0.68 ± 0.20	85LYa
sp	5 NaClO ₄	6.584 NaClO ₄	25	0.62	0.50 ± 0.20	77ASH, 77AHa

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

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

³References for rejected data: [04KOH]^l, [12NFa]^l, [48FRa]^{c,e}, [49NAa]^b, [51NLb]^e, [51WYa]^h, [52BER]^{d,h}, [53NAb]^c, [54NKb]^c, [56KEb]^b, [58KEa,59RRc]^b, [65TSb]^d, [68PRd]^{d,h}, [69GAR]^e, [69IEe]^d, [69VSA]^{d,j}, [68HPd,70HPd]^h, [71MKf]^{g,h}, [71KVa, *I* = 5 mol dm⁻³ datum only; medium unclear], [73RMA]^j, [75YYa]^h, [79GCa]^{d,g}, [81ARc]^{d,j}, [81YYa]^h, [90SKg]^{d,k}, [90SMe]^{d,k}, [2002ZLa]^{d,h}.

⁴Data also reported at other temperatures and pressures.

⁵Graphically interpolated by the reviewers from the original authors' numerical data.

⁶Recalculated value to 25 °C assuming Δ_r*H* = 7.3 kJ mol⁻¹ (Table A2-11).

Table A2-8 Reported and selected stability constants for the system $\text{Cu}^{2+}\text{-H}^+\text{-PO}_4^{3-}$ at 25 °C.

Method	Ionic medium		<i>t</i> /°C	Log ₁₀ <i>K</i> (reported)	Log ₁₀ * <i>K</i> (accepted) ¹	Ref.
	Amount concn./mol dm ⁻³	Molality/ mol kg ⁻¹				
$\text{Cu}^{2+} + \text{HPO}_4^{2-} \rightleftharpoons \text{CuHPO}_4(\text{aq})^2$						
gl	0.10 NaNO ₃	0.101	25	3.33 ± 0.03	3.3 ± 0.1	96SSa
gl	0.10 NaClO ₄	0.101	25	3.2	3.2 ± 0.2	67SBc
gl	0.15 KNO ₃	0.151	37	3.25 ± 0.15	3.2 ± 0.3	70CHc
vlt	0.50 NaClO ₄	0.513	25	3.1	3.1 ± 0.2	73NMb
$\text{Cu}^{2+} + 2\text{HPO}_4^{2-} \rightleftharpoons \text{Cu}(\text{HPO}_4)_2^{2-3}$						
vlt	0.50 NaClO ₄	0.513	25	4.7	4.7 ± 0.3	73NMb
gl, ise	3.0 NaClO ₄	3.503	25	5.12 ± 0.15	5.1 ± 0.3	93Cic
		0 corr ⁴		7.36 ± 0.2		
$\text{Cu}^{2+} + \text{H}_2\text{PO}_4^- \rightleftharpoons \text{CuH}_2\text{PO}_4^+$ ⁵						
ise	NaH ₂ PO ₄	0 corr	25	- ⁶	1.6 ± 0.3 ⁷	45MEa
gl	0.15 KNO ₃	0.151	37	1.2 ± 0.2	1.2 ± 0.3	70CHc
gl, ise	3.0 NaClO ₄	3.503	25	0.64 ± 0.07	0.6 ± 0.2	93Cic
		0 corr ⁴		1.14 ± 0.15		
$\text{Cu}^{2+} + 2\text{H}_2\text{PO}_4^- \rightleftharpoons \text{Cu}(\text{H}_2\text{PO}_4)_2(\text{aq})^8$						
gl, ise	3.0 NaClO ₄	3.503	25	1.03 ± 0.06	1.0 ± 0.2	93Cic
		0 corr ⁴		1.9 ± 0.2		

¹Constant corrected from molar to molal units and including our assigned errors.²Reference for rejected data: [73RMa]^j.³References for rejected data: [2000BAa]^j, [73RMa]^j.⁴Extrapolated to *I* = 0 by the authors using SIT and estimated ion interaction coefficients.⁵References for rejected data: [2000BAa]^j, [73RMa]^j, [68KYa]^c.⁶The authors reported the formation of the single species, Cu(H₂PO₄)₂(aq) (log₁₀ *K*^o = 1.48 ± 0.08).⁷The reported primary data were re-evaluated by the reviewers using SIT functions. Up to *I*_c = 1.36 mol dm⁻³ NaH₂PO₄ the experimental data can be well reproduced by assuming the formation of CuH₂PO₄⁺.⁸Reference for rejected data: [68BUe]^{a,b,j}.**Table A2-9** Selected solubility constant data for CuO(s) (tenorite) and Cu(OH)₂(s).

Method	Ionic medium		<i>t</i> /°C	Log ₁₀ * <i>K</i> _{s0} (reported)	Log ₁₀ * <i>K</i> _{s0} (accepted) ¹	Ref.
	Amount concn./mol dm ⁻³	Molality/ mol kg ⁻¹				
$\text{CuO}(\text{s}) + 2\text{H}^+ \rightleftharpoons \text{Cu}^{2+} + \text{H}_2\text{O} (*K_{s0})^2$						
sol	0 corr	0 (corr)	25	7.50	7.50 ± 0.10	63FSa
sol	0 corr	0 (corr)	25	7.65 ± 0.06	7.65 ± 0.06	65SAc
sol	0.20 NaClO ₄	0.203 m	25	7.89 ± 0.05	7.89 ± 0.05	65SA
$\text{Cu}(\text{OH})_2(\text{s}) + 2\text{H}^+ \rightleftharpoons \text{Cu}^{2+} + 2\text{H}_2\text{O} (*K_{s0})^2$						
gl	0 corr	0 (corr)	25	8.68 ± 0.20	8.68 ± 0.20	64GAb
sol	0 corr	0 (corr)	25	8.68 ± 0.05	8.68 ± 0.05	65SA
sol	0.20 NaClO ₄	0.203	25	8.92 ± 0.04	8.92 ± 0.04	65SAc

¹Constant corrected from molar to molal units and including our assigned errors.²Reference for rejected data: [86VAa]^j, [73PBA]^j, [70OKa] [69HEa]^a, [60BBa]^j, [58BBa]^j, [56SPb]^j, [54DOa]^a, [50AFa]^a, [49NTa]^j, [47GSA]^a, [44FEa]^a, [38OKa]^j, [24JGa]^a, [23MUA]^a.

Table A2-10 Selected solubility constant data for $\text{Cu}_2\text{CO}_3(\text{OH})_2(\text{s})$ (malachite) and $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2(\text{s})$ (azurite).

Method	Ionic medium		$t/^\circ\text{C}$	$\text{Log}_{10} K_{\text{s0}}$ (reported)	$\text{Log}_{10} K_{\text{s0}}$ (accepted) ¹	Ref.
	Amount concn./mol dm ⁻³	Molality/ mol kg ⁻¹				
$\text{Cu}_2\text{CO}_3(\text{OH})_2(\text{s}) \rightleftharpoons 2\text{Cu}^{2+} + \text{CO}_3^{2-} + 2\text{OH}^- (K_{\text{s0}})^2$						
sol	0.2 NaClO ₄	0.202	25	-31.36 ± 0.08	-31.34 ± 0.1	68SRe
sol	0.72 NaClO ₄ ³	0.72	25	-32.00 ± 0.08^4	-31.20 ± 0.1	84SKb
$\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2(\text{s}) \rightleftharpoons 3\text{Cu}^{2+} + 2\text{CO}_3^{2-} + 2\text{OH}^- (K_{\text{s0}})^2$						
sol	0.20 NaClO ₄	0.202	25	-42.10 ± 0.09	-42.07 ± 0.1	68SRe

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

²References for rejected data: [08FRE]^a, [79SGf]^{a,j}, [58Sla]^m, [57SCa]^l.

³Reported on the molality (mol kg⁻¹) scale.

⁴Reported constants expressed in terms of $[\text{CO}_3^{2-}]_f$ where $[\text{CO}_3^{2-}] = [\text{CO}_3^{2-}]_f + [\text{NaCO}_3^-]$, and $[\text{CO}_3^{2-}] = [\text{CO}_3^{2-}]_f (1 + 4.25[\text{Na}^+])$.

Table A2-11 Selected enthalpies and entropies for the reaction $\text{Cu}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{CuSO}_4(\text{aq})$ in NaClO_4 or LiClO_4 media at 25 °C.

Method	Ionic medium		<i>t</i> /°C	$\Delta_r H_m^\circ /$ kJ mol ⁻¹ (reported) ¹	$\Delta_r H_m^\circ /$ kJ mol ⁻¹ (accepted) ²	$\Delta_r S_m^\circ /$ J K ⁻¹ mol ⁻¹ (reported) ¹	$\Delta_r S_m^\circ /$ J K ⁻¹ mol ⁻¹ (accepted) ²	Ref. ³
	Amount concn./ mol dm ⁻³	Molality/ mol kg ⁻¹						
cal ⁴	0 corr ⁵	0 corr ⁵	25	5.1 ± 0.1	5.1 ± 1.0	61.1 ± 0.8	61 ± 5	69IEe
cal ⁶	0 corr	0 corr	25	7.2 ± 0.8	7.2 ± 1.0	69.5 ± 3.8 ⁷	70 ± 5	70LAe
cal ⁸	0 corr	0 corr	25	6.7 ^{9,10}	6.7 ± 1.0	68.4 ^{9,10}	68 ± 5	73POa
cal ¹¹	0 corr	0 corr	25	10.2 ± 0.3	10.2 ± 1.0	ns ¹²		73HPa
cal ¹¹	0 corr	0 corr	25	9.5 ± 0.3	9.5 ± 1.0	ns		73HPa, 73POa
cal	0 corr	0 corr	25	5.7 ± 0.2	5.7 ± 1.0	ns		69IEc, 73POa
cal	0 corr	0 corr	25	8.1 ± 0.4	8.1 ± 1.0	ns		73AUS
<i>K</i> (<i>T</i>) ¹³	0 corr	0 corr	25	7.7 ± 0.4	7.7 ± 1.0	67.8 ± 2.1	68 ± 5	82DKb
<i>K</i> (<i>T</i>) ¹⁴	0 corr	0 corr	25	6.5 ⁹	6.5 ± 1.0	67.7 ⁹	68 ± 5	2005BES
<i>K</i> (<i>T</i>) ¹⁵	0 corr	0 corr	25	6.4 ± 0.9	6.4 ± 1.0	66.2	66 ± 5	2005MBa
<i>K</i> (<i>T</i>) ¹⁶	1 NaClO ₄	1.051	25	9.9 ⁹	10 ± 3	44.3 ⁹	44 ± 5	77ASH, 77AHa
cal	2 NaClO ₄	2.212	25	7.3 ± 0.4	7.3 ± 1.0	35.6 ± 1.7	36 ± 5	69BGa
cal	3 LiClO ₄	3.482	25	4.8 ± 0.2	4.8 ± 1.0	29 ± 4	29 ± 7	70BRe, 74BRb
<i>K</i> (<i>T</i>) ¹⁶	3 NaClO ₄	3.503	25	5.9 ⁹	6 ± 3	28.5 ⁹	29 ± 7	77ASH, 77AHa
<i>K</i> (<i>T</i>) ¹⁶	5 NaClO ₄	6.584	25	2.2 ⁹	2 ± 3	19.4 ⁹	19 ± 10	77ASH, 77AHa

¹Uncertainties as given by the original authors.²Reported values with the reviewer's assigned uncertainties.³Rejected data: [77KFa]^j, [79GCa]^{c,g}, [81ARc]^{d,j}, [83ADc]^j.⁴Titration calorimetry with simultaneous determination of *K*₁.⁵Stated [69IEe] as corrected to *I* = 0 but apparently not (see ref. 24 in [73POa]).⁶Recalculation using $\Delta_{\text{dil}}H$ data from various literature sources.⁷Estimated by the reviewer.⁸Recalculation using $\Delta_{\text{dil}}H$ and activity data from various literature sources.⁹Uncertainty not given.¹⁰ $\Delta_r C_p = 272 \text{ J K}^{-1} \text{ mol}^{-1}$ also given.¹¹Titration calorimetry using independently determined *K*₁.¹²ns = not stated.¹³Using spectrometric data from 10–40 °C along with $\Delta_{\text{dil}}H$ and other calorimetric literature data.¹⁴Using conductivity data from 5–35 °C.¹⁵Using spectrometric data from 25–200 °C; $\Delta_r C_p = 327 \pm 41 \text{ J K}^{-1} \text{ mol}^{-1}$ also given.¹⁶Using spectrometric data from 25–60 °C.

APPENDIX 3

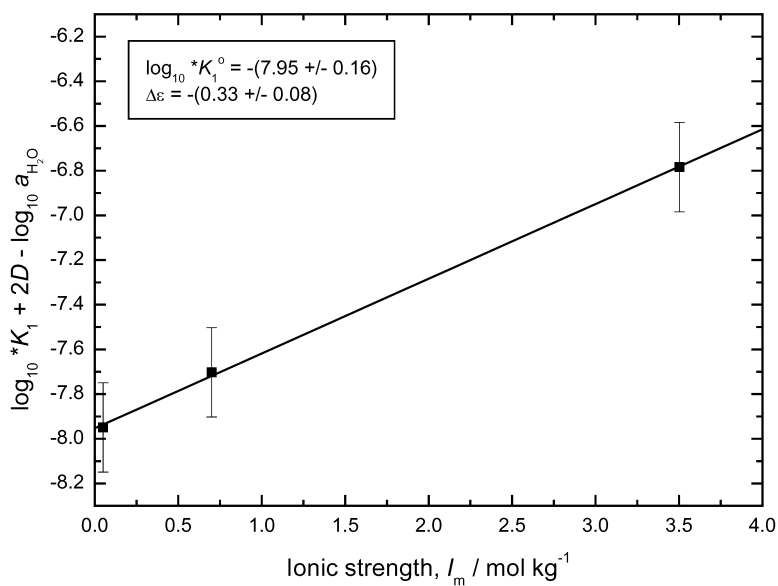
SIT plots for Cu^{2+} -L systems

Fig. A3-1 Extrapolation to $I_m = 0 \text{ mol kg}^{-1}$ of $\log_{10} {}^*K_1 - \Delta(z^2)D - \log_{10} a(\text{H}_2\text{O})$ (eq. 4, Section 5) for reaction 5 using selected data for NaClO_4 media, 25 °C, Table A2-1.

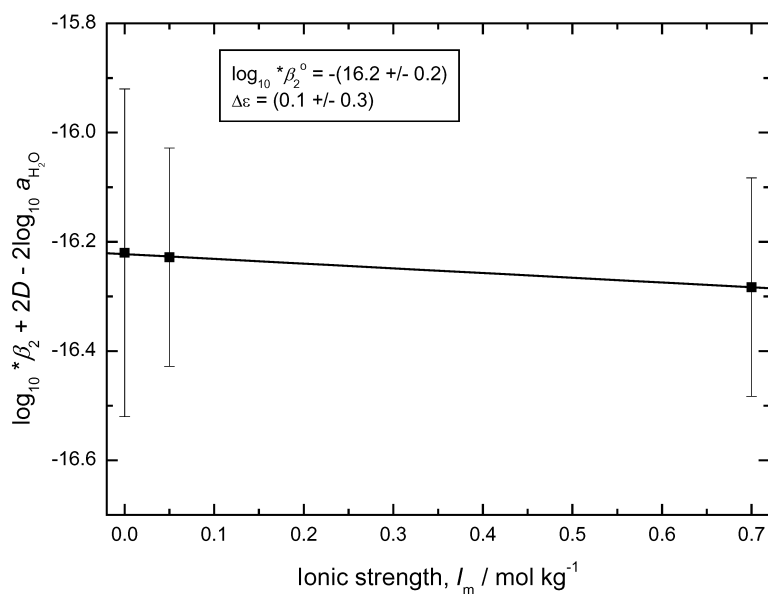


Fig. A3-2 Extrapolation to $I_m = 0 \text{ mol kg}^{-1}$ of $\log_{10} {}^*\beta_2 - \Delta(z^2)D - 2 \log_{10} a(\text{H}_2\text{O})$ for reaction 7 using selected data for NaClO_4 media, 25 °C (Table A2-2).

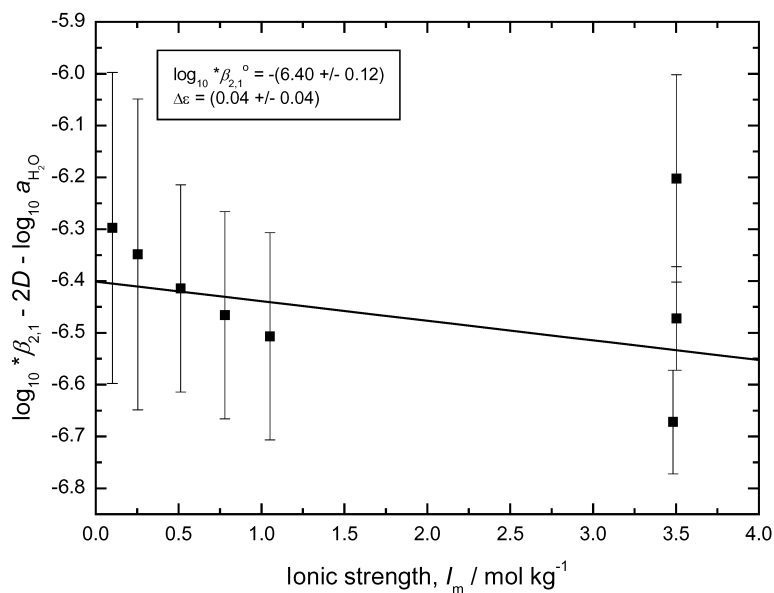


Fig. A3-3 Extrapolation to $I_m = 0 \text{ mol kg}^{-1}$ of $\log_{10} {}^* \beta_{2,1} - \Delta(z^2)D - \log_{10} a(\text{H}_2\text{O})$ for reaction 14 using selected data (Table A2-3) for NaClO_4 media at 25°C .

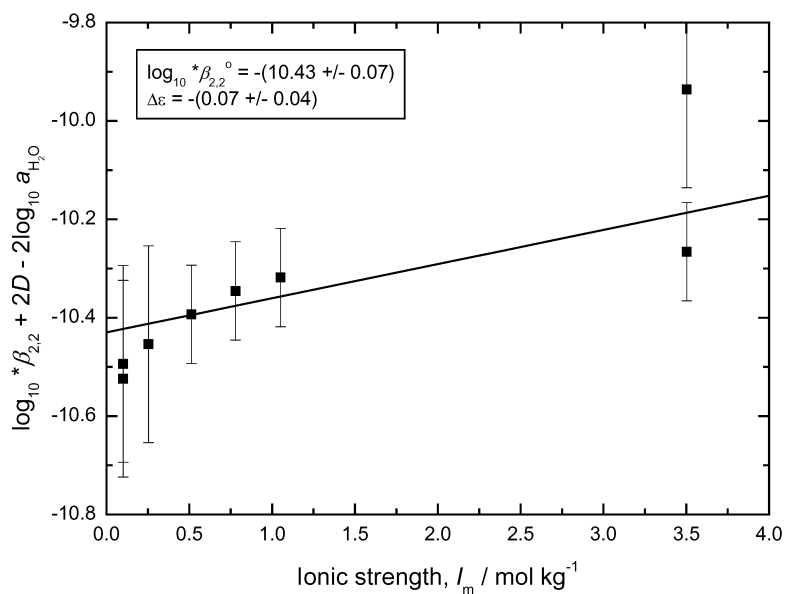


Fig. A3-4 Extrapolation to $I_m = 0 \text{ mol kg}^{-1}$ of $\log_{10} {}^* \beta_{2,2} - \Delta(z^2)D - 2 \log_{10} a(\text{H}_2\text{O})$ for reaction 15 using selected data for NaClO_4 media at 25°C (Table A2-3).

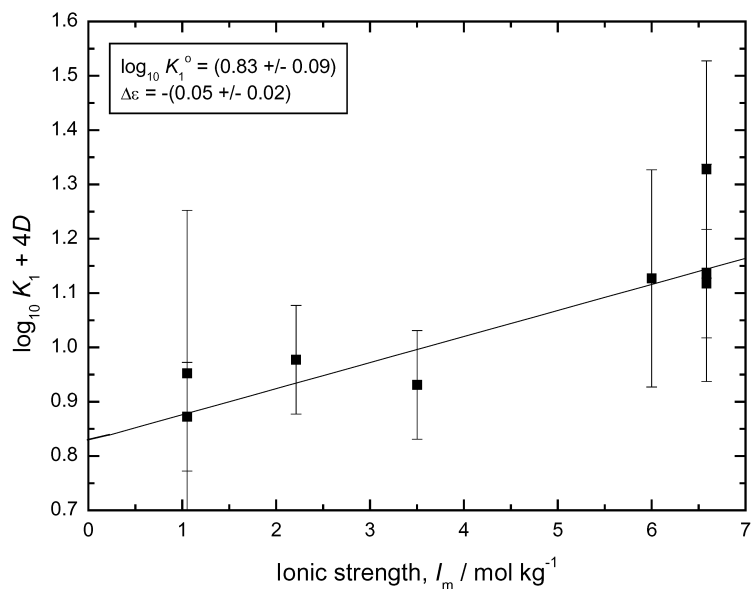


Fig. A3-5 Extrapolation to $I_m = 0 \text{ mol kg}^{-1}$ of $\log_{10} K_1 - \Delta(z^2)D$ for reaction 17 using selected data for NaClO_4 media at 25°C (Table A2-4).

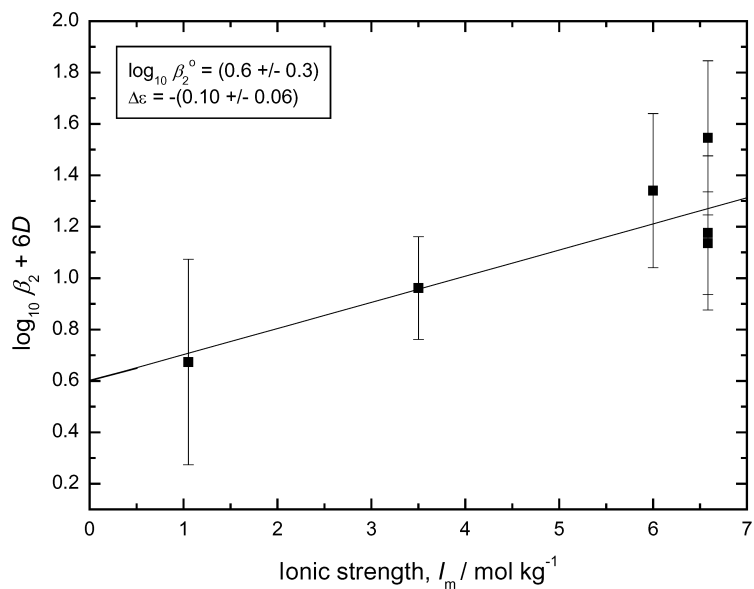


Fig. A3-6 Extrapolation to $I_m = 0 \text{ mol kg}^{-1}$ of $\log_{10} \beta_2 - \Delta(z^2)D$ for reaction 18 using selected data for NaClO_4 media at 25°C (Table A2-4).

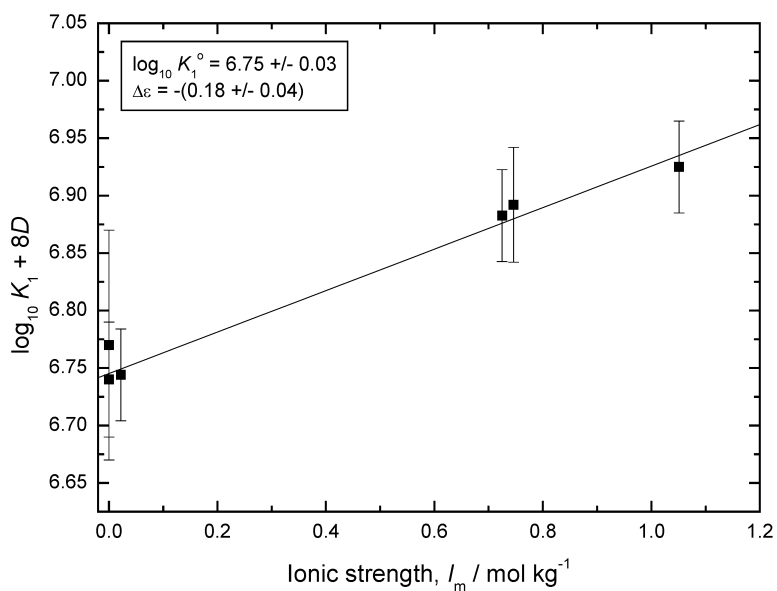


Fig. A3-7 Extrapolation to $I_m = 0 \text{ mol kg}^{-1}$ of $\log_{10} K_1 - \Delta(z^2)D$ for reaction 21 using selected data for NaClO_4 media at 25°C (Table A2-5).

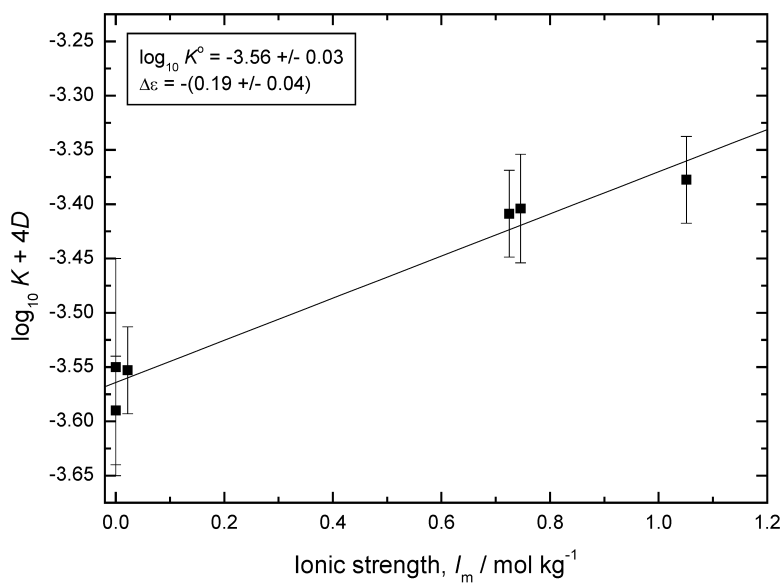


Fig. A3-8 Extrapolation to $I_m = 0 \text{ mol kg}^{-1}$ of $\log_{10} K - \Delta(z^2)D$ for reaction 22 using selected data for NaClO_4 media at 25°C (Table A2-6).

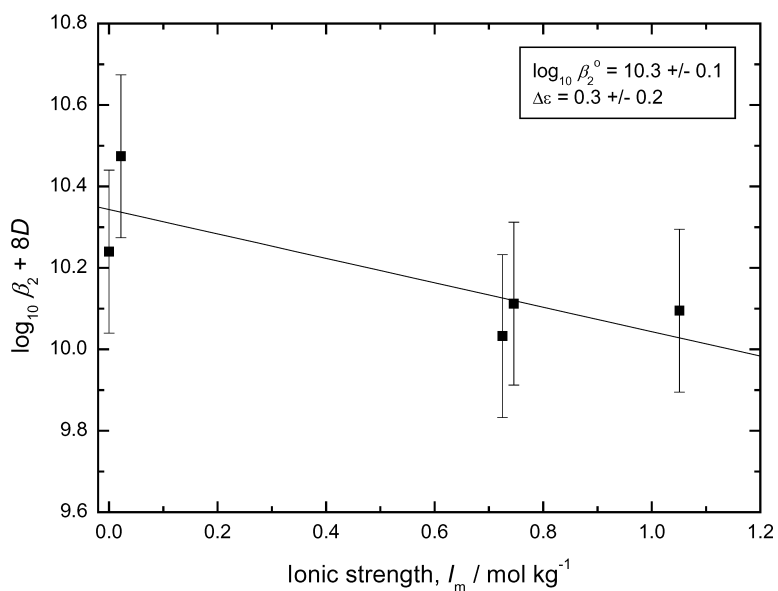


Fig. A3-9 Extrapolation to $I_m = 0 \text{ mol kg}^{-1}$ of $\log_{10} \beta_2 - \Delta(z^2)D$ for reaction 23 using selected data for NaClO_4 media at 25°C (Table A2-5).

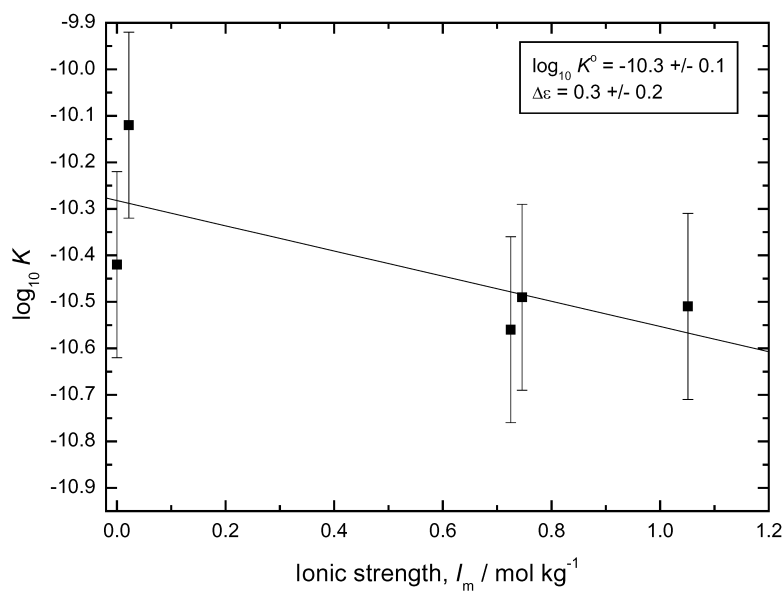


Fig. A3-10 Extrapolation to $I_m = 0 \text{ mol kg}^{-1}$ of $\log_{10} K - \Delta(z^2)D$ for reaction 25 using selected data for NaClO_4 media at 25°C (Table A2-6).

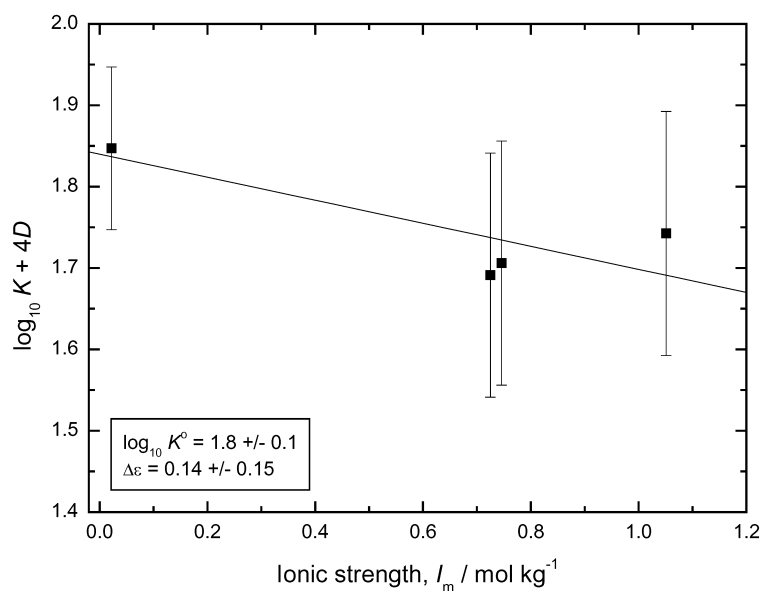


Fig. A3-11 Extrapolation to $I_m = 0 \text{ mol kg}^{-1}$ of $\log_{10} K - \Delta(z^2)D$ for reaction 26 using selected data for NaClO_4 media at 25 °C (Table A2-5).

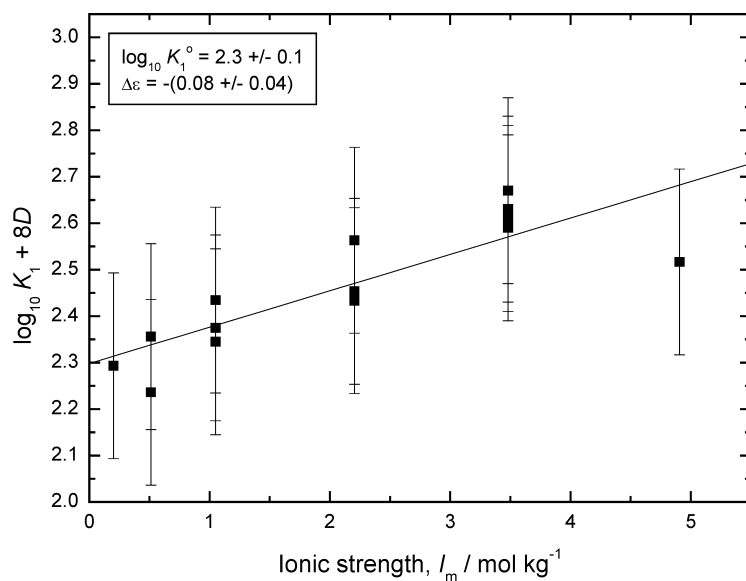


Fig. A3-12 Extrapolation to $I_m = 0 \text{ mol kg}^{-1}$ of $\log_{10} K_1 - \Delta(z^2)D$ for reaction 29 using selected data for LiClO_4 media at 25 °C (Table A2-7(b)).

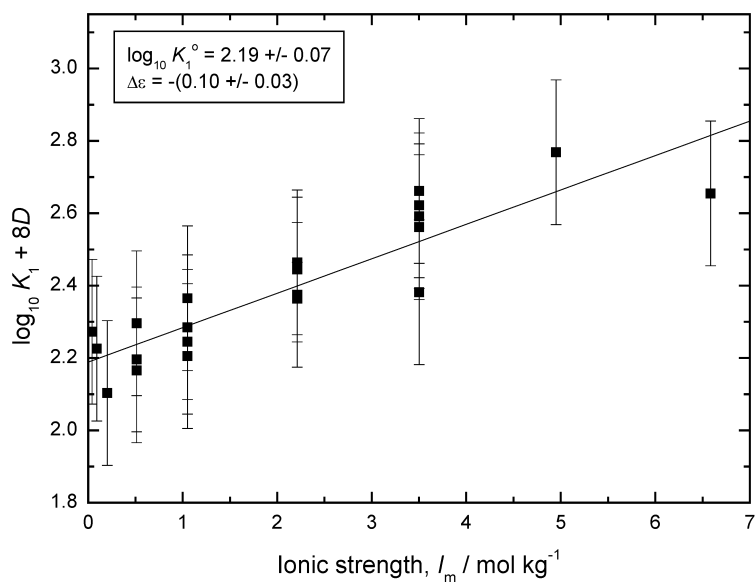


Fig. A3-13 Extrapolation to $I_m = 0 \text{ mol kg}^{-1}$ of $\log_{10} K_1 - \Delta(z^2)D$ for reaction 29 using selected data for NaClO_4 media at 25°C (Table A2-7(b)).

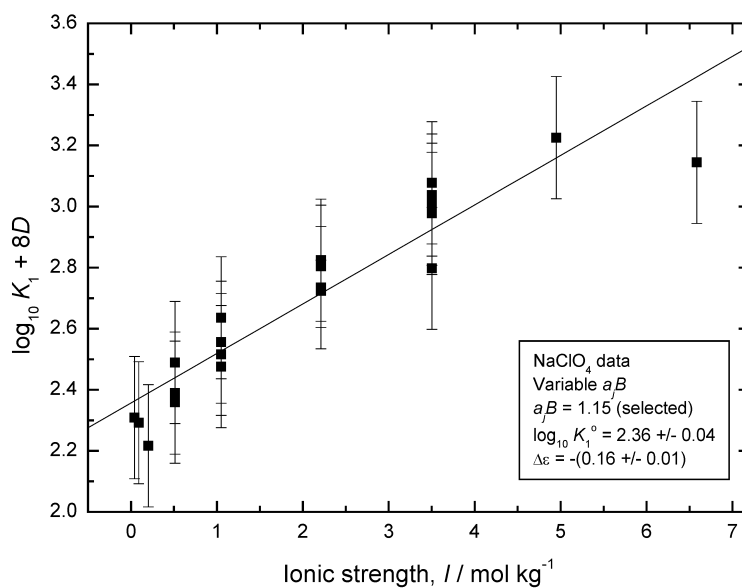


Fig. A3-14 Extrapolation to $I_m = 0 \text{ mol kg}^{-1}$ of $\log_{10} K_1 - \Delta(z^2)D$ for reaction 29 using the data for NaClO_4 media at 25°C (Table A2-7(b)) and the selected value of $a_\beta = 1.15$.