Sources of Pitzer parameters and equilibrium constants for the GEOTRACES core elements included in the SCOR Working Group 145 chemical speciation model

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Pitzer coefficients and equilibrium constants for the GEOTRACES core elements
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Contents

1. Introduction

SCOR Working Group 145 has so far published 3 papers describing the development of Pitzer models for seawater media based on the publications of Prof. Frank Millero and his group. Our Model I (22HW[1]) for artificial seawater is based on 13WMa, which was revised following review of all the original cited literature. Model II (22CW) is based on 17PM, which was revised in the same way. The two publications from the Millero group differ in their treatment of some key interactions in artificial seawater, so that Models I and II are kept distinct at this stage.

The fourth paper is planned to cover the GEOTRACES core elements together with Co^{2+} and Ni^{2+} since it makes good sense to treat the divalent cations of the first transition series as a group. The document therefore covers the cations Al^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} in seawater, together with phosphoric and silicic acids and their anions. These elements are included in the initial release of the Working Group 145 software, which predates the publication of the planned fourth paper. The following pages contain full documentation of the sources of equilibrium constant and Pitzer parameters for the GEOTRACES core elements that are included in the first software release. This material is planned to be included as part of the Supplementary Information for the fourth paper.

When extending Model II to trace elements, it became clear that the description of trace element chemistry in 17PM is both overcomplex and outdated, being based to a large extent on 98MP. The model described in 17PM uses a combination of Pitzer coefficients and equilibrium constants to describe many of the trace metal interactions with chloride and sulphate ions. Although equilibrium constants have been widely used for these interactions with chloride and sulphate, there are extensive published data on the osmotic coefficients and activity coefficients of most of these salts covering a much wider range of conditions than the corresponding equilibrium constant measurements. We have therefore taken advantage of these data and thus followed the normal approach for Pitzer-based models by describing weaker interactions with Pitzer coefficients where the relevant data are available. For most of the chloride and sulphate interactions with trace metal cations this represents a departure from many existing speciation models where these interactions are treated as complex formation.

Interactions of the trace metal ions with carbonate and hydroxide are treated as complexation reactions. Data on the interactions of the complexes with the major seawater ions are patchy, but the relevant Pitzer parameters are included where available. The weak interactions with bicarbonate are described with equilibrium constants due to paucity of data.

The meaning of the different Pitzer parameters is summarised in Table 1.1. The Pitzer equations can be found in 91P.

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[1] Literature citations in this document are in the form of codes with two digits for the publication year and one or two letters: the references ordered by code can be found in section 10.

Table 1.1 Explanation of the Pitzer parameters

$\beta_{ca}^{(0)}$, $\beta_{ca}^{(1)}$, $\beta_{ca}^{(2)}$, C^{ϕ} $C_{ca}^{(0)}$, $C_{ca}^{(1)}$	For interactions between cation c and anion a. Not all of these may be used, e.g., $\beta^{(2)}_{ca}$ is usually for 2:2 charge types only (e.g., CaSO₄), and is set to zero otherwise. The parameter C^{ϕ}, which is independent of ionic strength, is replaced by the parameters $C_{ca}^{(0)}$, $C_{ca}^{(1)}$ in an ionic-strength dependent extension of the original equations (94CR). The choice of C parameter shown in the tables for the various interactions follow the source publication.
α_{ca}, $\alpha_{ca}^{(2)}$, ω_{ca}	Coefficients associated with the ionic strength terms in the functions that use parameters $\beta_{ca}^{(1)}$, $\beta_{ca}^{(2)}$, and $C_{ca}^{(1)}$, respectively.
$\theta_{cc'}$, $\theta_{aa'}$	For interactions between dissimilar cations c and c', and between dissimilar anions a and a', respectively.
$\psi_{cc'a}$, $\psi_{aa'c}$	For interactions between anion a and dissimilar cations c and c', and between cation c and dissimilar anions a and a', respectively.
λ_{nc}, λ_{na}	For interactions between neutral solute n and cation c, and between neutral solute n and anion a, respectively.
ζ_{nca}	For interaction between neutral solute n, cation c and anion a.

2. Data coverage

Where possible, we have made use of critical analyses that give a complete set of Pitzer coefficients and/or equilibrium constants for a given interaction, while recognising that there may be some minor inconsistencies where the published analysis is not fully compatible with Model II (e.g. in the calculation of the osmotic coefficient of an isopiestic reference salt). In a small number of cases where Pitzer coefficients are appropriate but there is no published critical compilation, we have carried out our own analysis of the available data.

The following tables summarise the data coverage in this document. The codes used to indicate the types of available data are:

- $\gamma(T)$ indicates that Pitzer coefficients are available over a temperature range
- $\gamma(25)$ indicates that Pitzer coefficients are available at 25°C only
- $K(T)$ indicates that equilibrium constants are available over a temperature range
- $K(25)$ indicates that equilibrium constants are available at 25°C only
- θ, ψ, λ and ζ are used in the same way to indicate specific Pitzer coefficients

Table 2.1. Coverage of cation interactions with chloride, sulphate and fluoride

Cation	Chloride		Sulphate	Fluoride
	$M^{z+} - Cl^-$	Other interactions	$M^{z+} - SO_4^{2-}$	$M^{z+} - F^-$
Mn^{2+}	$\gamma(T)$		$\gamma(T)$	
Fe^{2+}	$\gamma(T)$	θ, ψ (25),(Na⁺, Mg²⁺, Ca²⁺, K⁺)	$\gamma(T)$	
Co^{2+}	$\gamma(T)$		$\gamma(T)$	
Ni^{2+}	$\gamma(T)$		$\gamma(T)$	
Cu^{2+}	$\gamma(T)$		$\gamma(T)$	
Zn^{2+}	$\gamma(T)$		$\gamma(T)$	
Cd^{2+}	$\gamma(T)$		$\gamma(T)$	
Pb^{2+}	$K(T)$, $\gamma(T)$	$\gamma(T)$ for complexes	$K(25)$	
Al^{3+}	$\gamma(T)$	θ, ψ (T) (Na⁺, H⁺, K⁺)	$\gamma(25)$	$K(25)$
Fe^{3+}	$\gamma(25)$	θ, ψ (25) (Na⁺, Mg²⁺, Ca²⁺, K⁺)	$\gamma(25)$	$K(25)$

Table 2.2. Coverage of cation interactions with hydroxide, carbonate and bicarbonate

Cation	Hydroxide		Carbonate		Bicarbonate
	M^{z+} - OH^-	Other interactions	M^{z+} - CO_3^{2-}	Other interactions	M^{z+} - HCO_3^-
Mn^{2+}	$K(T)$		$K(T)$	λ, ζ (25) (NaCl)	
Fe^{2+}	$K(T)$		$K(T)$		
Co^{2+}	$K(T)$		$K(T)$		
Ni^{2+}	$K(T)$		$K(T)$		
Cu^{2+}	$K(T)$	$\gamma(25)$ for complexes	$K(T)$	$\gamma(25)$ for complexes	$K(25)$
Zn^{2+}	$K(T)$	$\gamma(25)$ for complexes	$K(T)$		$K(25)$
Cd^{2+}	$K(T)$	$\gamma(25)$ for complexes	$K(T)$		
Pb^{2+}	$K(T)$		$K(T)$	λ, ζ (25) (NaCl)	$K(25)$
Al^{3+}	$K(T)$				
Fe^{3+}	$K(T)$	$\gamma(25)$ for complexes			

Table 2.3. Coverage of anion interactions with the major ions of seawater

Anion l	Proton	Sodium	Potassium	Magnesium	Calcium	Chloride	Sulphate
	X^{z-} - H^+	X^{z-} - Na^+	X^{z-} - K^+	X^{z-} - Mg^{2+}	X^{z-} - Ca^{2+}	X^{z-} - Cl^-	X^{z-} -SO_4^{2-}
PO_4^{3-}	$K(T)$	$\gamma(T)$ [a]	$\gamma(T)$			$\theta(25)$ [b]	$\theta(25)$ [b]
HPO_4^{2-}	$K(T)$	$\gamma(T)$ [a]	$\gamma(T)$	$K(25)$	$K(25)$	$\theta(25)$ [b]	$\theta(25)$ [b]
$H_2PO_4^-$	$K(T)$	$\gamma(T)$ [a]	$\gamma(T)$			$\theta(25)$ [b]	$\theta(25)$ [b]
$SiO(OH)_3^-$	$K(T)$	$\gamma(25)$					

[a] also triplet interactions $\psi(25)$ of these combinations with K^+
[b] also triplet interactions $\psi(25)$ of these combinations with Na^+ and K^+

Table 2.4. Coverage of neutral species interactions with the major ions of seawater

Neutral	Sodium	Potassium	Magnesium	Calcium	Chloride	Sulphate
	X^0 - Na^+	X^0 - K^+	X^0 - Mg^{2+}	X^0 - Ca^{2+}	X^0 - Cl^-	X^0 -SO_4^{2-}
$Si(OH)_4^0$	$\lambda(25)$	$\lambda(25)$	$\lambda(25)$	$\lambda(25)$	$\lambda(25)=0$	$\lambda(25)$

3. Chlorides

Isopiestic data for metal chloride solutions often extend to very high ionic strengths (20 mol kg^{-1} or more), which then require fourth or even fifth virial Pitzer parameters for satisfactory fits. Where we have carried out our own fits to determine the values of cation-anion interaction parameters we have restricted the ionic strength range to ensure a good fit with the standard Pitzer parameters $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$ where relevant, and $C^{(0)}$.

3.1 Mn(II)

There is no published critical evaluation of activity coefficients for MnCl$_2$. We have therefore carried out our own fitting at 25°C from published data as described in section 9.1.

For the temperature dependence we adopt the first derivatives of the Pitzer (p^L) , obtained from heat of dilution measurements (92SS), together with heat capacity parameters (p^J, which yield the second derivatives with respect to T) from 99CM.

Table 3.1 Mn^{2+} - Cl$^-$ interaction parameters

P [a]	q_1	P^{L} [b]	p^{J} [c]	α
$\beta^{(0)}$	0.3377 ± 0.0008	-1.677e-3	-2.5796e-5	
$\beta^{(1)}$	1.4645 ± 0.0117	2.34e-3	5.2114e-5	2.0
$C^{(0)}$	-0.00864 ± 0.00010	1.294e-4	0	

[a] $p = q_1 + q_2(1/T - 1/T_R) + q_3(T^2 - T_R^2)$ with T_R = 298.15 K
$\qquad q_2 = (p^J/3)T_R^3 - T_R^2 p_R^L; q_3 = p^J/6$
[b] from heat of dilution, σ = 30 J mol^{-1}
[c] from heat capacity, σ = 0.5 J mol^{-1} K^{-1}

3.2 Fe(II)

04MH determined Pitzer parameters for the Fe^{2+} - Cl$^-$ interaction at 25°C, and also parameters for the Fe^{2+}-M^{z+}-Cl$^-$ system where M^{z+} = Na$^+$, K$^+$, Mg^{2+}, Ca^{2+}. 20MM later determined the temperature dependence of the binary Fe^{2+} - Cl$^-$ parameters.

Table 3.2 Fe^{2+} - Cl$^-$ interaction parameters

P [a]	q_1	q_2	q_3	q_4	α
$\beta^{(0)}$	0.37324	0.00716	0.05840	-0.00203	
$\beta^{(1)}$	1.13499	0.00015	-0.02341	0.01709	2.0
C^{ϕ}	-0.0215243	0.03714	-0.00580	0.00016	

[a] $p = q_1 + q_2(1/T - 1/T_R) + q_3 \ln(T/T_R) + q_4(T - T_R)$ with T_R = 298.15 K

Table 3.3 Fe^{2+} - M^{z+} and Fe^{2+} - M^{z+} - Cl$^-$ interaction parameters at 25°C

Cation M^{z+}	θ (Fe^{2+} - M^{z+})	ψ (Fe^{2+} - M^{z+} - Cl$^-$)
Ca^{2+}	0.08112	-0.01599
K$^+$	0.02737	-0.02523
Mg^{2+}	0.14504	-0.02985
Na$^+$	0.10945	-0.01605

3.3 Co(II)

There is no published critical evaluation of activity coefficients for $CoCl_2$. We have therefore carried out our own fitting at 25°C from published data as described in section 9.2.

For the temperature dependence we adopt the first derivatives of the Pitzer (p^L) , obtained from heat of dilution measurements (92SS), together with heat capacity parameters (p^J, which yield the second derivatives with respect to T) from 99CM.

Table 3.4 Co^{2+} - Cl^- interaction parameters

P [a]	q_1	p^{L} [b]	p^{J} [c]	α
$\beta^{(0)}$	0.3558 ± 0.0038	-0.001273	-1.2414e-5	
$\beta^{(1)}$	1.475 ± 0.060	-0.00249	3.3193e-5	2.0
$C^{(0)}$	-0.00414 ± 0.00042	-0.0001929	0	

[a] $p = q_1 + q_2(1/T - 1/T_R) + q_3(T^2 - T_R^2)$ with T_R = 298.15 K
$\quad\quad q_2 = (p^J/3)T_R^3 - T_R^2 p_R^L; q_3 = p^J/6$
[b] from heat of dilution, σ = 15 J mol^{-1}
[c] from heat capacity, σ = 1.0 J mol^{-1} K^{-1}

3.4 Ni(II)

16DH have reviewed the available data for the $NiCl_2 - H_2O$ system, and have derived the following Pitzer parameters.

Table 3.5 Ni^{2+} - Cl^- interaction parameters

p [a]	q_1	q_2	q_3	α/ω
$\beta^{(0)}$	0.4196	-4314.0637	-1.2533e-5	
$\beta^{(1)}$	2.11	477.9627	3.5933e-5	2.0
$C^{(0)}$	-0.0071	6.5667	-6.9403e-8	
$C^{(1)}$	-1.2913	-1807.5940	-5.9847e-5	2.5 [b]

[a] $p = q_1 + q_2(1/T - 1/T_R) + q_3(T^2 - T_R^2)$ with T_R = 298.15 K
[b] the value of ω is not stated in the paper, and the authors have not replied to a request for confirmation. The standard value of 2.5 has therefore been assumed

3.5 Cu(II)

17YH have reviewed the data for aqueous $CuCl_2$, including the temperature variation of the interaction parameters based on extensive heat capacity measurements. The paper includes a parallel study on $CaCl_2$, which by comparison with literature data confirms the validity of the approach used.

Table 3.6 Cu^{2+} - Cl^- interaction parameters

P [a]	q_1	q_2	q_3	q_4	q_5	α
$\beta^{(0)}$	0.3992	-0.002446	3.6801e-6	-0.0026404	0.2531	
$\beta^{(1)}$	32.8563	-0.1987	0.0002941	0.0036331	1.9215	2.0
$C^{(0)}$	-0.02181	0.001341	-1.9857e-7	6.9327e-5	-0.0075696	

[a] $p = q_1(T/2 + T_R^2/2T - T_R) + q_2(T^2/6 + T_R^3/3T - T_R^2/2) + q_3(T^3/12 + T_R^4/4T - T_R^3/3) + q_4(T_R - T_R^2/T) + q_5$ with T_R = 298.15 K

3.6 Zn(II)

There is no published critical evaluation of activity coefficients for $ZnCl_2$. We have therefore carried out our own fitting at 25°C from published data as described in section 9.3.

The only determinations of the temperature dependency of these Pitzer parameters (93SD) have been analysed assuming that three parameters are used, i.e. excluding $\beta^{(2)}$. However, these same authors have noted that the heat of dilution measurements used are in general unable to provide temperature coefficients for $\beta^{(2)}$ (99SD). We therefore adopt the available temperature coefficients for the parameters that we have fitted, and retain a fixed $\beta^{(2)}$.

Table 3.7 Zn^{2+} - Cl^- interaction parameters

p	q_1	q_2	α
$\beta^{(0)}$	0.0098 ± 0.0018	-0.00927 ± 0.00089	
$\beta^{(1)}$	1.757 ± 0.013	0.0215 ± 0.0049	1.4
$\beta^{(2)}$	-1.192 ± 0.359		6.0
$C^{(0)}$	0.00463 ± 0.00015	0.00127 ±0.00002	

[a] $p = q_1 + q_2(T - T_R)$ with T_R = 298.15 K

3.7 Cd(II)

There is no published critical evaluation of activity coefficients for $CdCl_2$. We have therefore carried out our own fitting at 25°C from published data as described in section 9.3.

The only determinations of the temperature dependency of these Pitzer parameters (93SD) have been analysed assuming that three parameters are used, i.e. excluding $\beta^{(2)}$. However, these same authors have noted that the heat of dilution measurements used are in general unable to provide temperature coefficients for $\beta^{(2)}$ (99SD). We therefore adopt the available temperature coefficients for the parameters that we have fitted, and retain a fixed $\beta^{(2)}$.

Table 3.8 Cd^{2+} - Cl^- interaction parameters

p [a]	q_1	q_2 [b]	α
$\beta^{(0)}$	-0.0040 ± 0.0005	0.0007209	
$\beta^{(1)}$	-0.8179 ± 0.0106	-0.003179	1.4
$\beta^{(2)}$	-14.09 ± 0.38		6.0

[a] $p = q_1 + q_2(T - T_R)$ with T_R = 298.15 K
[b] from heat of dilution, σ = 22 J mol^{-1}

3.8 Pb(II)

07LM have provided a combined binding and Pitzer model for Pb^{2+}-Cl^- interactions. The authors' measurements in the range 15 - 45°C were combined with literature data to give an equation for $\log_{10}K$ for each complex in the temperature range 15 - 300°C. This equation takes the form $\log_{10} K = q_1 + q_2 T + q_3 \log_{10} T$. However, calculations show that this equation does not reproduce the author's measured equilibrium constants. Figure 9 of 07LM shows that the measured equilibrium constants in the range 15 – 45°C are linear functions of 1/T. A regression fitting with that equation reproduces the authors' measured equilibrium constants much more accurately (Table 3.9), so we adopt those values.

Table 3.9 Pb^{2+} - Cl^- equilibrium constants

Reaction	q_1	q_2
$Pb^{2+} + Cl^- = PbCl^+$	3.28 ± 0.05	-539.7
$Pb^{2+} + 2Cl^- = PbCl_2^0$	4.96 ± 0.04	-885.59
$Pb^{2+} + 3Cl^- = PbCl_3^-$	4.40 ± 0.06	-765.85

$$\log_{10} K = q_1 + q_2/T$$

07LM also provide Pitzer parameters for these complexes at four temperatures (their Table 5). These were fitted separately at the four temperatures studied, and show an incoherent variation with temperature, indicating possible overfitting. We have concluded that it will not be possible to obtain temperature-dependent Pitzer parameters without a reanalysis of the 07LM data, fitting all four temperatures simultaneously. At this stage, we therefore adopt the 25°C parameters given in 07LM, and neglect any variation with temperature. We have not adopted the parameters given for the $PbCl^+$ - Cl^- interaction since the parameters given in 07LM are unreasonably large.

Table 3.10 Pb^{2+} - Cl^- and Na^+ - $PbCl_3^-$ interaction parameters at 25°C

Cation	Anion	$\beta^{(0)}$	$\beta^{(1)}$	$C^{(0)}$	α
Pb^{2+}	Cl^-	0.2602	1.6425	-0.08798	2.0
Na^+	$PbCl_3^-$	-0.20 ± 0.08	1.11 ± 0.23	0.02 ± 0.01	2.0

Table 3.11 $PbCl_2^0$ interaction parameters at 25°C

λ Cl$^-$)	ζ (Cl$^-$, Na$^+$)
-0.19 ± 0.02	0.21 ± 0.07

$\lambda(Na^+)$ is set to zero

Subsequent to the work cited, 10BY have carried out a further review of lead chloride equilibrium constants at 25°C, leading to some differences in the equilibrium constants. However, we have chosen to adopt the results from 07LM who have fitted a complete model including both equilibrium constants and Pitzer parameters.

3.9 Al(III)

07CD studied this system and derived Pitzer parameters for both the cation-anion interactions and some mixing parameters.

Table 3.12 Al^{3+} -Cl^- interaction parameters

P [a]	q_1	q_2	q_3	α
$\beta^{(0)}$	-12.3369450	0.0201127032	2109.38737	
$\beta^{(1)}$	119.135056	-0.173302173	−18415.8656	2.0
C^ϕ	2.9900514	-0.0047078263	-474.566870	

[a] $p = q_1 + q_2 T + q_3/T$

Table 3.13 Al^{3+} - M^{z+} and Al^{3+} - M^{z+} - Cl^- interaction parameters

P [a]	q_1	q_2	q_3	q_4
θ(Al-H)	0.179086398			
ψ(Al-H-Cl)	−1.26910509	0.00217181206	183.332699	
θ(Al-K)	0.419552067			
ψ(Al-K-Cl)	29.8247471	0.0109536809	-667.124867	−5.43572997
θ(Al-Na)	0.335			
ψ(Al-Na-Cl)	−1.10588543	0.00171362150	157.980032	

[a] $p = q_1 + q_2 T + q_3/T + \ln T$

3.10 Fe(III)

04RH have derived parameters for this system, and also interactions with the major seawater cations at 25°C. We note that 04RH did not measure or control pH, so there is a risk that the Fe is partly hydrolysed. 07MP refitted the isopiestic data from 04RH and concluded that the $\beta^{(2)}$ term was not necessary: we use this reanalysis for Pitzer parameters at 25°C. 07MP then estimated the temperature dependence of these parameters using enthalpy and heat capacity data for the analogous salt $LaCl_3$.

Table 3.14 Fe^{3+} - Cl^- interaction parameters

P [a]	q_1	q_2	q_2	α
$\beta^{(0)}$	0.5382	2.6e-4	-1e-5	
$\beta^{(1)}$	6.3122	0.00802	-2.6e-5	2.0
C^{ϕ}	-0.0604	-0.00373	1.3e-5	

[a] $p = q_1 + q_2(T - T_R) + q_3(T - T_R)^2$ with $T_R = 298.15K$

Table 3.15 Fe^{3+} - M^{z+} and Fe^{3+} - M^{z+} - Cl- interaction parameters at 25°C

Cation M	θ (Fe^{3+} - M^{z+})	ψ (Fe^{3+} - M^{z+} - Cl^-)
Ca^{2+}	0.16291	-0.04910
K^+	0.14924	-0.03579
Mg^{2+}	0.15380	-0.07715
Na^+	0.25439	-0.02741

4. Sulphates

4.1 Mn(II)

12KT have reviewed the available data and fitted the data to obtain the following expressions for the Pitzer parameters.

Table 4.1 Mn^{2+} - SO_4^{2-} interaction parameters

P [a]	q_1	q_2	q_3	q_4	α
$\beta^{(0)}$	0.5246			-97.417	
$\beta^{(1)}$	92.1316	-0.235	1.992e-4	-10896.797	1.4
$\beta^{(2)}$	-182.7933			33186.707	12.0
C^ϕ	-0.1884			61.950	

[a] $p = q_1 + q_2 T + q_3 T^2 + q_4/T$

4.2 Fe(II)

20MM have reviewed the available data, and fitted the data to obtain the following expressions for the Pitzer parameters.

Table 4.2 Fe^{2+} - SO_4^{2-} interaction parameters

P [a]	q_1	q_2	q_3	q_4	α
$\beta^{(0)}$	0.28863	0.07759	-6.22314	0.01978	
$\beta^{(1)}$	2.70661	0.02505	-3.84957	0.00604	1.4
$\beta^{(2)}$	-42	0.00028	-0.03689	1.70108	12.0
C^ϕ	0.00748	-0.05429	1.13756	-0.00394	

[a] $p = q_1 + q_2(1/T - 1/T_R) + q_3 \ln(T/T_R) + q_4(T - T_R)$ with $T_R = 298.15$ K

4.3 Co(II)

21V reviewed the available data for aqueous $CoSO_4$ solutions, and fitted the data to obtain the following expressions for the Pitzer parameters.

Table 4.3 Co^{2+} - SO_4^{2-} interaction parameters

p [a]	q_1	q_2	q_3	q_4	q_5	α
$\beta^{(0)}$	0.4534 ± 0.0020			-78.21 ±0.59		
$\beta^{(1)}$	-1.1607 ± 0.0056			3439.95 ± 0.99	-672812 ± 1	1.4
$\beta^{(2)}$	-2588.76 ± 0.98	-2.054 ± 0.0032	552.14 ± 0.19			12.0
C^ϕ	-0.1086 ± 0.0015			40.11 ± 0.49		

[a] $p = q_1 + q_2 T + q_3 \ln T + q_4/T + q_5/T^2$

4.4 Ni(II)

Combining hygrometric measurements by 03EM, and enthalpy of dilution measurements by 99SD, yields the values below. 99SD note that their data did not allow them to estimate the temperature dependence of $\beta^{(2)}$.

Table 4.4 Ni^{2+} - SO_4^{2-} interaction parameters

p [a]	q_1	q_2 [b]	α
$\beta^{(0)}$	0.1625 ± 0.0019	7.5e-4	
$\beta^{(1)}$	2.903 ± 0.103	5.8e-5	1.4
$\beta^{(2)}$	-51.54 ± 7.81	0	12.0
C^ϕ	0.0389 ± 0.0013	-2.74e-5	

[a] $p = q_1 + q_2(T - T_R)$ with $T_R = 298.15$ K
[b] from heat of dilution, σ = 13 J mol^{-1}

4.5 Cu(II)

A recent reassessment by 22SS compared several different models and they recommend their Model 2, which we adopt.

Table 4.5 Cu^{2+} - SO_4^{2-} interaction parameters

p [a]	q_1	q_2	q_3	α
$\beta^{(0)}$	0.47563	-12.5928	-7.22e-04	
$\beta^{(1)}$	-1.20887		0.01293	1.4
$\beta^{(2)}$	-55.951			12.0
C^ϕ	-0.01312	7.40306		

[a] $p = q_1 + q_2/T + q_3T$
The goodness of fit is given as 0.0001 in a_{H2O}

4.6 Zn(II)

18HM have reviewed the available measurements for $ZnSO_4$ solutions, but their fit of the data included the unusual coefficient $\beta^{(3)}$, which is not compatible with standard Pitzer equations. Earlier reviews by 00AR and 03MNb included a fourth virial coefficient $D^{(0)}$, which is also not present in the standard Pitzer equations. However, a review of the aqueous $ZnSO_4 - H_2SO_4$ solutions by 18VS gives temperature-dependent Pitzer parameters $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, and C^ϕ (all present in the standard equations). We adopt these parameters.

Table 4.6 Zn^{2+} - SO_4^{2-} interaction parameters

p [a]	q_1	q_2	q_3	q_4	α
$\beta^{(0)}$	0.5468214	−112.68525			
$\beta^{(1)}$	156.87770	−17455.620	−0.45039814	0.0004408657	1.4
$\beta^{(2)}$	−109.50287	21332.288			12.0
C^ϕ	−0.16347515	59.798086			

[a] $p = q_1 + q_2/T + q_3T + q_4T^2$

4.7 Cd(II)

74PM and 78SP determined Pitzer parameters at 25°C, and their first derivatives with respect to temperature, respectively. 99MC reassessed the existing data together with their own emf measurements and presented a new fitting function at 25°C. This included a very high $\beta^{(2)}$ value (-134) together with a high α_2 value (16.1). Furthermore, the authors indicate that their fitting may not be optimal at intermediate ionic strengths (0.1 to 1m). We therefore adopt the parameters from 74PM and 78SP.

Table 4.7 Cd^{2+} - SO_4^{2-} interaction parameters

p [a]	q_1	q_2	α
$\beta^{(0)}$	0.2053	-0.00279	
$\beta^{(1)}$	2.617	0.0171	1.4
$\beta^{(2)}$	-48.07	-0.522	12.0
C^ϕ	0.0114	0.00261	

[a] $p = q_1 + q_2(T - T_R)$ with $T_R = 298.15$ K

4.8 Pb(II)

Since $PbSO_4$ is a sparingly soluble salt, it is not possible to prepare solutions with the range of concentrations needed to derive Pitzer parameters. The critical review 09PB determined a single equilibrium constant at 25°C, $\log_{10}K_1$ = 2.72. No data for temperature dependence have been found.

Table 4.8 Pb^{2+} - SO_4^{2-} equilibrium constant at 25°C

Reaction	$Log_{10}K$
$Pb^{2+} + SO_4^{2-} = PbSO_4^0$	2.72

4.9 Al(III)

88R has re-evaluated Pitzer parameters for this interaction at 25°C, resulting in the values given below. The author notes that the value of $\beta^{(2)}$ cannot be determined uniquely, but is an estimate based on solubility data.

Table 4.9 Al^{3+} - SO_4^{2-} interaction parameters at 25°C

Parameter	Value	α
$\beta^{(0)}$	0.854	
$\beta^{(1)}$	18.53	2
$\beta^{(2)}$	-500	50
C^ϕ	-0.0911	

4.10 Fe(III)

04RH have derived the following parameters for this system at 25°C. We note that 04RH did not measure or control pH, so there is a risk that the Fe is partly hydrolysed.

Table 4.10 Fe^{3+} - SO$_4^{2-}$ interaction parameters at 25°C

Parameter	Value	α
$\beta^{(0)}$	0.59625	
$\beta^{(1)}$	19.67406	1.559
$\beta^{(2)}$	74.06636	5.268
C^{ϕ}	-0.03227	

5. Hydroxides

For many of these cations the major source of information on hydrolysis at 25°C comes from the comprehensive 76BM review. A later paper by the same authors (81BM) provided data and estimates for enthalpy changes and heat capacities that can be used to calculate the temperature dependence of hydrolysis constants. With values of enthalpy change (ΔH / J mol^{-1}) and heat capacity change (ΔC_p / J K^{-1} mol^{-1}) at 25°C (i.e. T_R = 298.15 K), the value of $\log_{10} K$ at temperature T / kelvin can be calculated using the equation:

$$\log_{10} K(T) - \log_{10} K(T_R) = \frac{\Delta_r H(T_R)}{R \ln 10}\left(\frac{1}{T_R} - \frac{1}{T}\right) + \frac{\Delta_r C_p}{R \ln 10}\left(\frac{T_R}{T} + \ln\left[\frac{T}{T_R}\right] - 1\right)$$

The 81BM paper also contains equations for estimating values of $\Delta_r H$ and $\Delta_r C_p$ where these have not been measured:

- For the reaction $M(OH)_y^{(z-y)+} + H_2O = M(OH)_{y+1}^{(z-y-1)+} + H^+$, the value of $\Delta_r H$ / kcal mol^{-1} can be estimated using the equation

  $$\Delta_r H = -1.36 \log_{10} K(T_R) - 5.3 + 3.64(z - y)$$

- For estimation of $\Delta_r C_p$, 81BM provide in Table 8 estimates at 25°C for several values of the Pauling radius r / Å of the central metal ion. Where estimates are given at different ion radii we have fitted these to a linear regression. This results in the following values of $\Delta_r C_p$:

Reaction	$\Delta_r C_p$ / cal K^{-1} mol^{-1}
$M(OH)_{z-3}^{3+} + H_2O = M(OH)_{z-2}^{2+} + H^+$	$5\,r - 13.67$
$M(OH)_{z-2}^{2+} + H_2O = M(OH)_{z-1}^{+} + H^+$	$13.33\,r - 21.67$
$M(OH)_{z-1}^{+} + H_2O = M(OH)_{z}^{0} + H^+$	0
$M(OH)_{z}^{0} + H_2O = M(OH)_{z+1}^{-} + H^+$	-55

The ion radii used are given together with the data for each cation.

For the +2 cations, the third and fourth hydrolysis reactions can be very weak. Hydroxides with a stepwise formation constant of less than -11 $\log_{10}$ units have been excluded since they cannot make a significant contribution in seawater.

5.1 Mn(II)

76BM and 81BM give values for one weak hydroxide complex: the evidence for higher hydroxide constants was judged to be uncertain.

Table 5.1 Mn^{2+} - OH$^-$ equilibrium constants

Reaction [a]	$\log_{10} K$ (25°C)	$\Delta_r H$ / J mol^{-1}	$\Delta_r C_p$ / J K^{-1} mol^{-1}
$Mn^{2+} + H_2O = MnOH^+ + H^+$	-10.59	60 200	-49 [b]

[a] $\log_{10} K(T) - \log_{10} K(T_R) = \frac{\Delta_r H(T_R)}{R \ln 10}\left(\frac{1}{T_R} - \frac{1}{T}\right) + \frac{\Delta_r C_p}{R \ln 10}\left(\frac{T_R}{T} + \ln\left[\frac{T}{T_R}\right] - 1\right)$

[b] estimated according to 81BM with r = 0.75 Å

5.2 Fe(II)

76BM and 81BM give the following values.

Table 5.2 Fe^{2+} - OH$^-$ equilibrium constants

Reaction [a]	$\log_{10} K$ (25°C)	$\Delta_r H$ / J mol^{-1}	$\Delta_r C_p$ / J K^{-1} mol^{-1}
Fe^{2+} + H$_2$O = FeOH$^+$ + H$^+$	-9.5	55 200	-49 [b]
Fe^{2+} + 2H$_2$O = Fe(OH)$_2^0$ + 2H$^+$	-20.6	123 000	-49 [b]
Fe^{2+} + 3H$_2$O = Fe(OH)$_3^-$ + 3H$^+$	-29.0	134 000	-279 [b]

[a] $\log_{10} K(T) - \log_{10} K(T_R) = \frac{\Delta_r H(T_R)}{R \ln 1} \left(\frac{1}{T_R} - \frac{1}{T} \right) + \frac{\Delta_r C_p}{R \ln 10} \left(\frac{T_R}{T} + \ln \left[\frac{T}{T_R} \right] - 1 \right)$

[b] estimated according to 81BM with r = 0.75 Å

5.3 Co(II)

76BM and 81BM give the following values for the first two hydrolysis products. The formation of Co(OH)$_3^-$ is not included due to the large stepwise constant.

Table 5.3 Co^{2+} - OH$^-$ equilibrium constants

Reaction [a]	$\log_{10} K$ (25°C)	$\Delta_r H$ / J mol^{-1}	$\Delta_r C_p$ / J K^{-1} mol^{-1}
Co^{2+} + H$_2$O = CoOH$^+$ + H$^+$	-9.7	61 100	-47 [b]
Co^{2+} + 2H$_2$O = Co(OH)$_2^0$ + 2H$^+$	-18.8	117 000	-47 [b]

[a] $\log_{10} K(T) - \log_{10} K(T_R) = \frac{\Delta_r H(T_R)}{R \ln 10} \left(\frac{1}{T_R} - \frac{1}{T} \right) + \frac{\Delta_r C_p}{R \ln 1} \left(\frac{T_R}{T} + \ln \left[\frac{T}{T_R} \right] - 1 \right)$

[b] estimated according to 81BM with r = 0.79 Å

5.4 Ni(II)

76BM and 81BM give the following values for the first two hydrolysis products. The formation of Ni(OH)$_3^-$ is not included due to the large stepwise constant.

Table 5.4 Ni^{2+} - OH$^-$ equilibrium constants

Reaction [a]	$\log_{10} K$ (25°C)	$\Delta_r H$ / J mol^{-1}	$\Delta_r C_p$ / J K^{-1} mol^{-1}
Ni^{2+} + H$_2$O = NiOH$^+$ + H$^+$	-9.86	57 300	-44 [b]
Ni^{2+} + 2H$_2$O = Ni(OH)$_2^0$ + 2H$^+$	-19	103 000	-44 [b]

[a] $\log_{10} K(T) - \log_{10} K(T_R) = \frac{\Delta_r H(T_R)}{R \ln 10} \left(\frac{1}{T_R} - \frac{1}{T} \right) + \frac{\Delta_r C_p}{R \ln 10} \left(\frac{T_R}{T} + \ln \left[\frac{T}{T_R} \right] - 1 \right)$

[b] estimated according to 81BM with r = 0.83 Å

5.5 Cu(II)

The $\log_{10} K$ values at 25°C are not taken from 76BM in this case, but from a later reanalysis by 08SG, who also derived Pitzer parameters for the hydroxide complexes. The temperature dependence is taken from 81BM.

Table 5.5 Cu^{2+} - OH$^-$ equilibrium constants

Reaction [a]	$\log_{10} K$ (25°C)	$\Delta_r H$ / J mol^{-1}	$\Delta_r C_p$ / J K^{-1} mol^{-1}
Cu^{2+} + H$_2$O = CuOH$^+$ + H$^+$	-7.96	53 600	-42 [b]
Cu^{2+} + 2H$_2$O = Cu(OH)$_2^0$ + 2H$^+$	-16.23	93 700	-42 [b]

[a] $\log_{10} K(T) - \log_{10} K(T_R) = \frac{\Delta_r H(T_R)}{R \ln 1} \left(\frac{1}{T_R} - \frac{1}{T} \right) + \frac{\Delta_r C_p}{R \ln 10} \left(\frac{T_R}{T} + \ln \left[\frac{T}{T_R} \right] - 1 \right)$

[b] estimated according to 81BM with r = 0.87 Å

08SG have also derived Pitzer parameters in $NaClO_4$ solutions at 25°C. In the absence of other information we take the perchlorate parameters as valid for chlorides.

Table 5.6 CuOH⁺ - Cl⁻ interaction parameters at 25°C

Parameter	value
$\beta^{(0)}$	0.1192
C^ϕ	-0.002

Table 5.7 Cu(OH)$_2^0$ interaction parameters at 25°C

parameter	value
$\lambda(Na^+)$ [a]	0.2005
$\zeta(Na^+, Cl^-)$	-0.1724

[a] $\lambda(Cl^-)$ is set to zero

5.6 Zn(II)

76BM and 81BM give the following values for the first two hydrolysis products. The formation of $Zn(OH)_3^-$ and $Zn(OH)_4^{2-}$ are not included due to the large stepwise constants.

Table 5.8 Zn²⁺ - OH⁻ equilibrium constants

Reaction [a]	$\log_{10} K$ (25°C)	$\Delta_r H$ / J mol⁻¹	$\Delta_r C_p$ / J K⁻¹ mol⁻¹
$Zn^{2+} + H_2O = ZnOH^+ + H^+$	-8.96	56 200	-42 [b]
$Zn^{2+} + 2H_2O = Zn(OH)_2^0 + 2H^+$	-16.76	89 500	-42 [b]

[a] $\log_{10} K(T) - \log_{10} K(T_R) = \frac{\Delta_r H(T_R)}{R\,1}\left(\frac{1}{T_R} - \frac{1}{T}\right) + \frac{\Delta_r C_p}{R\ln}\left(\frac{T_R}{T} + \ln\left[\frac{T}{T_R}\right] - 1\right)$

[b] estimated according to 81BM with r = 0.88 Å

08SG indicate that the Pitzer parameters derived for Cu hydrolysis provide a reasonable description for this system.

Table 5.8 ZnOH⁺ - Cl⁻ interaction parameters at 25°C

Parameter	value
$\beta^{(0)}$	0.1192
C^ϕ	-0.002

Table 5.9 Zn(OH)$_2^0$ interaction parameters at 25°C

parameter	value
$\lambda(Na^+)$ [a]	0.2005
$\zeta(Na^+, Cl^-)$	-0.1724

[a] $\lambda(Cl^-)$ is set to zero

5.7 Cd(II)

76BM give $\log_{10}K$ = -10.8 and -20.35 for the first two hydrolysis reactions. 91RFa studied the solubility of $Cd(OH)_2$ but were unable to characterise $CdOH^+$. For $Cd(OH)_2^0$ they give $\log_{10}K$ = 20.87 and $\lambda(Cd(OH)_2^0 - Na^+)$ = -0.2. We adopt the 76BM constants for a consistent description.

Table 5.10 Cd^{2+} - OH$^-$ equilibrium constants

Reaction [a]	log$_{10}$ K (25°C)	$\Delta_r H$ / J mol^{-1}	$\Delta_r C_p$ / J K^{-1} mol^{-1}
Cd^{2+} + H$_2$O = CdOH$^+$ + H$^+$	-10.08	54 800	-30 [b]
Cd^{2+} + 2H$_2$O = Cd(OH)$_2$^{0} + 2H$^+$	-20.35	106 000	-30 [b]

[a] $\log_{10} K(T) - \log_{10} K(T_R) = \frac{\Delta_r H(T_R)}{R \ln 1}\left(\frac{1}{T_R} - \frac{1}{T}\right) + \frac{\Delta_r C_p}{R \ln 10}\left(\frac{T_R}{T} + \ln\left[\frac{T}{T_R}\right] - 1\right)$

[b] estimated according to 81BM with r = 1.09 Å

08SG indicate that the Pitzer parameters derived for Cu hydrolysis provide a reasonable description for this system.

Table 5.11 CdOH$^+$ - Cl$^-$ interaction parameters at 25°C

Parameter	value
$\beta^{(0)}$	0.1192
C^ϕ	-0.002

Table 5.12 Cd(OH)$_2$^{0} interaction parameters at 25°C

parameter	value
λ(Na$^+$) [a]	0.2005
ζ(Na$^+$,Cl$^-$)	-0.1724

[a] λ(Cl$^-$) is set to zero

5.8 Pb(II)

The log$_{10}$ K values at 25°C are not taken from 76BM in this case, but from a later critical review by 09PB. The temperature dependence is taken from 81BM. The complex Pb(OH)$_3$$^-$ is not included due to a large stepwise constant.

Table 5.13 Pb^{2+} - OH$^-$ equilibrium constants

Reaction [a]	log$_{10}$ K (25°C)	$\Delta_r H$ / J mol^{-1}	$\Delta_r C_p$ / J K^{-1} mol^{-1}
Pb^{2+} + H$_2$O = PbOH$^+$ + H$^+$	-7.46	35 500	-16 [b]
Pb^{2+} + 2H$_2$O = Pb(OH)$_2$^{0} + 2H$^+$	-16.94	67 300	-16 [b]

[a] $\log_{10} K(T) - \log_{10} K(T_R) = \frac{\Delta_r H(T_R)}{R \ln 10}\left(\frac{1}{T_R} - \frac{1}{T}\right) + \frac{\Delta_r C_p}{R \ln 10}\left(\frac{T_R}{T} + \ln\left[\frac{T}{T_R}\right] - 1\right)$

[b] estimated according to 81BM with r = 1.33 Å

5.9 Al(III)

76BM give values for a series of equilibrium constants at 25°C, which are combined with estimates of enthalpy and heat capacity from 81BM.

Table 5.14 Al^{3+} - OH$^-$ equilibrium constants

Reaction	$\log_{10} K$ (25°C)	$\Delta_r H$ / J mol^{-1}	$\Delta_r C_p$ / J K^{-1} mol^{-1}
Al^{3+} + H$_2$O = AlOH^{2+} + H$^+$	-4.97	49 800	-47
Al^{3+} + 2H$_2$O = Al(OH)$_2^+$ + 2H$^+$	-9.30	82 700	-110
Al^{3+} + 3H$_2$O = Al(OH)$_3^0$ + 3H$^+$	-15.00	108 000	-110
Al^{3+} + 4H$_2$O = Al(OH)$_4^-$ + 4H$^+$	-23.00	135 000	-340

^{a} $\log_{10} K(T) - \log_{10} K(T_R) = \frac{\Delta_r H(T_R)}{R \ln 1}\left(\frac{1}{T_R} - \frac{1}{T}\right) + \frac{\Delta_r C_p}{R \ln 10}\left(\frac{T_R}{T} + \ln\left[\frac{T}{T_R}\right] - 1\right)$

^{b} estimated according to 81BM with r = 0.50 Å

5.10 Fe(III)

07MP have published Pitzer coefficients for all four hydroxide complexes of Fe(III) in NaCl solutions. These coefficients were obtained from analysis of solubility data by 99LM for Fe(OH)$_3$ in NaCl. However, the Pitzer coefficients listed in 07MP are highly unusual to say the least: the interaction Fe(OH)$_2^+$ - Cl$^-$ is assigned a value of $\beta^{(2)}$ = -219.8, which would indicate a very strong complex formation (this Pitzer parameter is normally used only for 2:2 complexes and even there such a large negative value would be unusual). In addition, the neutral complex Fe(OH)$_3^0$ is assigned very large values of λ and ζ, indicating very strong interactions of this neutral species with Na$^+$ and Cl$^-$: interaction between neutral species and singly charged cations are normally considered weak in the Pitzer system with relatively small values of λ and ζ. The complexes' activity coefficients derived from solubility data, shown in Figure 8 of 07MP, reveal the basis for these extraordinary Pitzer parameters: the activity coefficients of the complexes Fe(OH)$_2^+$ and Fe(OH)$_3^0$ have by far the largest departure from unity, much larger than the doubly charged complex FeOH^{2+}.
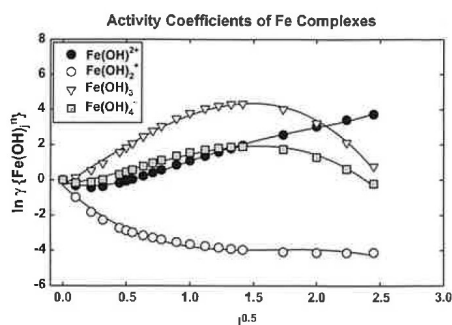

Fig. 8. The activity coefficient of FeOH^{2+}, Fe(OH)$_2^+$, Fe(OH)$_3$ and Fe(OH)$_4^-$ in NaCl solutions as a function of the square root of ionic strength at 25 °C.

Are these very unusual Pitzer parameters correct, or do they indicate a problem with using solubility data to estimate Pitzer parameters? The solubility measurements were carefully carried out, but the composition of the solid phase was not confirmed. There are indeed indications that the nature of the solid phase is not constant over the wide pH range studied:

- In the low pH region where the only complex formed is the reasonably well characterised FeOH^{2+}, the solubility should vary as $\log_{10}[Fe^{3+}] - 3$ pH for the solid phase Fe(OH)$_3$(s). However, the solubility is found to vary as $\log_{10}[Fe^{3+}] - 2.7$ pH. In their discussion of this question 00BL suggest that this could be attributed to "variations in the activity of the

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hydrous ferric oxide precipitates". In other words, variations in the nature of the solid phase, since solid phases are assigned unit activity.

- 00BL also cites a view that particle size is probably the major control on the thermodynamic stability of hydrous ferric oxides

- The measured iron solubilities in NaCl solutions show clear discontinuities at a number of pH values, indicating clearly that there are significant changes in the nature of the solid phase whose solubility is being measured. These effects are seen in Figures 5 and 6 from 99LM. Figure 6 shows a substantial pH shift in the minimum solubility as the ionic strength increases: it is the attempt to model this shift using activity coefficients that leads to the anomalous activity coefficients in Figure 8 from 07MP shown above.

Fig. 5. The effect of temperature on the solubility of Fe(III) as a function of pH in 0.7 M NaCl at 25°C.

Fig. 6. The effect of ionic strength on the solubility of Fe(III) as a function of pH in 0.7 M NaCl at 25°C.

We have therefore concluded that these solubility measurements cannot provide a sound basis for the derivation of Pitzer parameters for the various hydroxide complexes of Fe(III). Given the uncertainties in the equilibrium constants for $Fe(OH)^{2+}$, $Fe(OH)_3^0$ and $Fe(OH)_4^-$, we have not attempted to provide Pitzer coefficients for these complexes.

For the complex $FeOH^{2+}$ there is a set of potentiometric measurements in up to 6 molal NaCl at 25°C from 05BY. Analysis of these data results in values for the equilibrium constant and Pitzer parameters for the interaction of $FeOH^{2+}$ with Cl^- (Tables 5.14 and 5.15). 00BL have derived a value of ΔH = 10.2 kcal mol^{-1} for this complex formation. The lower value of ΔH given in 05BY includes correction for chloride complexation of Fe^{3+}, which is not treated as complexation in our Pitzer model. For the remaining ΔH and ΔC_p valueswe use the empirical relationships from 81BM described in section 5.

There is significant uncertainty over the values of the other three thermodynamic equilibrium constants. 07MP have compiled a number of estimates which are summarised the figure below. These constants are for the reaction of Fe^{3+} with OH^- rather than the normal formulation of reaction with water and loss of H^+. This approach gives confirmation that there is a consistent pattern of weaker complex formation with each added hydroxide: we adopt the mean value of each set of values for the second, third and fourth complexes. For the temperature dependence of these constants, we use the empirical relationships from 81BM described in section 5.
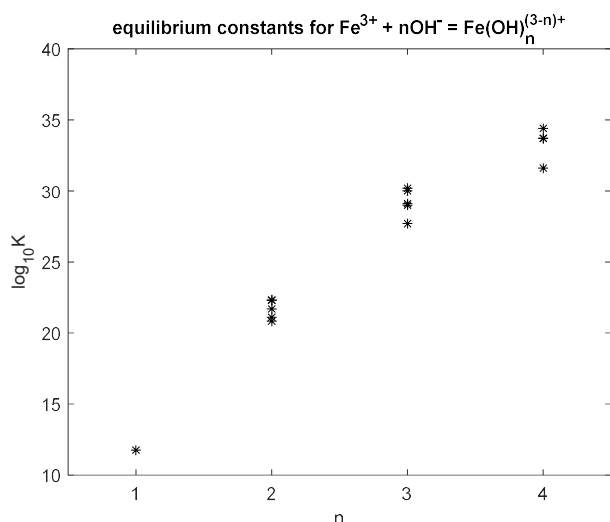
equilibrium constants for $Fe^{3+} + nOH^- = Fe(OH)_n^{(3-n)+}$

Table 5.14 Fe^{3+} - OH^- equilibrium constants

Reaction [a]	$\log_{10} K$ (25°C)	$\Delta_r H$ / J mol^{-1}	$\Delta_r C_p$ / J K^{-1} mol^{-1}
$Fe^{3+} + H_2O = FeOH^{2+} + H^+$	-2.25 [b]	42 700 [c]	-43 [d]
$Fe^{3+} + 2H_2O = Fe(OH)_2^+ + 2H^+$	-6.35	74 300 [d]	-95 [d]
$Fe^{3+} + 3H_2O = Fe(OH)_3^0 + 3H^+$	-12.8	104 000 [d]	-95 [d]
$Fe^{3+} + 4H_2O = Fe(OH)_4^- + 4H+$	-22.65	138 000 [d]	-325 [d]

[a] $\log_{10} K(T) - \log_{10} K(T_R) = \frac{\Delta_r H(T_R)}{R \ln 10}\left(\frac{1}{T_R} - \frac{1}{T}\right) + \frac{\Delta_r C_p}{R \ln 10}\left(\frac{T_R}{T} + \ln\left[\frac{T}{T_R}\right] - 1\right)$

[b] derived from data of 05BY

[c] ref. 00BL

[d] estimated according to 81BM with r = 0.69 Å

Table 5.15 Pitzer coefficients for $FeOH^{2+}$ (from analysis of data in ref. 05BY)

Parameter	Value	α
$\beta^{(0)}$	0.500	
$\beta^{(1)}$	2.949	2.0
$C^{(0)}$	-0.0207	

6. Carbonate and bicarbonate

For many cations the information on carbonate complexes consists at best of an equilibrium constant at 25°C, even for cations where carbonate complexation plays a significant role. The enthalpy of formation of $CuCO_3^0$ has been estimated by 89SB as 2.5 ± 0.3 kcal mol^{-1} (10.5 kJ mol^{-1}) This temperature dependence is used for other carbonate complexes where no other information is available. The equilibrium constants for the first carbonate complexes (MCO_3^0) are therefore given by the equation:

$$\log_{10} K = q_1 + q_2(1/T - 1/T_R) \text{ with } T_R = 298.15 \text{ K}$$

Where $q_2 = -\Delta H/(R \ln 10) = -546 \pm 66$

Where a second carbonate complex is formed we have no information on the enthalpy for the addition of the second carbonate ion, but retain the enthalpy for the addition of the first carbonate ion.

Bicarbonate complexes are relatively weak: in only in a few cases is an equilibrium constant at 25°C available.

6.1 Mn(II)

03LM studied the solubility of $MnCO_3(s)$ at 25°C, and determined both $\log_{10} K(MnCO_3^0)$ and the Pitzer coefficients given below.

Table 6.1 Mn^{2+} - CO_3^{2-} equilibrium constant

Reaction [a]	q_1	q_2
$Mn^{2+} + CO_3^{2-} = MnCO_3^0$	4.8 ± 0.1	-546 ± 66

[a] $\log_{10} K = q_1 + q_2(1/T - 1/T_R)$ with T_R = 298.15 K

Table 6.2 $MnCO_3^0$ interaction parameters at 25°C

Parameter	Value
$\lambda(Na^+)$ [a]	0.24
$\zeta(Na^+,Cl^-)$	0.04

[a] $\lambda(Cl^-)$ is set to zero

6.2 Fe(II)

02SL studied the solubility of $FeCO_3(s)$ and derived values for $\log_{10} K$ for $FeCO_3^0$ formation.

Table 6.3 Fe^{2+} - CO_3^{2-} equilibrium constant

Reaction [a]	q_1	q_2
$Fe^{2+} + CO_3^{2-} = FeCO_3^0$	6.3 ± 0.2	-546 ± 66

[a] $\log_{10} K = q_1 + q_2(1/T - 1/T_R)$ with T_R = 298.15 K

6.3 Co(II)

We have not been able to find measurements of this constant, and so use the value at 25°C estimated by 81TW from a linear free energy relationship

Table 6.4 Co^{2+} - CO_3^{2-} equilibrium constant

Reaction [a]	q_1	q_2
$Co^{2+} + CO_3^{2-} = CoCO_3^0$	4.91	-546 ± 66

[a] $\log_{10} K = q_1 + q_2(1/T - 1/T_R)$ with T_R = 298.15 K

6.4 Ni(II)

We have not been able to find measurements of this constant, and so use the value at 25°C estimated by 81TW from a linear free energy relationship.

Table 6.5 Ni^{2+} - CO_3^{2-} equilibrium constant

Reaction [a]	q_1	q_2
$Ni^{2+} + CO_3^{2-} = NiCO_3^0$	5.37	-546 ± 66

[a] $\log_{10} K = q_1 + q_2(1/T - 1/T_R)$ with T_R = 298.15 K

6.5 Cu(II)

10MS have studied this system in $NaClO_4$ medium at 25°C: We adopt their equilibrium constants and Pitzer parameters, assuming that the perchlorate parameters are also valid for chloride in the absence of other information.

Table 6.6 Cu^{2+} - CO_3^{2-} and Cu^{2+} - HCO_3^- equilibrium constants

Reaction [a]	q_1	q_2
$Cu^{2+} + CO_3^{2-} = CuCO_3^0$	6.74 ± 0.01	-546 ± 66
$Cu^{2+} + 2CO_3^{2-} = Cu(CO_3)_2^{2-}$	10.52 ± 0.06	-546 ± 66
$Cu^{2+} + HCO_3^- = CuHCO_3^+$	1.87 ± 0.01	

[a] $\log_{10} K = q_1 + q_2(1/T - 1/T_R)$ with T_R = 298.15 K

Table 6.7 $CuCO_3^0$ interaction parameters at 25°C

$\lambda(Na^+)$ [a]	0.0179
$\zeta(Na^+, Cl^-)$	0.0707

[a] $\lambda(Cl^-)$ is set to zero

Table 6.8 $Cu(CO_3^{2-})_2^{2-}$ and $CuHCO_3^+$ interaction parameters at 25°C

Cation	Anion	$\beta^{(0)}$	$\beta^{(1)}$	α
Na+	$Cu(CO_3)_2^2$	-0.590	-5.542	2.0
$CuHCO_3^+$	Cl^-	-0.0802	2.714	2.0

6.6 Zn(II)

We adopt the equilibrium constants recommended in the review by 13PB.

Table 6.9 Zn^{2+} - CO_3^{2-} and Zn^{2+} - HCO_3^- equilibrium constants

Reaction [a]	q_1	q_2
$Zn^{2+} + CO_3^{2-} = ZnCO_3^0$	4.75 ± 0.05	-546 ± 66
$Zn^{2+} + HCO_3^- = ZnHCO_3^+$	1.62 ± 0.1	0

[a] $\log_{10} K = q_1 + q_2(1/T - 1/T_R)$ with T_R = 298.15 K

6.7 Cd(II)

91RFb derived parameters for Cd^{2+} in carbonate media at 25°C. The $\log_{10}$ equilibrium constants are 4.7 and 6.4 for $CdCO_3^0$ and $Cd(CO_3)_2^{2-}$ respectively. A small number of interaction parameters were derived: $\beta^0(Cd(CO_3)_2^{2-} - Na^+) = -0.14$; $\beta^0(Cd(CO_3)_2^{2-} - K^+) = -0.06$.

The review by 11PB gave a recommended value of 4.4 for $\log_{10} K$ for $CdCO_3^0$, while the review by 11GM gave values of 4.4 and 6.53 for $\log_{10} K$ of $CdCO_3^0$ and $Cd(CO_3)_2^{2-}$, respectively. The review by 11GM, based on solubility data, is considered to provide the best summary.

Table 6.10 Cd^{2+} - CO_3^{2-} equilibrium constant

Reaction [a]	q_1	q_2
$Cd^{2+} + CO_3^{2-} = CdCO_3^0$	4.4 ± 0.2	-546 ± 66
$Cd^{2+} + 2CO_3^{2-} = Cd(CO_3)_2^2$	6.53 ± 0.2	-546 ± 66

[a] $\log_{10} K = q_1 + q_2(1/T - 1/T_R)$ with T_R = 298.15 K

6.8 Pb(II)

13WMb provides a description of the $PbCO_3^0$ complex in chloride media at 25°C. This is supplemented by equilibrium constants for $Pb(CO_3)_2^{2-}$ and $PbHCO_3^+$ from the critical review of 09PB.

Table 6.11 Pb^{2+} - CO_3^{2-} and Pb^{2+} - HCO_3^- equilibrium constants

Reaction [a]	q_1	q_2
$Pb^{2+} + CO_3^{2-} = PbCO_3^0$	6.87 ± 0.72	-546 ± 66
$Pb^{2+} + 2CO_3^{2-} = Pb(CO_3)_2^{2-}$	10.13 ± 0.24	-546 ± 66
$Pb^{2+} + HCO_3^- = PbHCO_3^+$	1.86 ± 0.2	

[a] $\log_{10} K = q_1 + q_2(1/T - 1/T_R)$ with T_R = 298.15 K

Table 6.12 $PbCO_3^0$ interaction parameters at 25°C

Parameter	Value
$\lambda(Cl^-)$ [a]	-0.020
$\zeta(Na^+,Cl^-)$	-0.145

[a] $\lambda(Na^+)$ is set to zero

7. Fluorides

7.1 Al(III)

08CO have studied the fluoride complexation of aluminium in $NaClO_4$ at ionic strengths of 1, 2 and 3 mol L^{-1} at 25°C. They used a modified Bromley method to estimate the equilibrium constants at zero ionic strength. We adopt these values: with measurements only at three ionic strengths there are insufficient data to estimate Pitzer parameters for the complexes formed.

Table 7.1 Al^{3+} - F^- equilibrium constants at 25°C

Reaction	$Log_{10}K$
$Al^{3+} + F^- = AlF^{2+}$	6.72 ± 0.07
$Al^{3+} + 2F^- = AlF_2^+$	12.08 ± 0.06
$Al^{3+} + 3F^- = AlF_3^0$	16.09 ± 0.06
$Al^{3+} + 4F^- = AlF_4^-$	18.63 ± 0.07
$Al^{3+} + 5F^- = AlF_5^{2-}$	20.79 ± 0.07
$Al^{3+} + 6F^- = AlF_6^{3-}$	21.69 ± 0.08

7.2 Fe(III)

96SB have made measurements of Fe(III) fluoride complexation in 0.68 molal $NaClO_4$ at 25°C, obtaining stoichiometric values of $log_{10}K$ = 5.15, 9.10, 11.96 and 13.7 for complexes $FeF_n^{(3-n)+}$. The last two complexes have very small stepwise formation complexes and are therefore not relevant in seawater. The stoichiometric constants for the first two complexes can be corrected to zero ionic strength using the following Pitzer parameters for perchlorate solutions:

Table 7.2 Perchlorate Pitzer parameters at 25°C

Cation	Anion	$\beta^{(0)}$	$\beta^{(1)}$	C^ϕ	Source
Na^+	ClO_4^-	0.0554	0.2755	-0.00118	07MP
Fe^{3+}	ClO_4^-	0.7213	7.2456	-0.0360	07MP
$FeOH^{2+}$	ClO_4^-	0.500	2.949	-0.0207 [a]	Assumed equal to $FeOH^{2+}$ - Cl^-

[a] $C^{(0)}$

This gives the following values:

Table 7.3 Fe(III) fluoride equilibrium constants at 25°C

Reaction	$Log_{10}K$
$Fe^{3+} + F^- = FeF^{2+}$	6.05
$Fe^{3+} + 2F^- = FeF_2^+$	10.2

Table 7.4 Pitzer parameters at 25°C, assumed equal to those for $FeOH^{2+}$ - Cl^-

Cation	Anion	$\beta^{(0)}$	$\beta^{(1)}$	$C^{(0)}$
$FeOH^{2+}$	F^-	0.500	2.949	-0.0207

8. Phosphate and silicate

8.1 Phosphates

Temperature dependent functions for the three dissociation constants of phosphoric acid have been derived by 95YM: these functions are also recommended by 07DS and are adopted here. Note that the subtraction of 0.015 natural log units by 07DS to correct for changes in pH scale has not been implemented since we are using only the thermodynamic constants from these publications.

13SM have derived Pitzer parameters at 25°C for the interactions of Na^+ and K^+ with the three phosphate anions from their own isopiestic measurements and literature data. In a later paper (15SM) these authors derived mixing parameters in the same way.

Table 8.1 Phosphoric acid equilibrium constants

Reaction [a]	q_1	q_2	q_3
$H_3PO_4 = H_2PO_4^- + H^+$	115.54	-4576.752	-18.453
$H_2PO_4^- = HPO_4^{2-} + H^+$	172.1033	-8814.715	-27.927
$HPO_4^{2-} = PO_4^{3-} + H^+$	-18.126	-3070.75	

[a] $\ln K = q_1 + q_2/T + q_3 \ln T$

Table 8.2 Cation – phosphate anion interaction coefficients at 25°C

Cation	Anion	$\beta^{(0)}$	$\beta^{(1)}$	C^ϕ	α
Na^+	PO_4^{3-}	0.15641	3.9397	-0.03498	2.0
Na^+	HPO_4^{2-}	-0.01720	1.2116	0.00585	2.0
Na^+	$H_2PO_4^-$	-0.04360	-0.03389	0.00605	2.0
K^+	PO_4^{3-}	0.24164	5.65323	-0.00944	2.0
K^+	HPO_4^{2-}	0.05884	1.06932	0.00012	2.0
K^+	$H_2PO_4^-$	-0.11116	0.04699	0.0197	2.0

Cations		Anion	ψ
K^+	Na^+	PO_4^{3-}	0
K^+	Na^+	HPO_4^{2-}	0.00099
K^+	Na^+	$H_2PO_4^-$	-0.01143

Table 8.2 Anion – phosphate anion interaction coefficients at 25°C

Anions		θ
PO_4^{3-}	Cl^-	0.24341
HPO_4^{2-}	Cl^-	0.07083
$H_2PO_4^-$	Cl^-	0.10037
PO_4^{3-}	SO_4^{2-}	1.09665
HPO_4^{2-}	SO_4^{2-}	0.09124
$H_2PO_4^-$	SO_4^{2-}	0.13769

Cation	Anion	$\psi(Cl^-)$	$\psi(SO_4^{2-})$
K^+	PO_4^{3-}	-0.01632	0
K^+	HPO_4^{2-}	-0.00736	0.01100
K^+	$H_2PO_4^-$	-0.01199	-0.03650
Na^+	PO_4^{3-}	-0.00243	-0.28058
Na^+	HPO_4^{2-}	-0.00883	-0.01911
Na^+	$H_2PO_4^-$	-0.01208	-0.01414

For Ca^{2+} and Mg^{2+} complexation with the phosphate anions, the review by 08DF gave thermodynamic equilibrium constants for Mg, Ca and Sr that decrease with increasing ion size. This follows the expected sequence for complexes with a significant electrostatic component, although we note that potentiometric measurements by 79JW and 76AC showed an opposite effect. Potentiometric measurements by 68CM gave values for all three Ca complexes with phosphate anions: the equilibrium constant for $CaH_2PO_4^+$ $CaHPO_4^0$ were adopted by 08DF. 68CM made measurements at 25°C and 37°C which were used to estimate values of ΔH for the Ca complexes: these values are also adopted for the Mg complexes.

Table 8.3 Ca^{2+} and Mg^{2+} phosphate equilibrium constants [a]

Cation	Anion	q_1	Source for q_1	q_2 (from 68CM)
Ca^{2+}	$H_2PO_4^-$	1.41	68CM, 08DF	-743
Ca^{2+}	HPO_4^{2-}	2.64	68CM, 08DF	-721
Ca^{2+}	PO_4^{3-}	6.46	68CM	-677
Mg^{2+}	$H_2PO_4^-$	1.6	08DF	-743
Mg^{2+}	HPO_4^{2-}	2.85	08DF	-721
Mg^{2+}	PO_4^{3-}	6.66	Estimated [b]	-677

[a] $\log_{10} K = q_1 + q_2(1/T - 1/T_R)$ with T_R = 298.15 K
[b] estimated using an offset of ≈ 0.2 between Mg and Ca complexes

89HM also studied phosphate dissociation in NaCl and $MgCl_2$ and derived Pitzer parameters for the interactions of Mg^{2+} with phosphate anions. The values are very unusual (large negative values for $\beta^{(0)}$), and are not included here.

We adopt the values shown in Table 8.3, but note that more work is needed on the alkali metal phosphates.

8.2 Silicates

A temperature dependent function for the dissociation of silicic acid has been derived by 95YM: this function is also recommended by 07DS and is adopted here. Note that the subtraction of 0.015 natural log units by 07DS to correct for changes in pH scale has not been implemented since we are using only the thermodynamic constant from these publications. The second ionisation of silicic acid is not considered relevant in seawater conditions.

Table 8.4 Silicic acid equilibrium constant

Reaction [a]	q_1	q_2	q_3
$Si(OH)_4 = SiO(OH)_3^- + H^+$	117.40	-8904.2	-19.334

[a] $\ln K = q_1 + q_2/T + q_3 \ln T$

The parameters for the interactions of the major seawater ions with neutral silicic acid have been summarised by 97A, and parameters for the interaction between $SiO(OH)_3^-$ and Na^+ have been estimated by 86HM. 74SS have determined the constants for the complexation of $SiO(OH)_3^-$ by Ca^{2+} and Mg^{2+}: these complexes are too weak to be relevant in seawater conditions.

Table 8.5 Si(OH)$_4$ interaction coefficients at 25°C

Ion	λ
Na$^+$	0.0925
K$^+$	0.03224
Mg^{2+}	0.2925
Ca^{2+}	0.2925
Cl$^-$	0.0
SO$_4^{2-}$	-0.13963

Table 8.6 SiO(OH)$_3^-$ interaction coefficients

Parameter	Value	α
$\beta^{(0)}$	0.043	
$\beta^{(1)}$	0.24	2.0

9. Appendix: coefficient derivations

Here we describe the derivation of Pitzer parameters in those cases where there is not a comprehensive publication available.

9.1 Manganese(II) chloride

Isopiestic measurements on $MnCl_2$ at 25°C have been made by 40RSa, 73D and 84R. In addition, 72D has measured Harned cell potentials in the $MnCl_2$ – HCl system. These data sets have been combined to derive Pitzer parameters at 25°C. The Harned cell data from the $MnCl_2$ – HCl system were analysed by comparing the values of $\ln(\gamma_H\gamma_{Cl})$ calculated from the Harned cell data with $\ln(\gamma_H\gamma_{Cl})$ calculated using Model II assuming that all the Mn – Cl parameters are zero. The symbols used for the various Pitzer parameters are described in 91P.

- The additional term specific to $\ln(\gamma_H)$ is $2m_{Mn}\theta_{Mn,H}$, assuming in the first instance that $\psi_{H,Mn,Cl} = 0$.
- The additional terms specific to $\ln(\gamma_{Cl})$ are $2m_{Mn}\beta^{(0)} + 2m_{Mn}g(x)\beta^{(1)} + Zm_{Mn}C^{(0)}$
- The terms affecting both $\ln(\gamma_H)$ and $\ln(\gamma_{Cl})$ are $m_{Mn}m_{Cl}g'(x)\beta^{(1)}/I + m_{Mn}m_{Cl}C^{(0)}$

Where g and g′ are the usual functions of $\alpha\sqrt{I}$ with α=2.

The full expression is then

$$\Delta \ln \gamma_H\gamma_{Cl} = 2m_{Mn}\beta^{(0)} + (2m_{Mn}\ g(x) + 2m_{Mn}m_{Cl}\ g'(x)/I)\beta^{(1)} + (Zm_{Mn} + 2m_{Mn}m_{Cl})C^{(0)} + 2m_{Mn}\theta_{Mn,H} \tag{2}$$

Although the factors multiplying $\beta^{(0)}$ and $\theta_{MN,H}$ are the same for the Harned cell data, they can be distinguished since they have different values for the isopiestic data.

An unweighted regression combining the isopiestic data up to a molality of 2.5 mol kg^{-1} with the values of $\Delta\ln(\gamma_H\gamma_{Cl})$ gave the following values.

Table 9.1 Results of regression analysis for the Mn^{2+} -Cl$^-$ interaction

p	Value	Std.error	t-statistic
$\beta^{(0)}$	0.3377	0.0008	406.3
$\beta^{(1)}$	1.4645	0.0117	124.9
$C^{(0)}$	-0.008642	0.000096	-90.4
θ	0.070	0.001	72.4

The residuals in both potential and osmotic coefficient are satisfactory:

MnCl$_2$: Residuals in osmotic coefficient: -0.000+/-0.002

MnCl$_2$ + HCl: Residuals in Harned cell potential: -0.00+/-0.06
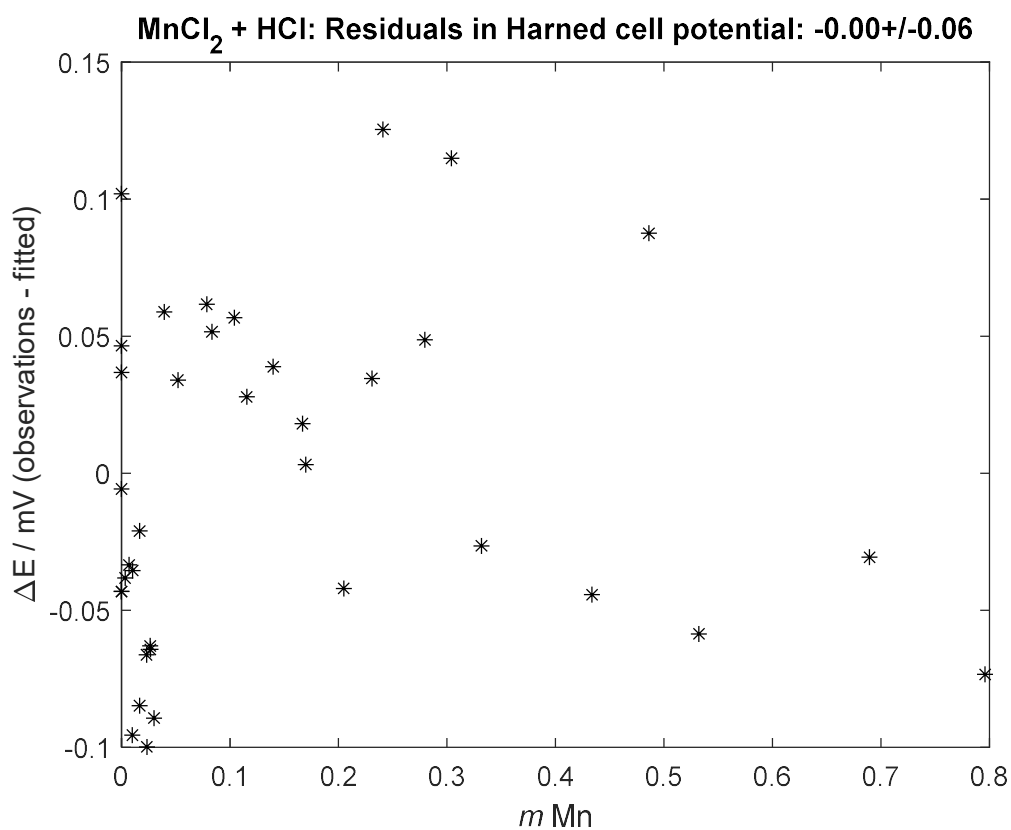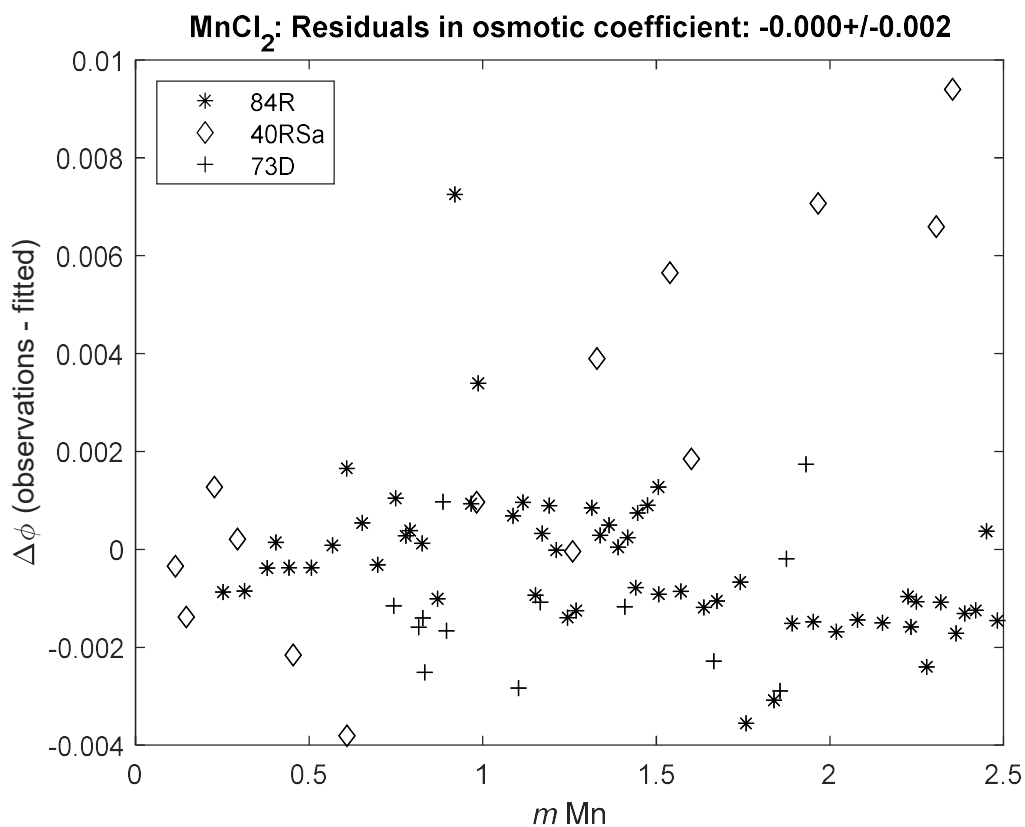
9.2 Cobalt(II) chloride

Isopiestic measurements on $CoCl_2$ at 25°C have been made by 48RB and 75D. These are consistent with one another, and the data with a maximum molality of 2.5 mol kg^{-1} can be described relatively well by the Pitzer equation with the following parameters.

Table 9.2 Results of regression analysis for the Co^{2+} -Cl^- interaction

p	Value	Std.error	t-statistic
$\beta^{(0)}$	0.3558	0.0038	93.2
$\beta^{(1)}$	1.4750	0.0603	24.4
$C^{(0)}$	-0.004140	0.000422	-9.8
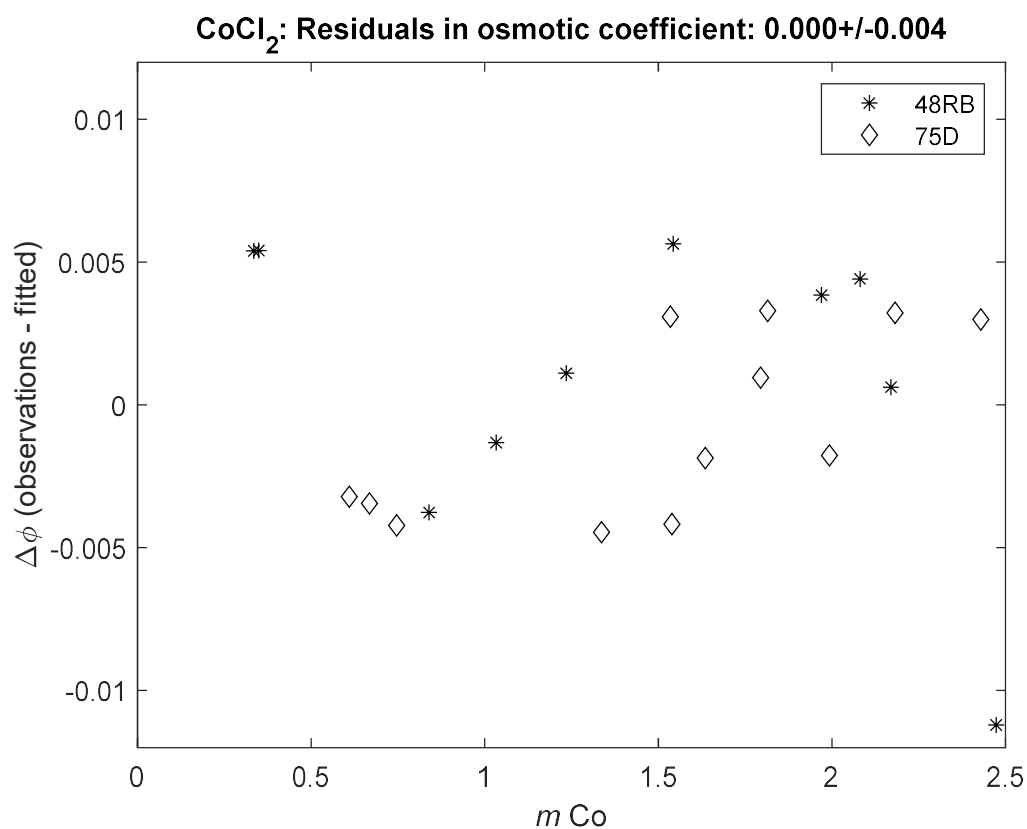
9.3 Zn(II) chloride

Isopiestic measurements at 25°C have been carried out by 40RSa, 87PA, 89RM and 03MNa. Fitting the combined data set to a standard Pitzer equation gives a poor fit. 89RM showed that a better fit can be obtained when restricting the molality to a maximum of 1.5 mol kg-1, but there are still significant residuals:

We have therefore investigated adding a $\beta^{(2)}$ coefficient, which results in a good fit to the whole data set. We have used values of $\alpha_1 = 1.4$ and $\alpha_2 = 6$ as used previously for 2:1 ionic interactions (borate interactions with Mg^{2+} and Ca^{2+}).

This gave a good fit with the following values:

Table 9.3 Results of regression analysis for the Zn^{2+} -Cl^- interaction

p	Value	Std.error	t-statistic
$\beta^{(0)}$	0.0098	0.0018	5.6
$\beta^{(1)}$	1.7573	0.0132	133.5
$\beta^{(2)}$	-1.1924	0.3594	-3.3
$C^{(0)}$	0.004626	0.000153	30.1
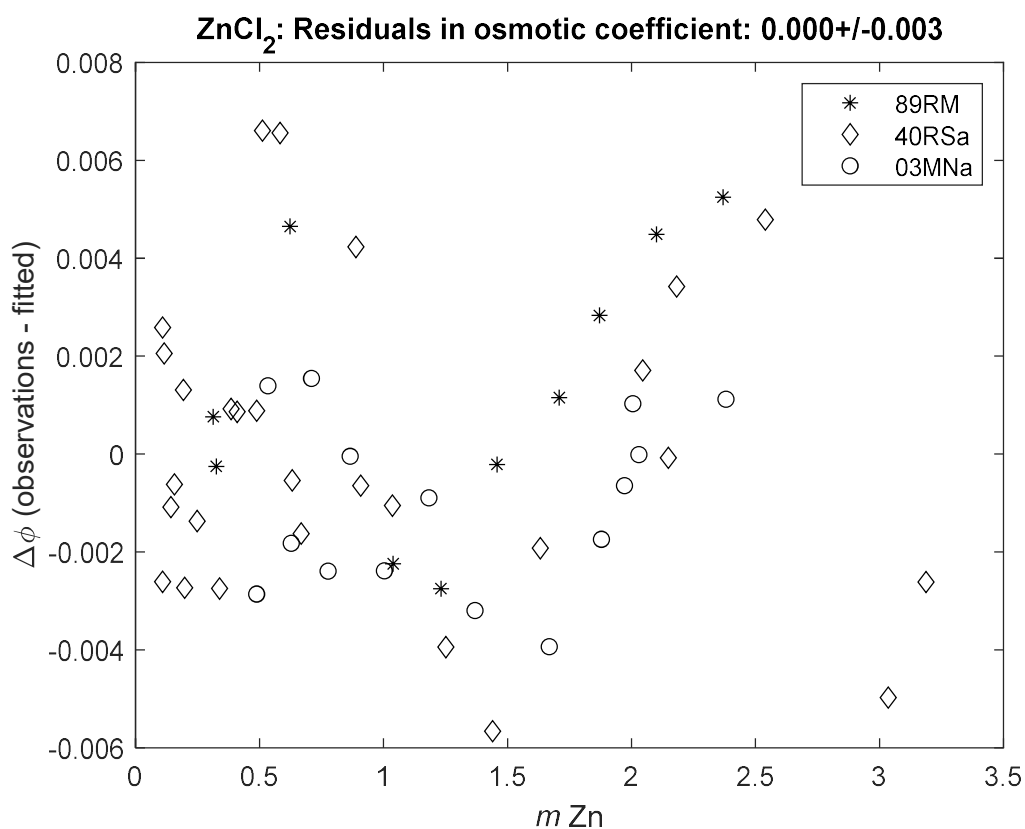
9.4 Cd(II) chloride

Isopiestic measurements on $CdCl_2$ at 25°C have been carried out by 40R and 75D. The available data up to a molality of 2.5 have been fitted in the same way as for $ZnCl_2$, i.e. including a $\beta^{(2)}$ coefficient with alpha values of 1.4 and 6.

Table 9.4 Results of regression analysis with 4 variables for the Cd^{2+} -Cl^- interaction
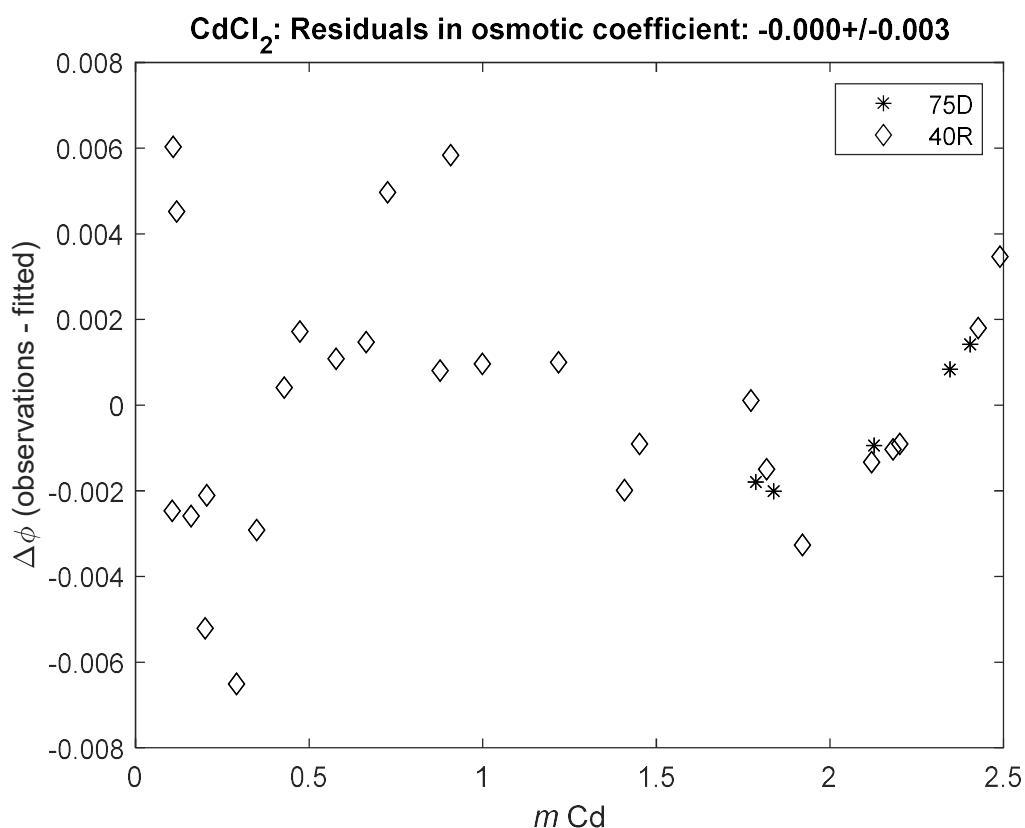
p	Value	Std.error	t-statistic
$\beta^{(0)}$	-0.0048	0.0037	-1.3
$\beta^{(1)}$	-0.8131	0.0244	-33.3
$\beta^{(2)}$	-14.1523	0.4759	-29.7
$C^{(0)}$	0.0000779	0.0003519	0.2

These results are not acceptable since Neither $\beta^{(0)}$ nor $C^{(0)}$ is statistically significant: we have therefore investigated omitting $C^{(0)}$, which results in three statistically significant parameters.

Table 9.5 Results of regression analysis with 3 variables for the Cd^{2+} -Cl^- interaction

p	Value	Std.error	t-statistic
$\beta^{(0)}$	-0.0040	0.0005	-8.3
$\beta^{(1)}$	-0.8179	0.0106	-77.3
$\beta^{(2)}$	-14.0918	0.3833	-36.8

The results shown in Table 9.5 are adopted.

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