The Sensitivity of Calculated Seawater pH (Total and Free Scales), and Calcite and Aragonite Saturation, to Pitzer Model Parameters. Recommendations for New Measurements of Thermodynamic Properties

I. Calculations for S = 35, and 1 atm. pressure at 25 °C. Recommendations for 25 °C and other temperatures.

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Overview

This draft document describes a study to identify what data, and new thermodynamic measurements, are needed to improve chemical speciation models of seawater based upon the Pitzer equations. Papers describing the application of the model to seawater should be consulted for discussions of its current accuracy with regard to pH and other quantities at different temperatures and salinities (e.g., Millero and Pierrot, 1998; Waters and Millero, 2013). The ultimate aim of model development is to create a tool that meets the needs of chemical oceanographers in many sub-disciplines – from estuarine water quality to paleo-oceanography – and which is also the equal of the various empirical relationships (such as in CO2SYS, for calculating the speciation of the marine carbonate system) that have been developed for particular ranges of salinity and temperature and which assume a normal seawater composition.

Our approach is a simple one: we have ranked (highest to lowest) the magnitudes of the contributions of the binary and ternary interactions in the Pitzer activity coefficient model to calculated pH ("total" scale) and the $Ca^{2+} \times CO_3^{2-}$ activity product (as a surrogate of the degree of saturation with respect to calcite or aragonite). The calculated quantities will be most sensitive to errors in the highest ranked contributions. We then briefly summarise the thermodynamic data from which each of the interaction parameters in the model have been determined. In section 5 recommendations for new measurements, based upon the rankings and summaries, are made.

It is expected that later versions of this document will extend the study to include buffer solutions used for the calibration of pH instruments, the effects of temperature (in greater detail than covered here), the effects of pressure, and minor interactions in the Pitzer model of seawater that are currently set to zero.

It is hoped that this document will stimulate discussion and, particularly, encourage those research groups with a capability to measure thermodynamic properties of electrolyte solutions (especially water and solute activities, and thermal properties) to act on some of the recommendations made here and so contribute to a better chemical speciation model for seawater. Please contact me (Simon Clegg), or the Chair of WG145 (David Turner, david.turner@marine.gu.se) if you wish to do so.

1. Background

The form in which a trace element or other component of seawater is present, and its tendency to react, depends on its *activity*. This is the product of its concentration (usually molality, m) and an activity coefficient (γ) which is a complex function of temperature, pressure, and salinity (or, more generally, solution composition). Note that concentrations are generally expressed as mol per kg of seawater by marine chemists, rather than molality, but conversion between the two scales is straightforward. Important reactions in seawater include complexation of trace metals (by a variety of ligands), and acid-base equilibria – for example with carbonate, borate, sulphate, and fluoride ions. Take, for example, this general reaction:

$$A_{(aq)} + B_{(aq)} \leftrightarrow C_{(aq)} \qquad (1)$$

The thermodynamic (K) and stoichiometric (K^*) equilibrium constants are defined by:

$$K = \gamma C\, mC / (\gamma A\, mA \cdot \gamma B\, mB) \qquad (2a)$$

$$K^* = mC/(mA \cdot mB) = K \cdot (\gamma A \cdot \gamma B / \gamma C) \qquad (2b)$$

The thermodynamic equilibrium constant varies with temperature and pressure only. The product $\gamma \cdot m$ for any species is its *activity*. The commonly measured stoichiometric equilibrium constant, which expresses speciation in terms of concentration directly, varies with solution composition as expressed in the activity coefficient term in eq (2b). Thus, if the values of K are known for the reactions of interest, the chemical equilibria in natural waters of any composition can be determined if the activity coefficients γ of the reactants and products can be calculated. The Pitzer model is used for this purpose (Pitzer, 1991). Its application to the chemistry of natural waters is described by Clegg and Whitfield (1991), and its application to seawater by Clegg and Whitfield (1995) and in many papers by Millero and co-workers (Waters and Millero, 2013, and references therein).

The Pitzer model equations contain sets of parameters, which are functions of T and P, of two kinds: "pure" solution parameters ($\beta_{ca}^{(0-2)}$, $C_{ca}^{(0-1)}$) whose values are determined by fitting to data for solutions containing single electrolytes consisting of cation 'c' and anion 'a'; and "mixture" parameters ($\Theta_{ii'}$, $\psi_{ii'j}$) whose values are determined from measurements containing typically two different electrolytes with a common ion (i.e., c-c'-a, or a-a'-c). There are also a small number of parameters for the interactions of uncharged solute species 'n' (e.g., the self interaction $\lambda_{nn'}$) and for interactions between uncharged solute species and ions (e.g., $\lambda_{n,c}$, $\lambda_{n,a}$, and ζ_{nca}). The data that are used to build a model of a relatively complex mixture such as seawater include: solvent and solute activities, apparent molar enthalpies and heat capacities (yielding the variation of the model parameters with temperature T), apparent molar volumes (the variation of the parameters with pressure P), salt solubilities, liquid/liquid phase partitioning, equilibrium partial pressures of volatile solutes, and others.

The major effort in constructing a Pitzer model for any solution is the determination of the parameter values, including the resolution of differences between inconsistent sets of data, obtaining approximate values of parameters for which there are no data, and relating uncertainties in calculated properties to those in the data upon which the model is based. There are a great many possible model parameters in a model of seawater, which contains the solute species H^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Cl^-, Br^-, OH^-, HCO_3^-, $B(OH)_4^-$, HSO_4^-, SO_4^{2-}, CO_3^{2-}, CO_2, and $B(OH)_3$. However, it is the ions present at the highest concentrations that have the greatest influence on the activity coefficients (γ) of all species. The dominant ions are, first, Na^+, Mg^{2+}, Cl^-, and SO_4^{2-}, followed by Ca^{2+} and K^+, and then HCO_3^-. This reduces the number of chemical systems that need to be studied, and parameters determined, to obtain an accurate model. This document addresses the question: what interactions in the Pitzer model (i.e., the parameters and the data they were determined from) are the calculated pH and calcium carbonate saturation in seawater most sensitive to? The answer to this question tells us where – on which pure solutions and mixtures – to focus our efforts in gathering available thermodynamic data and making new measurements to improve the accuracy of the model.

The sensitivity calculations are described in the next section. They have been carried out for S = 35 seawater at 25 ^{o}C. Data needs for other temperatures are discussed individually for each of the key chemical systems identified for further work. The two quantities for which sensitivities are assessed are pH on the total scale (defined here on a molality basis, rather than mol per kg of seawater, so that $10^{-pH} = m\text{H}^+ + m\text{HSO}_4^-$), and the activity product of Ca^{2+} and CO_3^{2-} ions (representing a calculation of calcite or aragonite saturation in seawater).

2. Description of the Calculations

The base composition of seawater for these calculations (to yield a calculated pH of close to 8) is given below. The temperature is 25 °C, and all concentrations are molalities (*m*, moles per kg of pure water).

mH	0.60239E-08	mBr	0.87202E-03
mNa	0.48614E+00	mB(OH)4	0.10053E-03
mMg	0.54742E-01	mF	0.70815E-04
mCa	0.10657E-01	mOH	0.38699E-05
mK	0.10580E-01	mHSO4	0.17643E-08
mSr	0.93961E-04	mB(OH)3	0.32706E-03
mCl	0.56578E+00	mCO2	0.10524E-04
mSO4	0.29264E-01	mHF	0.13039E-09
mHCO3	0.18852E-02		
mCO3	0.23350E-03		

The sensitivity calculations were carried out by setting each parameter (or group in the case of $\beta^{(0-2)}$ and $C^{(0-1)}$ for +/– interactions) successively to zero, and then recalculating the equilibrium composition of the system to yield pH and the activity product of Ca^{2+} and CO_3^- ($a\text{Ca} \cdot a\text{CO}_3$). The differences from the case in which all parameters are included were then noted. Section 3 shows the results for pH, ordered by the strength of the influence, both in absolute terms and also normalised to unity for the strongest influence (Na^+ - CO_3^{2-} interactions). We have used the Clegg and Whitfield (1995) seawater model for these calculations (plus parameters from Harvie et al. (1984) for the components of the carbonate system). The results we obtain should be broadly applicable to all Pitzer models of seawater. Note that parameters that are equal to zero in the model (either intentionally, or simply because their values are unknown) will not appear in the tables.

We believe that, for some of the interactions identified in the tables below as high sensitivity, further thermodynamic data (new measurements) will be needed so that parameters can be determined more "accurately" at all temperatures of interest (0°C, or below, up to about 40 °C). We put "accurately" in quotes because its exact definition for each interaction – i.e., how accurate is accurate enough? – requires sensitivity analyses to relate uncertainties in the data to which a parameter is fitted to the effect on the calculated quantity of interest.

The main papers describing the Pitzer model of seawater developed by Millero and co-workers (the "Miami" model) are Waters and Millero (2013) (seawater without carbonate), and before that Millero and Pierrot (1998) (with carbonate). In between these studies Millero et al. (2007) published measurements of carbonic acid dissociation in NaCl(aq) from 0 to 50 °C and up to 6 mol kg^{-1}, made by potentiometric titration. They combined the results with those of several other studies to re-derive parameters for Na^+ - CO_3^{2-} and Na^+ - HCO_3^- interactions up to 250 °C. The purpose of the work was to enable calculations to be extended to hydrothermal brines. It isn't clear whether current (i.e., 2016) seawater model of Millero has been revised to include these new parameters.

A new notes for non-modellers: electromotive force (emf) measurements yield activities of the species to which the two electrodes are sensitive (usually H^+ and Cl^-, although SO_4^{2-} electrodes can be used too). Osmotic coefficients (ϕ, from isopiestic measurements) yield water activities which are the other main source of data from which cation-anion interaction parameters are determined for most solutes. Measured enthalpies of dilution ($\Delta_{\text{dil}}H$) yield the first differential of solute or solvent activities with respect to temperature, and heat capacities (C_p) yield the second differential with respect to temperature. Thus, Pitzer models to calculate activities of solvent and solutes as a function of concentration, and over a range of temperatures, are most tightly constrained by a combination of activities and osmotic coefficients, and thermal data.

3. Results for pH

In the table below "ΔpH(Tot)" is the change in calculated pH on the total scale at 25 °C caused by setting the Pitzer model parameters for the indicated interaction to zero, and re-calculating the equilibrium speciation of the artificial seawater solution. It is an absolute value (the sign of the change has not been retained). The quantity ΔpH(Tot) is a simple measure of the sensitivity of the modelled pH to errors and uncertainties associated with each interaction. The column "ΔpH(Tot,norm)" presents the same information, but normalised to unity for the maximum case (the cation-anion interaction Na^{+} - CO$_3^{2-}$, row 1). Blank lines at the 10% and 1% levels in the ΔpH(Tot,norm) column have been added, for convenience. There are notes on the next page regarding the sources of parameters for the first 25 interactions below, which corresponds to ΔpH(Tot) ≥ 0.001699.

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 id     interaction       ΔpH(Tot) ΔpH(Tot,norm) sp1     sp2     sp3
  1 B(ca), C(ca)  (+ -  )  0.1601630  1.00000000   NA      CO3
  2 B(ca), C(ca)  (+ -  )  0.1243410  0.77634035   MG      CO3
  3 B(ca), C(ca)  (+ -  )  0.1115020  0.69617827   H       CL
  4 B(ca), C(ca)  (+ -  )  0.0749040  0.46767356   CA      CO3
  5 B(ca), C(ca)  (+ -  )  0.0314830  0.19656850   NA      SO4
  6 B(ca), C(ca)  (+ -  )  0.0193950  0.12109538   NA      HSO4
  7 B(ca), C(ca)  (+ -  )  0.0176810  0.11039379   NA      CL
  8 B(ca), C(ca)  (+ -  )  0.0168680  0.10531771   MG      HCO3

  9 B(ca), C(ca)  (+ -  )  0.0125590  0.07841387   MG      CL
 10 B(ca), C(ca)  (+ -  )  0.0121900  0.07610996   MG      HSO4
 11 B(ca), C(ca)  (+ -  )  0.0118770  0.07415570   MG      SO4
 12 Theta(cc')    (+ +  )  0.0118050  0.07370616   H       NA
 13 B(ca), C(ca)  (+ -  )  0.0116420  0.07268845   NA      HCO3
 14 B(ca), C(ca)  (+ -  )  0.0110350  0.06889856   MG      B(OH)4
 15 Theta(aa')    (- -  )  0.0096530  0.06026985   CL      HCO3
 16 B(ca), C(ca)  (+ -  )  0.0087650  0.05472550   CA      HCO3
 17 Theta(aa')    (- -  )  0.0080200  0.05007399   CL      B(OH)4
 18 Theta(aa')    (- -  )  0.0068000  0.04245675   CL      CO3
 19 B(ca), C(ca)  (+ -  )  0.0054880  0.03426509   CA      B(OH)4
 20 B(ca), C(ca)  (+ -  )  0.0041460  0.02588613   K       CO3
 21 Theta(cc')    (+ +  )  0.0036810  0.02298284   H       MG
 22 B(ca), C(ca)  (+ -  )  0.0025500  0.01592128   CA      CL
 23 B(ca), C(ca)  (+ -  )  0.0023300  0.01454768   CA      HSO4
 24 Theta(aa')    (- -  )  0.0022080  0.01378596   CL      SO4
 25 Lambda(N,c)   (n +  )  0.0016990  0.01060794   CO2     NA

 26 B(ca), C(ca)  (+ -  )  0.0013530  0.00844764   H       SO4
 27 Psi(aa'c)     (- - +)  0.0011750  0.00733628   CL      HCO3    NA
 28 B(ca), C(ca)  (+ -  )  0.0011450  0.00714897   CA      SO4
 29 Lambda(N,a)   (n -  )  0.0010750  0.00671191   B(OH)3  SO4
 30 B(ca), C(ca)  (+ -  )  0.0010470  0.00653709   NA      OH
 31 B(ca), C(ca)  (+ -  )  0.0008480  0.00529461   NA      B(OH)4
 32 Psi(aa'c)     (- - +)  0.0008470  0.00528836   CL      HCO3    MG
 33 Psi(aa'c)     (- - +)  0.0007080  0.00442050   CL      CO3     NA
 34 Theta(aa')    (- -  )  0.0006640  0.00414578   CL      HSO4
 35 B(ca), C(ca)  (+ -  )  0.0006590  0.00411456   K       SO4
 36 Theta(cc')    (+ +  )  0.0006580  0.00410831   H       CA
 37 Lambda(N,c)   (n +  )  0.0006460  0.00403339   B(OH)3  NA
 38 Psi(cc'a)     (+ + -)  0.0003680  0.00229766   H       NA      CL
 39 Theta(aa')    (- -  )  0.0003510  0.00219152   SO4     CO3
 40 Lambda(N,c)   (n +  )  0.0003400  0.00212284   CO2     MG
 41 B(ca), C(ca)  (+ -  )  0.0003240  0.00202294   K       CL
 42 Theta(aa')    (- -  )  0.0003010  0.00187934   CL      OH
 43 Psi(aa'c)     (- - +)  0.0002230  0.00139233   CL      B(OH)4  NA
 44 B(ca), C(ca)  (+ -  )  0.0001950  0.00121751   K       B(OH)4
 45 B(ca), C(ca)  (+ -  )  0.0001840  0.00114883   H       BR
 46 Theta(aa')    (- -  )  0.0001670  0.00104269   SO4     HCO3
 47 Psi(aa'c)     (- - +)  0.0001620  0.00101147   CL      HSO4    NA
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Below are notes on the sources of data for the different interactions in the table. In the model that has been used for these calculations, the interactions of Mg^{2+} and Ca^{2+} with CO$_3^{2-}$ are included as parameters rather than equilibrium constants (in contrast to the approach used in the Miami model, which is the focus of the discussion here). It is assumed that, for the purpose of these calculations, the results are equivalent. The sources of data and Pitzer parameters quoted below are those for the Miami model.

1. Na – CO_3 (+/–): the source is Peiper and Pitzer (1982). They include emf data from several sources, ϕ, $\Delta_{dil}H$, and C_p (C_p at 25 °C only). Fitted emfs at 0 °C and 50 °C show deviations of about 1 mV, apparently due to the assumption of constant $^{\phi}C_p$. Peiper and Pitzer state: "Although accurate thermodynamic information beyond 323 K is severely lacking, there is a need to measure the heat capacity of aqueous Na_2CO_3 and $NaHCO_3$ solutions and their mixtures with NaCl and other salts at molalities in excess of 1 mol kg^{-1} at 298.15 K and at all molalities at temperatures other than 298.15 K. In combination with a few additional measurements of the enthalpy of dilution at 298.15 K for solutions in excess of 1 mol kg^{-1}, extremely accurate thermodynamics for this system will be obtained."

2, 4. Mg and Ca – CO_3 (+/–): the Miami model includes these interactions as ion pair formation (although earlier versions appear to use strong interactions between the free ions instead). Millero and Pierrot (1998) give equations for these and other ion pairs in their Table II ($pK = A + CT$). They appear to refer to Millero and Roy (1997) as a source. These authors refer to Thurmond and Millero (1983) but that paper is for 25 °C only. I suggest that measurements are needed to determine the ion pairing constants over a range of T. Are emfs best for this?

3. H – Cl (+/–): the source for the Miami model is Campbell et al. (1993). They fitted emf data of Harned and co-workers and Bates and Bower (1954) (see p. 228 of Campbell et al., 1993). The Campbell et al. parameters are stated as being valid from 0-100 °C. The fit appears to have ignored (i.e., not included) $\Delta_{dil}H$, and C_p measurements (the latter have been determined at 10, 25 and 40 °C by Allred and Woolley (1981), and at 5 °C by Patterson et al.(2001)). It seems likely that an improved Pitzer model for $HCl_{(aq)}$ is possible, but new measurements are <u>not</u> high priority.

5. Na – SO_4 (+/–): the Miami model uses parameters of Holmes and Mesmer (1986) (acc. to Waters and Millero, 2013). More recently Rard et al. (2000) have re-fitted the Pitzer model from about 0 °C to 50 °C. No heat capacities appear to have been measured below 25 °C up to the year 1999 or so (none are cited by Rard et al.). Some further measurements in this range (0 – 25 °C) would be valuable.

6. Na – HSO_4 (+/–): Waters and Millero (2013) cite Hovey and Hepler (1990) as the source of parameters, but no values are given (there are just blanks in their table). Campbell et al. (1993) determined these parameters as functions of temperature from emf measurements of Dickson (1990) (in artificial seawater) by assuming that parameters for Mg^{2+}, Ca^{2+} and K^+ – HSO_4^- interactions were invariant with T. However, the treatment of these other bisulphates is different in Waters and Millero. It is not obvious what to suggest here: other emf measurements in mixtures at low T? C_p of H_2SO_4-Na_2SO_4 mixtures at low T?

7. Na-Cl (+/–): Waters and Millero use Archer's treatment (Archer, 1992). This includes C_p data at 274 and 278 K, but only a very few heats of dilution below 25 °C. There have been some new measurements since Archer's paper, notably the study of Archer and Carter (2000) of low temperature C_p. It may be sensible to compare some representative data with the model.

8. Mg – HCO_3 (+/–): according to Millero and Pierrot (1998) the $Mg(HCO_3)_2$ parameters were recalculated using the results of Millero and Thurmond (1983) and are only valid at 25 °C.

9. Mg – Cl (+/–): Waters and Millero (2013) list de Lima and Pitzer (1983) as the source. These authors appear simply to have fitted Pitzer parameters at 25 °C from Rard and Miller (1981), and values at higher T from Rogers and Pitzer (1981). This does not seem likely to result in accurate predictions of interactions below 25 °C. In the comprehensive study by Wang et al. (1998) some freezing point depression data were included, although there appears (from their table) to be only a single set of C_p data below 25 °C (at 283 K, by Eigen and Wicke (1951)). Further measurements of C_p at low temperatures may be worthwhile, but perhaps not the highest priority.

10. Mg – HSO_4 (+/–): the parameters in Waters and Millero (2013) are taken from Rard and Clegg (1999) and are for 25 °C only. The earlier Millero and Pierrot (1998) paper cites a submitted ms. by Pierrot et al. (1998) and states a range of validity of 0 – 50 °C. However, this other study appears never to have been published, and Millero and

Pierrot (1998) only tabulate parameters for 25 °C citing Harvie et al. (1984) as source. Measurements that yield this interaction at temperatures other than 25 °C are needed.

11. Mg – SO_4 (+/–): Waters and Millero (2013) list Phutela and Pitzer (1986) as the source. Their paper is mainly concerned with high T although their Pitzer model does yield osmotic coefficients at the freezing point in good agreement with measurements. It isn't clear from this paper what – if any – low T thermal data there are. I think we can assume that there are no C_p data below 25 °C, so new measurements would be valuable.

12. H – Na (++): Waters and Millero (2013) cite Campbell et al. (1993) who fitted results from the Harned and Owen (1958) textbook, though the real source is likely to be Harned and Mannweiler (1935) emf data (0 – 60 °C) for "ionized water in NaCl solutions". Robinson (1980) (who also addresses the temperature effect in this system) is cited too. There is probably no need for new data.

13. Na – HCO_3 (+/–): the source is Peiper and Pitzer (1982). See item (1) above.

14. Mg – $B(OH)_4$ (+/–): Millero and Pierrot (1998) take their parameters are taken from Simonson et al. (1987a) ("1987b" in their paper, not 1988 as stated). The parameters are valid from 5 to 55 °C. Simonson et al. measured emfs in a cell without liquid junction. A $\beta^{(2)}$ term is used because of the ion pairing that takes place. The nature of the solutions, and the analysis, means that there are dependencies on other data.

15. Cl – HCO_3 (– –): Millero and Pierrot (1998) take parameter $\Theta_{Cl-HCO3}$ (and Θ_{Cl-CO3}, $\psi_{Cl-HCO3-Na}$, and $\psi_{Cl-CO3-Na}$) from Roy et al. (1982) and Peiper and Pitzer (1982). The parameters are stated to be reliable from 0 to 60 °C. Peiper and Pitzer, whose paper follows that of Roy et al. in the printed journal, treats all the results. Roy et al.'s experiments were at 5, 25, and 45 °C.

16. Ca –HCO_3 (+/–): Millero and Pierrot (1998) state that these $Ca(HCO_3)_2$ parameters are taken from Harvie et al. (1984) and are only valid at 25 °C. Harvie et al. analysed calcite solubilities in a number of mixtures to obtain estimates of these parameters, but note discrepancies and state a need for further data. This ought to be explored.

17. Cl – $B(OH)_4$ (– –): Millero and Pierrot (1998) determined $\Theta_{Cl-B(OH)4}$ and $\psi_{Cl-B(OH)4-Na}$ from 0 to 45 °C from the work of Owen and King (1943) and Hershey et al. (1986). Measured emfs (5 to 55 °C) are not tabulated by Owen and King, but coefficients of fitted equations are given. From their description, there appear to be some systematic deviations. However, the results are from King's thesis (Yale University), and the original measurements are tabulated there. Hershey et al. (1986) used a glass pH electrode and made measurements at 25 °C only. Solutions including Mg^{2+} and Ca^{2+} ions were studied by them.

18. Cl – CO_3 (– –): see item (15) above.

19. Ca – $B(OH)_4$ (+/–): see item (14) above (the study of Simonson et al. (1987) included Ca^{2+} as well as Mg^{2+}).

20. K – CO_3 (+/–): Millero and Pierrot (1998) adopt parameters determined by Simonson et al. (1987b). The lowest temperature in their experiments is 338 K, and they use parameter values for 298.15 K from another study. In their discussion Simonson et al. report comparing excess thermodynamic properties with those calculated from previously reported parameters (Roy et al., 1984) to 278.15 K. (Roy et al. measured emfs in cells containing K, Cl, CO_3, and HCO_3 from 5 to 45 °C.) Simonson et al. (1987b) also note that some of their choices of fitting parameters are somewhat arbitrary, and suggest further data are needed to more directly determine values for K_2CO_3 and $KHCO_3$.

21. Mg - H (+ +): Waters and Millero (2013) adopt parameters from the study of Roy et al. (1980) on H-Mg-Cl-H_2O solutions. They measured emfs from 5 to 45 °C. There will be dependencies on the parameters used for $HCl_{(aq)}$ and $MgCl_{2(aq)}$.

22. Ca – Cl (+/–): the parameters used by Waters and Millero (2013) come from Greenberg and Moller (1989), which appear to be a partial re-fit of work originally done by Moller (1988). Moller's study adopts parameters of Phutela and Pitzer (1983), from 25 to 250 °C. Moller's study is for high temperatures. It is well known that the activity data for $CaCl_2$(aq) cannot be accurately fitted by the Pitzer model beyond 4 mol kg^{-1} or so. Our interest is mainly in lower concentrations. It seems possible that the model parameters adopted by Waters and Millero (2013) will not be accurate at low temperatures.

23. Ca –HSO_4 (+/–): Waters and Millero (2013) list their parameters for this interaction as coming from Harvie et al. (1984) (a 25 ^{o}C value), but with "Data extrapolated to temperatures other than 25 °C using calorimetric data from Pitzer (1991)." The Pitzer reference is his book chapter (in *Activity Coefficients in Electrolyte Solutions*, 2nd Edn.). I haven't been able to find any relevant information there, and the note of Waters and Millero appears to refer to $CaSO_4$ and not the bisulphate. This set of parameters should perhaps be treated as being "25 ^{o}C only".

24. Cl –SO_4 (– –): Waters and Millero (2013) use the 25 ^{o}C value of Harvie et al. (1984). However, Millero and Pierrot (1998) cite the studies of Moller (1988) and Greenberg and Moller (1989). The latter apparently use a fixed value of this parameter for temperatures below 150 ^{o}C (but this is not the same as Harvie et al.'s value). I conclude that the variation with temperature of this parameter is not known, though it also may not be significant.

25. CO_2 – Na (neutral +): Millero and Pierrot (1998) take their values ("from 0 to 50 ^{o}C") from the study of Peiper and Pitzer (1982), see item 1.

The same calculation as that above has also been carried out for pH on the free scale (pH(free) = $-\log_{10}(m\mathrm{H}^+)$), see below. Almost the only difference from the same calculation for pH on the total scale is that interactions which significantly affect the activity coefficients of HSO_4^- and SO_4^{2-} do <u>not</u> influence pH(free). Thus, they do not appear in the list below. (The most important of these interactions are those of HSO_4^- and SO_4^{2-} with cations Na^+ and Mg^{2+}.)

```
interaction                ΔpH(free)  ΔpH(free,norm)  sp1      sp2     sp3
1  B(ca), C(ca)  (+ -  )    0.160145   1.0              NA       CO3
2  B(ca), C(ca)  (+ -  )    0.139389   0.87039          H        CL
3  B(ca), C(ca)  (+ -  )    0.124346   0.77645          MG       CO3
4  B(ca), C(ca)  (+ -  )    0.074904   0.46772          CA       CO3
5  B(ca), C(ca)  (+ -  )    0.024422   0.15249          NA       CL
6  B(ca), C(ca)  (+ -  )    0.017312   0.10810          MG       CL
7  B(ca), C(ca)  (+ -  )    0.016877   0.10538          MG       HCO3

8  Theta(cc')    (+ +  )    0.015202   0.09492          H        NA
9  B(ca), C(ca)  (+ -  )    0.011647   0.07272          NA       HCO3
10 B(ca), C(ca)  (+ -  )    0.011033   0.06889          MG       B(OH)4
11 Theta(aa')    (- -  )    0.009652   0.06027          CL       HCO3
12 B(ca), C(ca)  (+ -  )    0.008768   0.05475          CA       HCO3
13 Theta(aa')    (- -  )    0.008018   0.05006          CL       B(OH)4
14 Theta(aa')    (- -  )    0.006801   0.04246          CL       CO3
15 B(ca), C(ca)  (+ -  )    0.005492   0.03429          CA       B(OH)4
16 Theta(cc')    (+ +  )    0.004754   0.02968          H        MG
17 B(ca), C(ca)  (+ -  )    0.004147   0.02589          K        CO3
18 B(ca), C(ca)  (+ -  )    0.003576   0.02232          NA       SO4
19 B(ca), C(ca)  (+ -  )    0.003496   0.02183          CA       CL
20 B(ca), C(ca)  (+ -  )    0.001748   0.01091          H        SO4
21 Lambda(N,c)   (n +  )    0.001698   0.01060          CO2      NA

22 Psi(aa'c)     (- - +)    0.001174   0.00733          CL       HCO3       NA
23 Lambda(N,a)   (n -  )    0.001066   0.00665          B(OH)3   SO4
24 B(ca), C(ca)  (+ -  )    0.001044   0.00651          NA       OH
25 B(ca), C(ca)  (+ -  )    0.000852   0.00532          NA       B(OH)4
26 Theta(cc')    (+ +  )    0.000850   0.00530          H        CA
27 Psi(aa'c)     (- - +)    0.000843   0.00526          CL       HCO3       MG
28 Psi(aa'c)     (- - +)    0.000706   0.00440          CL       CO3        NA
29 Lambda(N,c)   (n +  )    0.000648   0.00404          B(OH)3   NA
30 Psi(cc'a)     (+ + -)    0.000476   0.00297          H        NA         CL
31 B(ca), C(ca)  (+ -  )    0.000447   0.00279          K        CL
32 Theta(aa')    (- -  )    0.000353   0.00220          SO4      CO3
33 Lambda(N,c)   (n +  )    0.000339   0.00211          CO2      MG
34 B(ca), C(ca)  (+ -  )    0.000324   0.00202          CA       SO4
35 Theta(aa')    (- -  )    0.000303   0.00189          CL       OH
36 B(ca), C(ca)  (+ -  )    0.000238   0.00148          H        BR
37 B(ca), C(ca)  (+ -  )    0.000231   0.00144          MG       SO4
38 Psi(aa'c)     (- - +)    0.000224   0.00139          CL       B(OH)4     NA
39 B(ca), C(ca)  (+ -  )    0.000195   0.00121          K        B(OH)4
40 Theta(aa')    (- -  )    0.000166   0.00103          SO4      HCO3
```

interaction	ΔpH(free)	ΔpH(free,norm)	sp1	sp2	sp3
41 Psi(cc'a) (+ + -)	0.000144	0.00089	H	MG	CL
42 B(ca), C(ca) (+ -)	0.000137	0.00085	K	HCO3	
43 Lambda(N,c) (n +)	0.000115	0.00071	B(OH)3	K	
44 Psi(cc'a) (+ + -)	0.000101	0.00063	H	NA	SO4
45 Lambda(N,a) (n -)	0.000094	0.00058	CO2	CL	
46 Lambda(N,a) (n -)	0.000094	0.00058	CO2	SO4	
47 Theta(aa') (- -)	0.000079	0.00049	SO4	B(OH)4	
48 Psi(aa'c) (- - +)	0.000072	0.00044	SO4	HCO3	MG
49 B(ca), C(ca) (+ -)	0.000065	0.00040	K	SO4	
50 Lambda(N,c) (n +)	0.000065	0.00040	CO2	CA	

4. Results for Calcium Carbonate Activity

These sensitivity calculations (below) were done in the same way as for pH: the parameters for each of the interactions in the table below were set to zero, and then the equilibrium speciation in the system recalculated for each case. In the table below "$\Delta\lg(a\mathrm{CaCO_3})$" is the change in the logarithm (base 10) of the calculated $a\mathrm{Ca} \cdot a\mathrm{CO_3}$ activity product at 25 ^{o}C caused by setting the parameters for the indicated interaction to zero. It is an absolute value (I have not retained the sign of the change). This quantity is a simple measure of the sensitivity of the modelled activity product to errors and uncertainties associated with each interaction. The column "$\Delta\lg(a\mathrm{CaCO_3})$(norm)" presents the same information, but normalised to unity for the maximum case (the cation-anion interaction $\mathrm{Ca^{2+}}$ - $\mathrm{Cl^-}$, row 1).

The column id(pH) is the pH sensitivity ranking for the same interaction. Thus, high rankings in both id and id(pH) columns – for example for $\mathrm{Na^+}$ - $\mathrm{CO_3^{2-}}$ – mean that the interaction is very important for both quantities.

id	id(pH)	interaction	$\Delta\lg(a\mathrm{CaCO_3})$	$\Delta\lg(a\mathrm{CaCO_3})$(norm)	sp1	sp2	sp3
1	22	B(ca), C(ca) (+ -)	0.4367960	1.00000000	CA	CL	
2	1	B(ca), C(ca) (+ -)	0.1685990	0.38599026	NA	CO3	
3	2	B(ca), C(ca) (+ -)	0.1314670	0.30098032	MG	CO3	
4	4	B(ca), C(ca) (+ -)	0.0815200	0.18663175	CA	CO3	
5	7	B(ca), C(ca) (+ -)	0.0541200	0.12390223	NA	CL	
6	9	B(ca), C(ca) (+ -)	0.0383910	0.08789229	MG	CL	
7	-	Theta(cc') (+ +)	0.0294980	0.06753267	NA	CA	
8	28	B(ca), C(ca) (+ -)	0.0174600	0.03997289	CA	SO4	
9	14	B(ca), C(ca) (+ -)	0.0098750	0.02260781	MG	B(OH)4	
10	5	B(ca), C(ca) (+ -)	0.0079440	0.01818698	NA	SO4	
11	8	B(ca), C(ca) (+ -)	0.0076660	0.01755053	MG	HCO3	
12	18	Theta(aa') (- -)	0.0072220	0.01653403	CL	CO3	
13	17	Theta(aa') (- -)	0.0071760	0.01642872	CL	B(OH)4	
14	16	B(ca), C(ca) (+ -)	0.0061650	0.01411414	CA	HCO3	
15	13	B(ca), C(ca) (+ -)	0.0052490	0.01201705	NA	HCO3	
16	19	B(ca), C(ca) (+ -)	0.0051440	0.01177666	CA	B(OH)4	
17	15	Theta(aa') (- -)	0.0044120	0.01010083	CL	HCO3	
18	20	B(ca), C(ca) (+ -)	0.0043480	0.00995430	K	CO3	
19	25	Lambda(n,c) (n +)	0.0013000	0.00297622	CO2	NA	
20	41	B(ca), C(ca) (+ -)	0.0009660	0.00221156	K	CL	
21	29	Lambda(n,c) (n -)	0.0009500	0.00217493	B(OH)3	SO4	
22	30	B(ca), C(ca) (+ -)	0.0009310	0.00213143	NA	OH	
23	-	Psi(cc'a) (+ + -)	0.0008970	0.00205359	NA	CA	CL
24	31	B(ca), C(ca) (+ -)	0.0007620	0.00174452	NA	B(OH)4	
25	33	Psi(cc'a) (- - +)	0.0007380	0.00168958	CL	CO3	NA
26	-	B(ca), C(ca) (+ -)	0.0005900	0.00135074	CA	BR	
27	37	Lambda(n,c) (n +)	0.0005770	0.00132098	B(OH)3	NA	
28	33	Psi(cc'a) (- - +)	0.0005390	0.00123399	CL	HCO3	NA
29	-	Psi(cc'a) (+ + -)	0.0004490	0.00102794	NA	CA	SO4
30	11	B(ca), C(ca) (+ -)	0.0004410	0.00100962	MG	SO4	

Interactions ranked 18 and higher have an effect of $\geq$ 1% of the most important interaction (Ca^{2+} - Cl^{-}). All of these interactions, with the exception of Ca^{2+} - SO_4^{2-} and Na^{+} - Ca^{2+}, are also in the top 25 of those affecting pH. The sources of the parameters for these interactions are described in section 3 above. Details for $CaSO_4$ are below:

7. Na - Ca (+ +): the value of this parameter in the Miami model is fixed, and was determined in the study of Moller (1988). It was determined from solubility data and was found to be satisfactory over a very wide range of temperatures. There appear to be some isopiestic or vapour pressure data at room temperature (and some high temperature studies) from which the parameter could be determined independently. (See the references in Gruszkiewicz et al., 2007).

8. Ca – SO_4 (+/–): Waters and Millero (2013) list Harvie et al. (1984) as the source of the parameter value for 25 °C. In the same way as for the HSO_4^{-} interaction (see item 23 in the previous section) they add "Data extrapolated to temperatures other than 25 °C using calorimetric data from Pitzer (1991)" which implies that the parameters for this interaction vary with temperature. The Pitzer reference is his book chapter (in *Activity Coefficients in Electrolyte Solutions*, 2nd Edn.), see Table 13 in that work.

5. Draft Recommendations for New Measurements

The sensitivities ΔpH(Tot) and Δlg($a$$CaCO_3$) listed in the tables are relative, not absolute. They simply establish a ranking of the magnitude of the contributions of the different interactions to the calculation of the two quantities. One might expect, perhaps, that a change in the parameter(s) for a particular interaction of 10% might cause changes in the contributions to ΔpH(Tot) and Δlg($a$$CaCO_3$) of the order of 10% of those listed (because the sensitivity calculations involved a 100% change), but this has not yet been investigated. However, working on the assumption that obvious or likely data gaps identified in the notes above should be addressed in the order of sensitivity (the rank order in the tables), the following "top ten" interactions are suggested for further measurement and investigation.

(i) Na^{+} - HCO_3^{-} and Na^{+} - CO_3^{2-} interactions. See the text for item 1 in the pH section. It seems sensible to follow the recommendations of Peiper and Pitzer (1982) noted there, and quoted again below:

Recommendation: "there is a need to measure the heat capacity of aqueous Na_2CO_3 and $NaHCO_3$ solutions and their mixtures with NaCl and other salts at molalities in excess of 1 mol kg^{-1} at 298.15 K and at all molalities at temperatures other than 298.15 K."

(ii) $CaCl_2$(aq) – literature data for the thermodynamic properties of solutions of this salt seem to be almost entirely for 25 °C and above. Thus the Spencer et al. (1990) low temperature Pitzer model parameterised Ca^{2+} - Cl^{-} interactions for T < 25 °C by making use of freezing point data.

Recommendation: C_p measurements for molalities up to 4-6 mol kg^{-1} at different temperatures below 25 °C.

(iii) Mg^{2+} - CO_3^{2-} and Ca^{2+} - CO_3^{2-} interactions. Harvie et al. (1984) determined the Ca^{2+} - CO_3^{2-} ion-pairing constant (at 25 °C) from a consideration of calcite solubilities in water and NaCl(aq) at various fixed pCO_2, and from emf measurements of Reardon and Langmuir (1974). These authors studied both ion pairs, in experiments from 10 to 50 °C in aqueous K_2CO_3 solutions, and obtained the pK as functions of temperature.

Recommendation: emf studies of HCl in NaCl and Na_2CO_3 media at temperatures below 25 °C.

(iv) Na_2SO_4(aq) – this salt is quite insoluble (1.97 mol kg^{-1} at 25 °C, falling to about 0.35 at 0 °C), but supersaturated solutions can be produced. There do not appear to be any C_p data below 25 °C.

Recommendation: C_p measurements at different temperatures below 25 °C, up to (or beyond) saturation with respect to the solid salt.

(v) Na^{+} - HSO_4^{-} interactions. The variation of these parameters with temperature in the Miami model (see note 6 in section 3 above) involves a number of assumptions. Data at other temperatures are needed.

Recommendation: C_p of H_2SO_4-Na_2SO_4 aqueous solution mixtures, and emfs of H^{+}-Na^{+}-SO_4^{2-}-Cl^{-} solutions, at different temperatures, in the range 0 to 40 °C. If the emf measurements could be made using a sulphate electrode in place of the chloride one, Cl^{-} could be omitted from the solutions. This would simplify the modelling and probably reduce the uncertainties in the fitted parameters.

(vi) Mg^{2+} - HCO_3^- interactions. Values of the parameters appear to be available for 25 °C only, and were determined from emf measurements of carbonic acid ionisation in Na^+-Mg^{2+}-Cl^- aqueous solutions by Millero and Thurmond (1983).

Recommendation: further emf measurements, similar to those of Millero and Thurmond (1983), at temperatures other than 25 °C.

(vii) $MgCl_2$(aq) – as noted in item 9 in section 3, there only appears to be one set of measured C_p (at 10 °C) below 25 °C. Given the dependence of the determination of parameters for other interactions – for example Mg^{2+} - HCO_3^- as described above – on an accurate treatment of $MgCl_{2(aq)}$ further data for low temperatures would be worthwhile.

Recommendation: C_p measurements for molalities at different T from 0 to 40 °C, especially below 25 °C.

(viii) Mg^{2+} - HSO_4^- interactions. There appear to be parameters for 25 °C only. The recommendation below is similar to that for Na^+ - $HSO4^-$, with Mg^{2+} replacing Na^+.

Recommendation: C_p of H_2SO_4-$MgSO_4$ aqueous solution mixtures, and emfs of H^+-Mg^{2+}-SO_4^{2-}-Cl^- solutions, at different temperatures, in the range 0 to 40 °C. If the emf measurements could be made using a sulphate electrode in place of the chloride one, Cl^- could be omitted from the solutions. This would simplify the modelling and probably reduce the uncertainties in the fitted parameters.

(ix) Ca^{2+} - SO_4^{2-} interactions. First derivatives with respect to temperature of two parameters ($\beta^{(1)}_{CaSO4}$, $\beta^{(2)}_{CaSO4}$) are listed by Pitzer (1991; Table 13), with a maximum molality of 0.02. It is clear from the discussion in Moller (1988) of the determination of these parameters (from solubility data) that it is difficult or impossible to determine them uniquely. $CaSO_4$-Na_2SO_4 solutions were her favoured system. Some discussion regarding further work, and whether $MgSO_{4(aq)}$ can be used as an analogue in some way, is needed.

Recommendation: nothing yet.

(x) $MgSO_{4(aq)}$ – there don't appear to be thermal data below 25 °C, and the existing Pitzer parameterisations for this solute are mainly intended for 25 °C and above.

Recommendation: new C_p measurements for molalities at different temperatures from 0 to 40 °C, especially below 25 °C.

6. References

G. C. Allred and E. M. Woolley (1981) *J. Chem. Thermodyn*. **13**, 155– 164.

D. G. Archer (1992) *J. Phys. Chem. Ref. Data* **21** (4), 793-829.

D. G. Archer and R. W. Carter (2000) *J. Phys. Chem. B* **104**, 8563-8584.

R. G. Bates and V. E. Bower (1954) *J. Res. Natl. Bur. Stand*. **53**, 283-290.

D. M. Campbell, F. J. Millero, R. N. Roy, L. Roy, M. Lawson, K. M. Vogel and C. P. Moore (1993) *Mar. Chem.* **44**, 221-233.

S. L. Clegg and M. Whitfield (1991) Activity coefficients in natural waters. In '*Activity Coefficients in Electrolyte Solutions*', 2nd Edn., Ed. K. S. Pitzer, CRC Press, Boca Raton, p279-434.

S. L. Clegg and M. Whitfield (1995) *Geochim. et Cosmochim. Acta* **59**, 2403-2421.

A. G. Dickson (1990) *J. Chem. Thermodyn*. **22**, 113-127.

V. M. Eigen and E. Wicke (1951) *Electrochem.* **55**, 354.

J. P. Greenberg, N. Moller (1989) *Geochim. Cosmochim. Acta* **53**, 2503–2518.

M. S. Gruszkiewicz, D. A. Palmer, R. D. Springer, P. Wang, and A. Anderko (2007) *J. Solut. Chem*. **36**, 723-765.

H. S. Harned and B. B. Owen (1958) *The Physical Chemistry of Electrolytic Solutions*. Am. Chem. Soc. Monogr., Reinhold, London, pp. 748.

H. S. Harned and G. Mannweiler (1935) *J. Amer. Chem. Soc.* **57**, 1873-1876.

C. E. Harvie, N. Moller and J. H. Weare (1984) *Geochim. et Cosmochim. Acta* **48**, 723-751.

J. P. Hershey, M. Fernandez, P. J. Milne, and F. J. Millero (1986) *Geochim. et Cosmochim. Acta* **50**, 143-148.

H. Holmes and R. E. Mesmer (1986) *J. Solut. Chem*. **15**, 495-517.

J. K. Hovey and L. G. Hepler (1990) *J. Chem. Soc. Faraday Trans.* **16**, 2831-2839.

M. Ca. P. de Lima and K. S. Pitzer (1983) *J. Solut. Chem*. **12**, 187-199.

F. J. Millero and D. Pierrot (1998) *Aquatic Geochem*. **4**, 153-199.

F. J. Millero, F. Huang, T. Graham, and D. Pierrot (2007) *Geochim. et Cosmochim. Acta* **71**, 46-55.

F. J. Millero and R. N. Roy (1997) *Croatica Chemica Acta* **70** (1), 1-38.

F. J. Millero and V. Thurmond (1983) *J. Solut. Chem*. **12**, 401-412.

N. Moller (1988) *Geochim. et Cosmochim*. Acta **52**, 821-837.

B. B. Owen, and E. J. King (1943) *J. Amer. Chem. Soc*. **65**, 1612–1620.

B. A. Patterson, T. G. Call, J. J. Jardine, M. L. Origlia-Luster, and E. M. Woolley (2001) *J. Chem. Thermodyn*. **33**(10), 1237-1262.

J. C. Peiper and K. S. Pitzer (1982) *J. Chem. Thermodyn.* **14**, 613-638.

R. C. Phutela and K. S. Pitzer (1983) *J. Solut. Chem.* **12**, 201-207.

R. C. Phutela and K. S. Pitzer (1986) J. *Phys. Chem*. **90**, 895-901.

K. S. Pitzer (1991) Ion interaction approach: theory and data correlation. In '*Activity Coefficients in Electrolyte Solutions*', 2nd Edn., Ed. K. S. Pitzer, CRC Press, Boca Raton, p75-154.

J. A. Rard, S. L. Clegg and D. A. Palmer (2000) *J. Solut. Chem*. **29**, 1-49.

J. A. Rard and D. G. Miller (1981) *J. Chem. Eng. Data* **26**, 38.

E. J. Reardon and D. Langmuir (1974) *Am. J. Sci*. **274**, 599-612.

R. A. Robinson (1980) *J. Solut. Chem*. **9**, 449-454.

P. S. Z. Rogers and K. S. Pitzer (1981) *J. Phys. Chem*. **85**, 2886.

R. N. Roy, J. J. Gibbons, J. K. Trower, G. A. Lee, J. J. Hartley, and J. G. Mack. (1982) *J. Chem. Thermodyn*. **14**, 473–482.

R. N. Roy, J. J. Gibbons, R. Williams, L. Godwin, G. Baker, J. M. Simonson and K. S. Pitzer (1984) *J. Chem. Thermodyn***.** **16**, 303.

R. N. Roy, J. J. Gibbons, D. P. J Bliss, R. G. Casebolt, and B. K. Baker (1980) *J. Solut. Chem*. **9** (12), 911–930.

Møller, N. (1988) . *Geochim.Cosmochim. Acta* **52**, 821–837.

J. M. Simonson, R. N. Roy, J. Connole, L. N. Roy, and D. A. Johnson, D. A. (1987a) *J. Solution Chem*. **16**, 791–803.

J. M. Simonson, R. N. Roy, and J. J. Gibbons (1987a) *J. Chem. Eng. Data* **32**, 41–45.

R. Spencer, N. Moller, and J. H. Weare (1990) *Geochim. et Cosmochim. Acta* **54**, 575-590.

P. Wang, K. S. Pitzer and J. M. Simonson (1981) *J. Phys. Chem. Ref. Data* **27**, 971-991.

J. F. Waters and F. J. Millero (2013) *Mar. Chem*. **149**, 8-22.