

## Consistency issues of aqueous solubility data and solution thermodynamics of electrolytes\*

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*Abstract:* For the calculation of aqueous solubility of electrolytes, thermodynamic data from different sources are required. This can lead to errors if the data are inconsistent. This study reveals that some often-used semi-empirical equations for CO<sub>2</sub> solubility and other equilibria are inconsistent with CODATA (Committee on Data for Science and Technology) key thermodynamic data. The equations were recalculated to make them consistent with CODATA. Combining standard thermodynamic data of NaCl with the Pitzer model leads to significant deviations from the accepted experimental value at 25 °C. Owing to the inadequacy of the Pitzer model at molalities exceeding 6 mol kg<sup>-1</sup>, this model leads to poor predictions of the HCl vapor pressure in equilibrium with highly concentrated aqueous HCl solutions. A long-standing inconsistency problem is related to the solubility of calcium carbonate. The main problem is disagreement on the existence of the CaHCO<sub>3</sub><sup>+</sup> ion pair. It is shown that the inconsistency largely disappears if it is assumed that the CaHCO<sub>3</sub><sup>+</sup> exists at low ionic strength, but becomes less stable at higher ionic strength.

*Keywords:* solubility; electrolytes; modeling; Pitzer parameters; thermodynamics.

### INTRODUCTION

For the calculation of the aqueous solubility of electrolytes, thermodynamic data are needed for the pure compound and for the species formed in aqueous solution. As most of these dissolved species are ions, in the case of a salt, a model is needed to account for the nonideality of the solution. Unless the ionic strength of the solution is low, a model accounting for specific ion interactions like the model of Pitzer [1] with experimentally derived parameters [2] will be required for accurate calculations. As data from different sources is needed to calculate the solubility, internal consistency of the data used is not guaranteed.

In 1989, the Committee on Data for Science and Technology (CODATA) published a set of internationally agreed values for the thermodynamic properties of a number of key chemical substances [3]. This data set is considered to be highly internally consistent, but it is limited to about 150 species only. Furthermore, the reference data refer to 298.15 K, so additional information on heat capacities is required for calculations at other temperatures. As a practical result, other sources of information are often used for solubility calculations, and even for the data analysis of primary solubility data. This can lead to consistency issues.

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\*Paper based on a presentation at the 11<sup>th</sup> International Symposium on Solubility Phenomena (11<sup>th</sup> ISSP), Aveiro, Portugal, 25–29 July 2004. Other presentations are published in this issue, pp. 513–665.

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The most widely used parameter set for the Pitzer model is the one compiled by Pitzer himself [4]. However, several authors have suggested alternative sets [5–7], some of them applicable in a wide temperature range [8,9]. It is unclear to what extent these parameter sets lead to comparable results.

This paper discusses some of the main sources of inconsistency and error relevant to solubility problems, and points at future research for resolving those inconsistency issues.

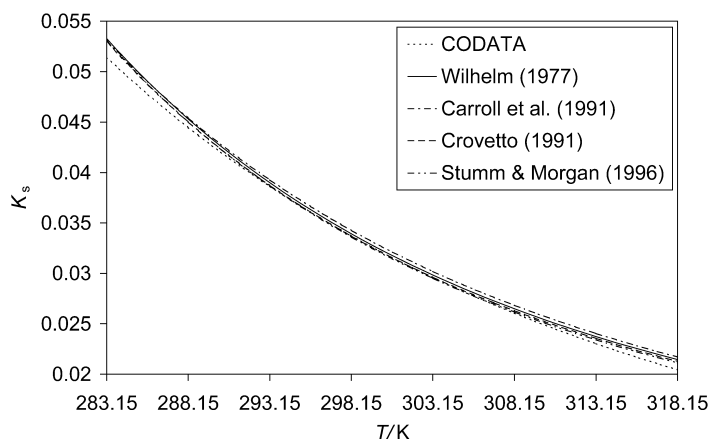
### CONSISTENCY BETWEEN CODATA AND OTHER THERMODYNAMIC DATA

The calculation of equilibrium constants based on the CODATA key thermodynamic data is limited to  $T = 298.15$  K, unless the heat capacity change of the reaction is accounted for. Therefore, semi-empirical equations are often used for the calculation of equilibrium constants. Not all numerical data found in the literature are consistent with CODATA. The aquatic chemistry of  $\text{CO}_2$  will be used as an illustration here.

The equilibrium constant,  $K_s$ , of the dissolution reaction,



is given by  $m(\text{CO}_2) \gamma(\text{CO}_2) p^0/[m^0 \phi(\text{CO}_2) p(\text{CO}_2)]$ , with  $m$  molality,  $p$  pressure (bar),  $\gamma$  activity coefficient, and  $\phi$  fugacity coefficient.  $K_s$  was calculated as a function of temperature, based on CODATA (assuming no changes of the heat capacity), and based on semi-empirical equations proposed by refs. [10–13]. The result is shown in Fig. 1. The curves should coincide at 298.15 K. However, small deviations can be observed. In order to check if these differences are significant, the enthalpy and entropy of dissolution at 298.15 K was calculated for each equation, and compared with the CODATA values. The result is shown in Table 1. The uncertainty estimates of the CODATA values were calculated assuming no correlation between the data, and therefore represent an upper bound of the uncertainty. While the dissolution enthalpies calculated from the semi-empirical equations are within the CODATA uncertainty limits, the dissolution entropies are outside the acceptable range in the case of Carroll et al. [13] and Stumm & Morgan [11].



**Fig. 1** Solubility constant of  $\text{CO}_2$  calculated from CODATA thermodynamic values and from various semi-empirical equations.

**Table 1** Enthalpy and entropy of CO<sub>2</sub> dissolution at 298.15 K estimated by CODATA, compared with values calculated from various semi-empirical equations.

	$\Delta_r H^\circ/\text{kJ mol}^{-1}$	$\Delta_r S^\circ/\text{J mol}^{-1} \text{K}^{-1}$
CODATA	$-19.75 \pm 0.33$	$-94.425 \pm 0.61$
Wilhelm (1977)	-19.78	-94.36
Carroll et al. (1991)	-19.43	-93.21
Crovetto (1991)	-19.79	-94.56
Stumm & Morgan (1996)	-19.98	-95.24

A similar calculation was made for the acid dissociation constants of CO<sub>2</sub>-carbonic acid ( $K_1$  and  $K_2$ ), comparing the Stumm and Morgan [11] equations with CODATA. The results are shown in Table 2. For these reactions, the former are consistent with CODATA thermodynamic values within the uncertainty limits.

**Table 2** Enthalpy and entropy of CO<sub>2</sub> dissociation at 298.15 K estimated by CODATA, compared with values calculated from semi-empirical equations.

	$\Delta_r H^\circ/\text{kJ mol}^{-1}$	$\Delta_r S^\circ/\text{J mol}^{-1} \text{K}^{-1}$
$\text{CO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) = \text{H}^+(\text{aq}) + \text{HCO}_3^-(\text{aq})$		
CODATA	$9.16 \pm 2.24$	$-90.91 \pm 1.13$
Stumm & Morgan (1996)	9.109	-91.052
$\text{HCO}_3^-(\text{aq}) = \text{H}^+(\text{aq}) + \text{CO}_3^{2-}(\text{aq})$		
CODATA	$14.70 \pm 2.25$	$-148.4 \pm 1.5$
Stumm & Morgan (1996)	14.901	-147.766

To conclude, data on the dissociation of water was investigated in the same manner. CODATA values were compared with an empirical equation suggested by Stumm and Morgan [11], and with  $K_w$  values of Marshall and Franck [14] recommended in *The CRC Handbook of Chemistry and Physics* [15]. The latter provides values of  $\text{p}K_w$  at 5 °C intervals. The data at 0–50 °C were used to fit an equation of the following form:

$$\lg K_w = A + B/(T/K) + C(T/K) + D \ln T/K + E/(T/K)^2 \quad (2)$$

Deviation between  $\text{p}K_w$  values provided by CRC [15] and values calculated with eq. 2 was on the order of 0.001. A comparison of thermodynamic data is shown in Table 3. It is clear that both Stumm and Morgan [11] and CRC [15] yield values that are inconsistent with CODATA. The CODATA values might be questioned here, because they lead to a  $\text{p}K_w$  value of 14.0014 at 298.15 K, whereas experimental values obtained by several authors are slightly below 14 [14,16,17]. The equation Marshall and Franck [14] fitted to the  $K_w$  data contains the density of the water. Consequently, further inconsistencies might potentially be introduced by using different equations of state for water.

**Table 3** Enthalpy and entropy of water dissociation at 298.15 K estimated by CODATA, compared with values calculated from semi-empirical equations

	$\Delta_r H^\circ/\text{kJ mol}^{-1}$	$\Delta_r S^\circ/\text{J mol}^{-1} \text{K}^{-1}$
CODATA	55.815 ± 0.08	-80.85 ± 0.23
Stumm & Morgan (1996)	55.906	-80.511
CRC	55.578	-81.522

To find out what is the cause of the inconsistencies, the primary data used by different sources should be compared in future research. In the meantime, it is useful to recalculate the empirical relations mentioned in this section, and force them through the CODATA value and slope at 298.15 K. This does not guarantee that the equations are correct, but it does guarantee that the equations are CODATA-consistent.

The results of such a recalculation is shown in Table 4, together with the original coefficients. The generic equation is of the following form:

$$\lg K = c_1 + c_2/(T/\text{K}) + c_3 T/\text{K} + c_4 \lg T/\text{K} + c_5/(T/\text{K})^2 + c_6/(T/\text{K})^3 \quad (3)$$

The standard deviation given in the table indicates the difference between the original and the recalculated equation, and does not necessarily reflect the actual accuracy of the equation. In the case of  $K_{\text{H}^+}$ , the use of the recalculated equation of Crovetto [12] is recommended because of the small correction needed in the recalculation. In the case of  $K_{\text{w}}$ , the proper choice is less clear-cut because of the possible overestimation of  $\text{p}K_{\text{w}}$  at 298.15 K by CODATA.

**Table 4** Coefficients of eq. 3 for various equilibria relevant for solubility: original data, followed by CODATA-consistent recalculations (bold). Note that  $\sigma$  signifies difference between original and recalculated equations (lg scale) and does not necessarily reflect accuracy of the equations.

	$c_1$	$c_2$	$c_3$	$c_4$	$c_5$	$c_6$	$\sigma$	$T$ range/ $^\circ\text{C}$	Ref.
<b>CO<sub>2</sub>(g) = CO<sub>2</sub>(aq)</b>									
	108.380 78	-6919.53	0.019 851	-40.451 54	669 365	-	-	-	[11]
	<b>7519.0886</b>	<b>-368 745.6</b>	<b>1.326 786</b>	<b>-2785.4522</b>	<b>18 939 340</b>	-	<b>0.003</b>	-	
	-0.340 255	-1708.688	-	-	408 797.14	-	-	0-80	[12]
	<b>-0.405 26</b>	<b>-1667.78</b>	-	-	<b>402 411.5</b>	-	<b>0.0009</b>	-	
	3.712 587 8	-5566.352	-	-	1 635 901	-1.30 158 × 10 <sup>8</sup>	-	0-160	[13]
	<b>2.1549</b>	<b>-3917.2</b>	-	-	<b>1 060 975</b>	<b>-6.4248 × 10<sup>7</sup></b>	<b>0.014</b>	-	
	-67.672 54	3796.3918	-0.000 479	21.668 955	-	-	-	0-80	[10]
	<b>-328.255 05</b>	<b>10 982.6</b>	<b>-0.071 246</b>	<b>125.7617</b>	-	-	<b>0.011</b>	-	
<b>CO<sub>2</sub>(aq) + H<sub>2</sub>O(l) = H<sup>+</sup>(aq) + HCO<sub>3</sub><sup>-</sup>(aq)</b>									
	-356.3094	21 834.37	-0.060 917	126.8339	-563 713	-	-	-	[11]
	<b>-5169.8296</b>	<b>252 830.5</b>	<b>-0.929 875</b>	<b>1915.6552</b>	<b>-13 106 717</b>	-	<b>0.003</b>	-	
<b>HCO<sub>3</sub><sup>-</sup>(aq) = H<sup>+</sup>(aq) + CO<sub>3</sub><sup>2-</sup>(aq)</b>									
	-107.8871	5151.79	-0.032 528	38.925 61	-1 684 915	-	-	-	[11]
	<b>1858.1688</b>	<b>-85 500.8</b>	<b>0.340 823</b>	<b>-697.0795</b>	<b>3 692 370</b>	-	<b>0.003</b>	-	
<b>H<sub>2</sub>O(l) = H<sup>+</sup>(aq) + OH<sup>-</sup>(aq)</b>									
	-283.971	13 323	-0.050 698	102.244 47	-1 119 669	-	-	-	[11]
	<b>-6349.0976</b>	<b>307 392.7</b>	<b>-1.130 594</b>	<b>2351.8194</b>	<b>-15 844 492</b>	-	<b>0.002</b>	-	
	744.0173	-32 750.0	0.151 078	-284.5121	959 560	-	-	0-50	[15]
	<b>-37 935.2884</b>	<b>1 820 707.1</b>	<b>-6.853 217</b>	<b>14 094.9688</b>	<b>-90 599 258</b>	-	<b>0.008</b>	-	

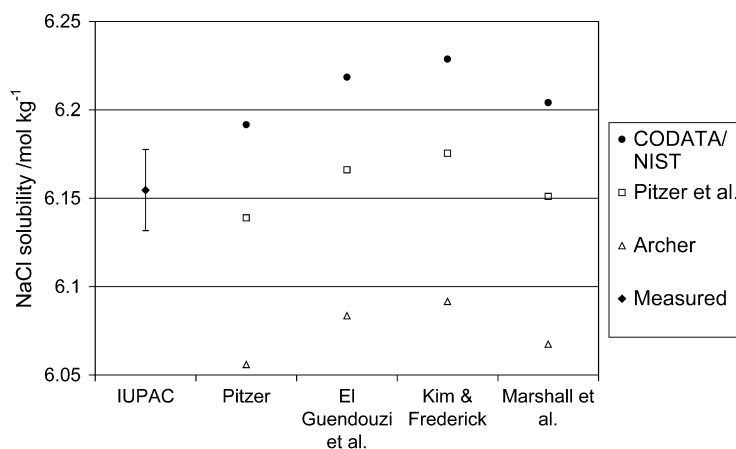
## AQUEOUS SOLUBILITY OF SODIUM CHLORIDE AND HYDROCHLORIC ACID

Before embarking on an investigation of the internal consistency of data related to electrolyte solubilities, a brief overview of the Pitzer model will be given. In this model, the mean activity coefficient of a pure electrolyte is given by:

$$\ln \gamma_{\pm} = |z_M z_X| f^{\gamma} + m \frac{2v_M v_X}{\nu} B_{MX}^{\gamma} + m^2 \frac{2(v_M v_X)^{2/3}}{\nu} C_{MX}^{\gamma} \quad (4)$$

where  $M$  and  $X$  in subscript denote cation and anion, respectively,  $z$  is charge number,  $m$  is molality of the compound,  $v_M$  and  $v_X$  are the number of cations and anions in the molecule, respectively,  $\nu = v_M + v_X$ .  $f^{\gamma}$  is a function of ionic strength that is independent of the electrolyte.  $B_{MX}^{\gamma}$  ( $\text{kg mol}^{-1}$ ) is the second interaction coefficient specific for the electrolyte  $MX$ , which contains an ionic-strength-independent part with coefficient  $\beta_{MX}^{(0)}$  and an ionic-strength-dependent part with coefficient  $\beta_{MX}^{(1)}$ .  $C_{MX}^{\gamma} = (3/2) C_{MX}^{\phi}$  ( $\text{kg}^2 \text{mol}^{-2}$ ) is the (ionic-strength-independent) third interaction coefficient. A convenient summary of the main aspects of the model is given by Pitzer [8].

We calculated the solubility of NaCl at 298.15 K using thermodynamic data of CODATA for  $\text{Na}^+(\text{aq})$  and  $\text{Cl}^-(\text{aq})$  and NIST for  $\text{NaCl}(\text{cr})$ , leading to  $\Delta_r G^{\circ} = -9.103 \text{ kJ mol}^{-1}$ . Alternative values of  $\Delta_r G^{\circ}$  were taken from Pitzer et al. [18] and from Archer [19]. The Pitzer model was used for calculating ion activity coefficients. Several sources of Pitzer parameters were tested [4,5,7,20]. The calculations were compared with measured values taken from the IUPAC Solubility Series [21]. The result is shown in Fig. 2.



**Fig. 2** Predicted values of NaCl solubility in water based on various sources of thermodynamic data (legend) and various sources of Pitzer parameters (X-axis); experimental value from IUPAC Solubility Data Series [21]. Error bar represents one standard deviation of data including all recommended values at 25 °C and excluding both tentative and aberrant values.

CODATA/NIST thermodynamic data lead to an overestimation of NaCl solubility. The difference is small (0.5–1 %) but significant. The calculated solubilities based on Pitzer et al.'s [18] thermodynamic data are acceptable. The values based on Archer's [19] data are too low by 1–1.5 %. Gibbs energies of formation of  $\text{Na}^+(\text{aq})$  and  $\text{Cl}^-(\text{aq})$  taken from Oelkers [22] were about 200  $\text{J mol}^{-1}$  different from values calculated from CODATA, but their sum was identical to the CODATA-derived sum.

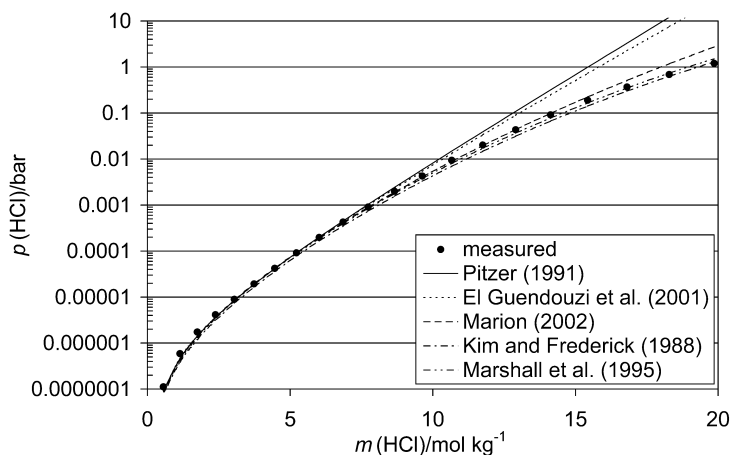
In view of the remarkable influence of different Pitzer parameter sets on the result, we tested these parameter values by comparing predictions of the mean activity coefficient of  $\text{NaCl}(\text{aq})$  with experimental values as compiled by Hamer and Wu [23] and by Robinson and Stokes [24]. The parameter sets

of Kim and Frederick [5] and by El Guendouzi et al. [7] systematically underestimate activity coefficients, typically by 0.005, and are not recommended. Pitzer's [4] own parameter values and those of Marshall et al. [20] show much better agreement.

For an exact match between the calculated solubility of NaCl and the value recommended by the IUPAC Solubility Data Series, a  $\Delta_f G^\circ$  value of  $-9.049 \text{ kJ mol}^{-1}$  is needed when Pitzer's [4] parameter values ( $\beta^{(0)} = 0.0765$ ,  $\beta^{(1)} = 0.2664$ ,  $C^\phi = 0.00127$ ) are used, and a value of  $-9.031 \text{ kJ mol}^{-1}$  is needed when Marshall et al.'s [20] parameters ( $\beta^{(0)} = 0.0771$ ,  $\beta^{(1)} = 0.26393$ ,  $C^\phi = 0.0011$ ) are used. Future research should be directed at the determination of the enthalpy and entropy contributions of these  $\Delta_f G^\circ$  values.

It is clear that careless use of thermodynamic data and Pitzer parameters can lead to incorrect calculations. Therefore, it would be useful if publications presenting Pitzer parameters would also present consistent thermodynamic properties.

Similarly, the equilibrium vapor pressure of HCl was calculated as a function of aqueous HCl molality. Thermodynamic data were taken from CODATA. Pitzer parameters were taken from various references [4,5,7,9]. The calculations were compared with measured values given by Liley et al. [25]. The result is shown in Fig. 3. None of the parameter sets is satisfactory over the entire concentration range. The parameter sets of Pitzer [4] and El Guendouzi et al. [7] were derived from data at molalities below  $6 \text{ mol kg}^{-1}$ , and do not extrapolate well at higher molalities. The parameter set of Kim and Frederick [5] is the most accurate set at  $20 \text{ mol kg}^{-1}$ , but is inaccurate at low molalities. Overall, the parameter set of Marshall et al. [20] yields the most accurate predictions. The parameter set of Marion [9] is almost as accurate, which is somewhat surprising because the main focus of this reference is on subzero temperatures.



**Fig. 3** HCl equilibrium partial pressure vs. aqueous HCl molality at  $25 \text{ }^\circ\text{C}$ , calculated with various sources of Pitzer parameters, together with experimental values compiled by Liley et al. [25].

The accuracy of the Pitzer model and even of simpler models is satisfactory in a large number of applications, but if activity coefficient models are used to derive thermodynamic data from primary measurements, the accuracy of the Pitzer model is barely sufficient at  $6 \text{ mol kg}^{-1}$ , and insufficient at higher molalities. Several suggestions have been made in the literature to improve the accuracy of the model. Weber [26] suggested an equation of the following form to calculate mean activity coefficients:

$$\ln(\gamma_{\pm}) = -\frac{A\sqrt{I}}{1+B\sqrt{I}} + CI + DI^2 + EI^3 + \dots \quad (5)$$

The disadvantage of this equation is that it cannot be considered as an extension of the Pitzer model. Applying this model means abandoning the Pitzer model with its extensive parameter set that cannot be used in Weber's formalism. An alternative was proposed by Pérez-Villaseñor et al. [27]. They used the Pitzer equations, but treated parameter  $b$ , which represents ionic diameter, as an adjustable parameter that can be different for each ion pair. The disadvantage of this method is that the electrostatic term is no longer the same for all electrolytes of the same charge, which raises the question of which mixing rules to use in the case of mixed electrolytes. Pitzer and Simonson [28,29] suggested an alternative model based on mole fractions. Another alternative, suggested by Pitzer et al. [30], treats the third interaction coefficients ( $C$ ) as ionic-strength-dependent, and even introduces fourth and fifth interaction coefficients. This method conserves the basic structure of the original Pitzer model, so existing interaction parameters can still be used by simply setting higher-order parameters equal to 0. However, the significance of fourth or higher virial coefficients, indicating quaternary or higher ion interactions, can be questioned. Their need probably arises due to the intrinsic nonlinearity of the molality scale, which goes to infinity as the mole fraction of the solute goes to unity. Therefore, it would be more appropriate to make the third virial coefficient ionic-strength-dependent in a way that compensates for the non-linearity of the molality scale.

### SPECIAL CASE: CALCIUM CARBONATE SOLUBILITY

Inconsistencies abounded for decades in the search for the thermodynamic solubility constant of the calcium carbonate polymorphs, especially calcite. The dissolution reaction is as follows:



However, the dominant reaction is [31]:



Calcium carbonate solubilities are generally determined in the pH range where  $\text{HCO}_3^{-}$  dominates the  $\text{CO}_2$  chemistry. In this case, it can be assumed that the charge balance is dominated by  $\text{Ca}^{2+}$  and  $\text{HCO}_3^{-}$  only. In that case, it follows that the equilibrium constant of reaction 6, denoted by  $K_s(\text{CaCO}_3)$ , can be approximated by the following relation:

$$K_s(\text{CaCO}_3) = \frac{K_2}{K_s(\text{CO}_2)K_1} \frac{\gamma(\text{Ca}^{2+})\gamma^2(\text{HCO}_3^{-})}{a(\text{H}_2\text{O})} \frac{S^3}{4p(\text{CO}_2)} \quad (8)$$

With  $K_1$  and  $K_2$  the first and second acid dissociation constant of  $\text{CO}_2(\text{aq})$ , respectively,  $K_s(\text{CO}_2)$  the solubility constant of  $\text{CO}_2$ ,  $\gamma(\text{Ca}^{2+})$  and  $\gamma(\text{HCO}_3^{-})$  the activity coefficient of  $\text{Ca}^{2+}$  and  $\text{HCO}_3^{-}$ , respectively,  $a(\text{H}_2\text{O})$  the water activity,  $S$  the solubility of  $\text{CaCO}_3$  in molality, and  $p(\text{CO}_2)$  the  $\text{CO}_2$  partial pressure. Ideal-gas behavior is assumed for  $\text{CO}_2$ . This equation is only approximate, as eq. 7 is not the only reaction occurring. Therefore, it should not be used to derive  $K_s(\text{CaCO}_3)$  from  $S$ . However, eq. 8 is a useful tool to assess potential errors in the determination of  $K_s(\text{CaCO}_3)$  from  $S$ .

Above, it was shown that there are significant differences between CODATA-derived values of  $K_s(\text{CO}_2)$  and values derived from other sources. This inconsistency will propagate to the value of  $K_s(\text{CaCO}_3)$  if different authors use different values of  $K_s(\text{CO}_2)$  for the calculation of  $K_s(\text{CaCO}_3)$ . The presence of  $a(\text{H}_2\text{O})$  in eq. 6 indicates that water activity changes need to be accounted for in the case of high ionic strengths. The presence of the activity coefficients  $\gamma(\text{Ca}^{2+})$  and  $\gamma(\text{HCO}_3^{-})$  is the main cause of inconsistencies, as will be explained below.

An examination of primary data from the literature revealed that literature calcite solubility data versus  $\text{CO}_2$  partial pressure at 298.15 K can be subdivided into two internally consistent, but mutually

inconsistent data sets [32]. At  $\text{CO}_2$  partial pressures around 1 atm both data sets are virtually identical, but at low partial pressures, there is a difference of 5–10 % between the data sets.

Another inconsistency in the literature with relevance to the solubility of calcium carbonate is on the existence of the  $\text{CaHCO}_3^+$  ion pair. The existence of this species has been asserted by different authors, and its stability constant has even been measured with different techniques [33,34]. Bicarbonate complexes of  $\text{Ba}^{2+}$  and  $\text{Sr}^{2+}$  have been observed as well [35–37]. However, several authors rejected the existence of  $\text{CaHCO}_3^+$  based on calcite solubility measurements [31,38]. Furthermore, Pitzer et al. [39] investigated the interaction between  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  in an electrochemical cell, and found positive values for  $\beta^{(0)}$  and  $\beta^{(1)}$  (0.28 and 0.3, respectively). Positive values mean that ions increase each other's activity coefficient, inconsistent with the existence of an ion pair. He and Morse [40] found similar results by studying the dissociation constants of carbonic acid in the presence of  $\text{CaCl}_2$  and  $\text{NaCl}$ . Remarkably, the calcite solubility data set with the lower solubilities is consistent with the existence of a  $\text{CaHCO}_3^+$  ion pair, whereas the other calcite solubility data set is consistent with ion behavior showing no complexation.

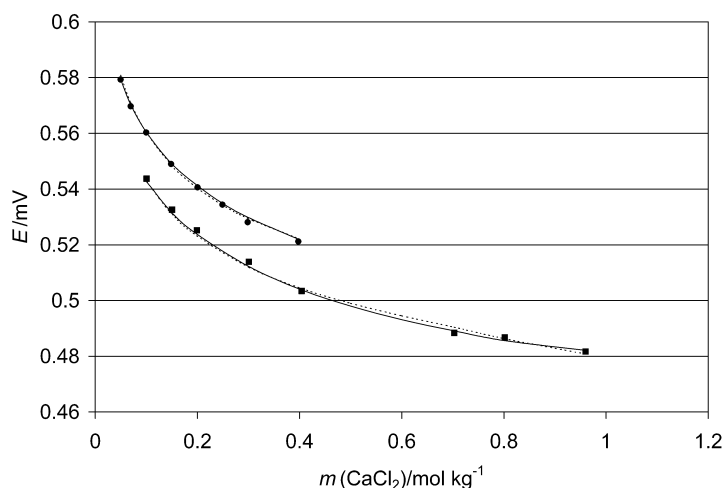
In a previous paper [32], we put forward a hypothesis that explained these inconsistencies, with the exception of Pitzer's electrochemical data. In this section, we will show that the hypothesis can be reconciled with those data as well. According to our hypothesis the calcite solubility data set showing the lower solubilities is the correct one. We assumed that the higher solubilities of the other data set were caused by crystal defects, for instance, in the form of a charged crystal surface. Surface-pitting processes can also lead to anomalous experimental results owing to the occurrence of metastable states [41]. Consequently, we hypothesized that  $\text{CaHCO}_3^+$  exists. The remaining issue is the electrochemical data of Pitzer et al. [39], which is not consistent with the hypothesis. However, Pitzer et al. [39] assumed that  $C^\phi = 0$  for the  $\text{Ca}^{2+}$ – $\text{HCO}_3^-$  interaction. This restriction introduces an apparent inconsistency with the solubility data we assumed to be correct, where in fact there is no inconsistency. In order to illustrate this, we generated a Pitzer parameter set that is consistent with both data sets. This could mean that the  $\text{CaHCO}_3^+$  ion pair is stable at low ionic strength and disappears at higher ionic strengths, but a more refined approach is needed to substantiate this.

Figure 4 shows the electrochemical data together with calculated values generated by the Pitzer model, using both the original and the new parameters. The parameter values are shown in Table 5. Figure 5 shows experimental data of aragonite solubility [34], together with model calculations using both Pitzer parameter sets. We use aragonite, another calcium carbonate polymorph, as an illustration here because Plummer and Busenberg [34] used these data to calculate the stability constant of  $\text{CaHCO}_3^+$ . They found a value of  $10^{1.14}$ , which approaches the range of values found from liquid-junction-corrected pH measurements of  $\text{CO}_2$ -saturated  $\text{Ca}(\text{HCO}_3)_2$  solutions ( $10^{1.21}$ – $10^{1.36}$ ). The results obtained with the two parameter sets are very similar, but Pitzer's parameters lead to an underestimation of the predicted  $\text{CO}_2$  partial pressure dependence of aragonite solubility, whereas the new parameter set accurately predicts the  $\text{CO}_2$  partial pressure dependence. The effect of the parameter set on the agreement between theory and experiment is more clear in Fig. 6, which shows the residuals  $r_s$  (predicted minus experimental solubility) expressed as a percent of the predicted solubility. Whereas Pitzer's parameters lead to systematic deviations, the residuals of the new parameter set are distributed more randomly.

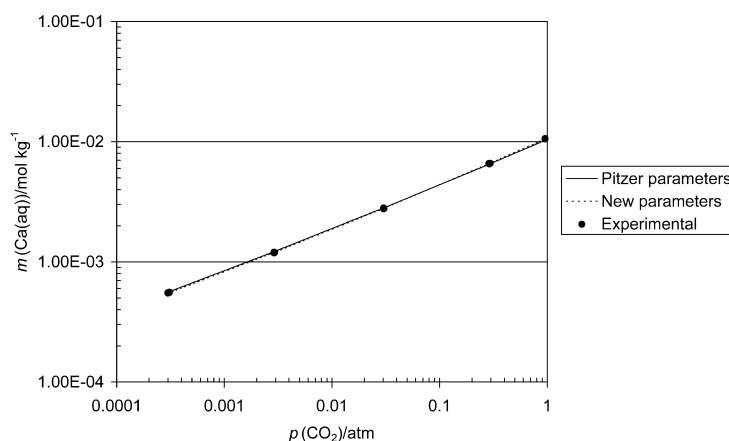
**Table 5** Pitzer parameters for the  $\text{Ca}^{2+}$ – $\text{HCO}_3^-$  ion pair

	Pitzer et al. (1985)	New parameters
$\beta^{(0)}$	0.28	1.45
$\beta^{(1)}$	0.3	–3.86
$C^\phi$	0	–1.01





**Fig. 4** Electromotive force of a  $\text{CaCl}_2 + \text{Ca}(\text{HCO}_3)_2$  system vs.  $\text{CaCl}_2$  molality at 25 °C [39]. Curves are predictions with parameters of Pitzer et al. [39] (solid curves) and the new parameter set (dotted curves). Squares are at  $m[\text{Ca}(\text{HCO}_3)_2] = 0.00062 \text{ mol kg}^{-1}$ , circles are at  $m[\text{Ca}(\text{HCO}_3)_2] = 0.00124 \text{ mol kg}^{-1}$ .

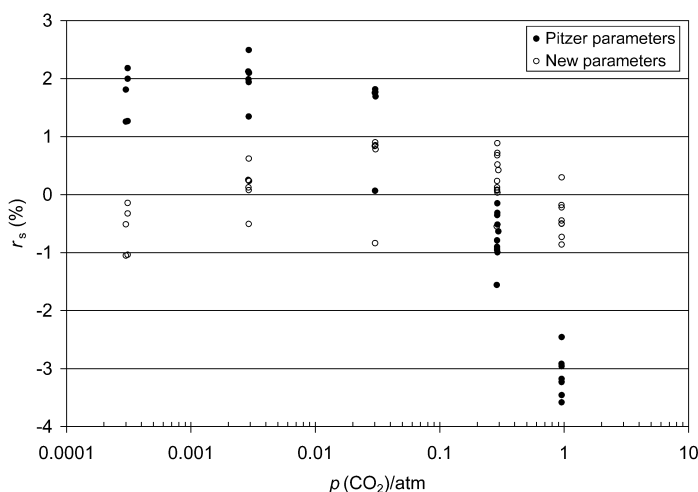


**Fig. 5** Aragonite solubility vs.  $\text{CO}_2$  partial pressure at 25 °C, measured by Plummer and Busenberg [34], and calculated with two Pitzer parameter sets.

The new Pitzer parameters are rather unusual. Especially  $C^\phi$  is outside the range normally encountered, and it can be expected that this parameter set is inapplicable at  $\text{CaCl}_2$  molalities exceeding  $1 \text{ mol kg}^{-1}$ . Nevertheless, the results show that the electrochemical data and the solubility data are not necessarily inconsistent. Future research should address the causes of those unusual Pitzer parameters. The introduction of a stability constant for  $\text{CaHCO}_3^+$  in the Pitzer framework might be helpful here.

Pitzer's original parameters are consistent with a  $K_s(\text{CaCO}_3)$  value of  $3.597 \times 10^{-9} = 10^{-8.444}$  for calcite, and  $4.996 \times 10^{-9} = 10^{-8.301}$  for aragonite, leading to  $\Delta_r G^\circ$  values of dissolution of  $48.199 \text{ kJ mol}^{-1}$  and  $47.384 \text{ kJ mol}^{-1}$ , respectively. The new parameters are consistent with  $K_s(\text{CaCO}_3)$  value of  $3.253 \times 10^{-9} = 10^{-8.488}$  for calcite, and  $4.640 \times 10^{-9} = 10^{-8.333}$  for aragonite, leading to  $\Delta_r G^\circ$  values of dissolution of  $48.448 \text{ kJ mol}^{-1}$  and  $47.568 \text{ kJ mol}^{-1}$ , respectively.

Königsberger et al. [42] investigated the  $\Delta_r G^\circ$  of the aragonite–calcite transition, and obtained a value of  $-830 \pm 20 \text{ J mol}^{-1}$ . The present analysis with the original Pitzer parameters and the new para-



**Fig. 6** Measured minus calculated aragonite solubility data at 25 °C, as a percentage of the calculated value ( $r_s$ ), with two parameter sets.

meters lead to  $\Delta_r G^\circ$  values of  $-815 \text{ J mol}^{-1}$  and  $-880 \text{ J mol}^{-1}$ , respectively. In spite of the better fit with the measured solubilities, the new Pitzer parameters lead to an inferior prediction of  $\Delta_r G^\circ$ .

## SUMMARY AND CONCLUSIONS

It was shown that several semi-empirical equations of equilibrium constants relevant for solubility calculations are inconsistent with the CODATA key thermodynamic values. NaCl solubility, calculated with CODATA/NIST thermodynamic values and the Pitzer model for ion activity coefficients, differs significantly from the accepted value from the IUPAC Solubility Data Series. Owing to the limited accuracy of the Pitzer model at high molalities, predictions of HCl solubility based on this model are poor. It was shown that electrochemical data, which were considered inconsistent with experimental calcium carbonate solubilities by Plummer and Busenberg [34], can be made consistent by assuming that the Pitzer parameter  $C^\phi(\text{Ca}^{2+}, \text{HCO}_3^-)$  differs from 0.

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