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Short Communication

Temperature extension of NaCl Pitzer coefficients and $\Delta_R G°$(NaCl)

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Abstract: The general temperature range for THEREDA is currently limited to 0 to about 110 °C. For the important electrolyte NaCl there are thermodynamic data available to 200 °C and above. To cover this larger temperature range for the Pitzer coefficients, a refit of the temperature functions of Greenberg, J. P. and Møller, N. (*Geochim. Cosmochim. Acta* 53 (1989) 2503-2518) is presented. A corresponding function for the solubility constant of NaCl is deduced from IUPAC recommended data. The data set for NaCl, thus extended in its range of validity up to 200°C, is implemented in THEREDA.

1 Introduction

The THEREDA database for the oceanic salt systems was designed such that the solid-liquid equilibria will be described as reliable and accurate as possible for the hexary system Na^+, K^+, Mg^{2+}, Ca^{2+} // Cl^-, SO_4^{2-} - H_2O and all its subsystems. To ensure the accuracy and considering the bases of experimental data, the temperature range was limited to 0 °C to about 110 °C. For some binary and ternary systems such as NaCl – H_2O and NaCl – KCl – H_2O thermodynamic data are available up to 200 °C and above. To cover this larger temperature range for the Pitzer coefficients and solubility constants, temperature functions with more than six terms (7 to 8) are required. However, the geochemical codes PHREEQC and Geochemist's Workbench, which are widely used and supported by THEREDA, support temperature functions with up to six temperature coefficients only. As for the important electrolyte NaCl it would be worthwhile to be able to describe the thermodynamic properties up to 200 °C, it was decided to extend the temperature functions implemented in THEREDA at present. Here the results of the refit of the eight-coefficient expression by Greenberg and Møller [GRE/MOL1989] to the six-coefficient temperature function in THEREDA are reported.

2 Fitting procedure and Results

The fitting strategy consisted in re-fitting the binary eight-coefficient temperature function for binary Pitzer coefficients given by Greenberg and Møller [GRE/MOL1989] to a six-coefficient temperature function implemented in THEREDA. With the new Pitzer coefficients a new temperature function for $\Delta_r G_m°$(NaCl) with

$$\Delta_r G_m^0(T) = -RT\ln K_s^0 \qquad (2\text{-}1)$$

for the reaction

$$Na^+ + Cl^- \rightleftharpoons NaCl(cr) \qquad (2\text{-}2)$$

was fitted against the experimental solubility data in the NaCl – H_2O system.

The equations of [GRE/MOL1989] were used to calculate the binary Pitzer coefficients in steps of 1 K between 273.15 K and 490.15 K.

Data in the range 273 to 393 K were given a double weight, in order to minimize changes in the former function [VOI2020]. The fitting program used was *gnuplot* [THO2011]. The fitted function was:

$$P=A + B \cdot T + C \cdot T \cdot \ln(T)+D \cdot T^2+E \cdot T^3+ \frac{F}{T} \qquad (2\text{-}3)$$

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The same procedure was also applied to the temperature function of [GRE/MOL1989] for $\Delta_r G_m°$of NaCl(cr). The resulting parametrization of equation (2-3) is used to calculate the dashed line in Figure 3.1. However, no numerical data of this refit are presented. This is due to the fact that a new function $\Delta_r G_m°(T)$ for NaCl(cr) is derived from experimental solubility data within the present work (cf. chapter 2.2).

2.1 Pitzer Parameter

The results for the refit of $\beta^{(0)}$, $\beta^{(1)}$, C^{Φ} according to equation (2-3)are listed in Table 2.1. The differences between the previous and new Pitzer coefficients of THEREDA in comparison to [GRE/MOL1989] are plotted in Figures 2.1 to 2.3.

Table 2.1: Temperature coefficients for the Pitzer parameter (equation (2-3)).

	$\beta^{(0)}$	$\beta^{(1)}$	C^{Φ}
A	9931.0954	27034.783	-4635.055
B	-223.8321	-611.8806	107.86756
C	37.468729	102.2781	-18.11616
D	-0.063524	-0.171355	0.0311444
E	$2.0008 \cdot 10^{-5}$	$5.4624 \cdot 10^{-5}$	$-9.9052 \cdot 10^{-6}$
F	-508663.3	-1335514	221646.78

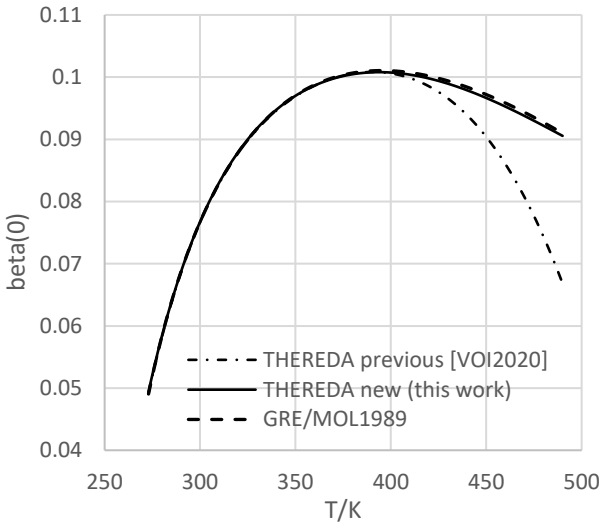

Figure 2.1: Temperature dependence of $\beta^{(0)}$ according to [GRE/MOL1989], the previous and new THEREDA function.

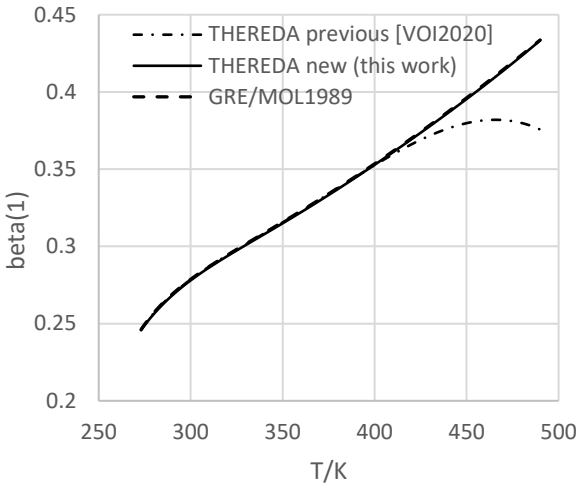

Figure 2.2: Temperature dependence of $\beta^{(1)}$ according to [GRE/MOL1989], the previous and new THEREDA function.

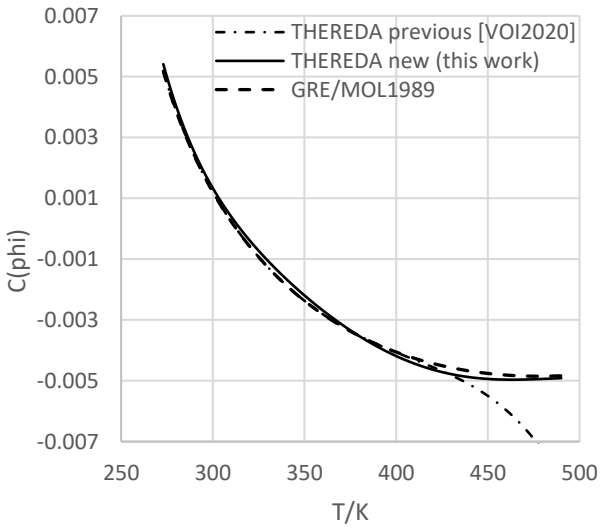

Figure 2.3: Temperature dependence of C^{Φ} according to [GRE/MOL1989], the previous and new THEREDA function.

2.2 New $\Delta_r G_m°(T)$ for NaCl(cr)

The description of the experimental solubility data of halite was not accurate enough with the new Pitzer coefficients and $\Delta_r G_m°(T)$ derived from [GRE/MOL1989] (cf. dashed line in Figure 3.1). Therefore the solubility data between 0 °C and 200 °C accepted by IUPAC [COH/LOR1991] were used to fit a new temperature function for $\Delta_r G_m°$(NaCl). (The experimental dataset of [COH/LOR1991] is part of the data compilation of [KRU2017]. All additional

data of other authors listed in [KRU2017] are represented well by the present fit – to be seen under application examples on THEREDA website.) Experimental solubility data were converted to $\Delta_r G_m°$ using equation (2-1). The results of the fit against equation (2-3) are given in Table 2.2.

Table 2.2: Temperature coefficients for $\Delta_r G_m°$(NaCl) (equation (2-3)).

A	$-1.585611 \cdot 10^6$
B	37614.26246
C	-6327.712366
D	11.10781391
E	-0.003763213
F	$7.1992993 \cdot 10^7$

The description quality of the NaCl solubility is demonstrated in Figure 3.1. As can be seen the experimental data are better reproduced than with the recommended IUPAC equation.

3 Comparison with the previous temperature function

The new temperature functions have some effect on the calculations of solubilities in higher component systems. The changes are generally small and do not justify the work for re-fitting the mixing parameters. Representative results calculated via the program ChemSage (nowadays distributed as FactSage, see [BAL/BEL2016]) are listed in Table 3.1 and Table 3.2.

The following abbreviations apply:

anh	anhydrite	gyp	gypsum
bi	bischofite	hal	halite
bloed	bloedite	mir	mirabilite
dans	d'ansite	then	thenardite
eps	epsomite	vant	van'thoffite
glas	glaserite	syl	sylvite

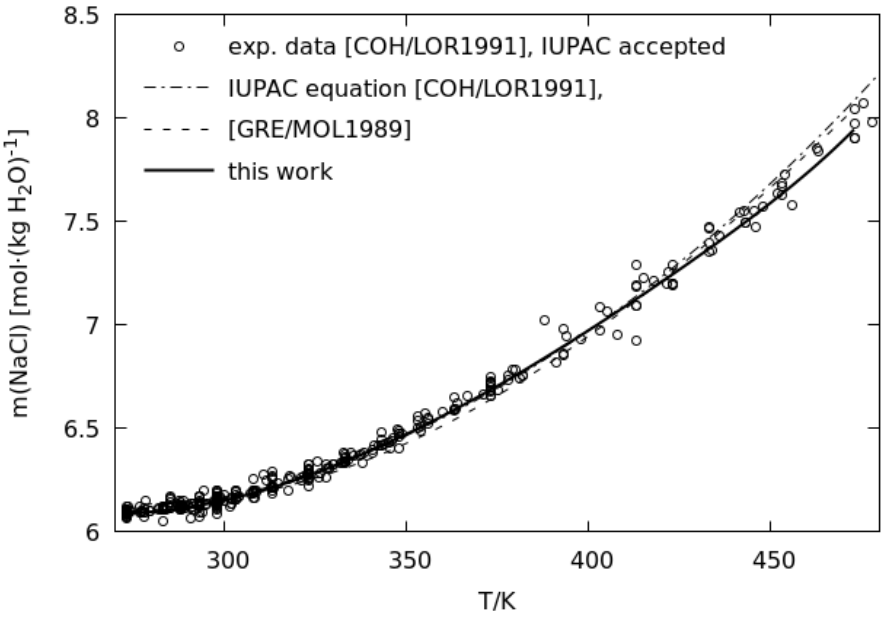

Figure 3.1: Solubility data for NaCl (Halite) in the system NaCl – H_2O. Comparison of experimental data [COH/LOR1991] with model results.

Table 3.1: Comparison of calculated saturation concentrations (mol/kgw) and osmotic coefficients (phi) according to the previous data set [VOI2020] and the updated one of this work.

(The osmotic coefficient phi is related to the water activity by $\varphi = \frac{-1000 \ln a_w}{M_w(\nu_1 m_1 + \nu_2 m_2)}$.)

NaCl-$MgCl_2$-H_2O						
	previous data set			**this work**		
	Na^+	**Mg^{2+}**	**phi**	**Na^+**	**Mg^{2+}**	**phi**
***T* = 0 °C, 1 bar**						
hal	2.6787	2.00 *)	1.7865	2.5218	2.00 *)	1.7923
bi	---	5.5215	3.6171	---	5.5215	3.6172
hal / bi	0.08171	5.4999	3.6079	0.080656	5.4999	3.6082
T = 25 °C, 1 bar						
hal	2.6787	2.00 *)	1.7447	2.6781	2.00 *)	1.7482
bi	---	5.7235	3.4695	---	5.7235	3.4695
hal / bi	0.09821	5.6997	3.4592	0.09742	5.6997	3.4594
***T* = 100 °C, 2 bar**						
hal	3.3825	2.00 *)	1.5587	3.4305	2.00 *)	1.5628
bi	----	7.5661	3.5027	----	7.5661	3.5027
hal / bi	0.1129	7.5691	3.4939	0.1153	7.5690	3.4937
NaCl-Na_2SO_4-H_2O						
	previous data set			**this work**		
	Cl^-	**SO_4^{2-}**	**phi**	**Cl^-**	**SO_4^{2-}**	**phi**
***T* = 0 °C, 1 bar**						
hal	6.0236	0.100 *)	1.2651	6.0054	0.100 *)	1.2745
mir	----	0.3300	0.6852	----	0.3300	0.6852
hal / mir	6.0010	0.1257	1.2639	5.9852	0.1229	1.2735
***T* = 25 °C, 1 bar**						
hal	5.8209	0.400 *)	1.2652	5.8089	0.400 *)	1.2708
mir	----	1.9268	0.6239	----	1.9268	0.6239
hal / mir	3.4432	1.4785	1.0614	3.4427	1.4654	1.0652
hal / then	5.5699	0.6928	1.2521	5.5680	0.6800	1.2582
NaCl-Na_2SO_4-H_2O						
	previous data set			**this work**		
	Cl^-	**SO_4^{2-}**	**phi**	**Cl^-**	**SO_4^{2-}**	**phi**
***T* = 100 °C, 1 bar**						
hal	6.4901	0.400 *)	1.1890	6.5455	0.400 *)	1.1946
then	---	2.9775	0.6329	---	2.9775	0.6329
hal / then	6.4646	0.4786	1.1781	6.5243	0.4657	1.1855

Table 3.1 (continued)

NaCl-$CaCl_2$-H_2O						
	previous data set			this work		
	Na^+	Ca^{2+}	phi	Na^+	Ca^{2+}	phi
***T* = 0 °C, 1 bar**						
hal	2.5719	2.00 *)	1.6884	2.5713	2.00 *)	1.6943
hal	0.1462	5.00 *)	2.7656	0.1451	5.00 *)	2.7659
***T* = 25 °C, 1 bar**						
hal	2.7794	2.00 *)	1.6719	2.7783	2.00 *)	1.6755
hal	0.2567	5.00 *)	2.6443	0.2556	5.00 *)	2.6447
***T* = 100 °C, 1 bar**						
hal **)	3.6405	2.00 *)	1.4789	3.6889	2.00 *)	1.4833
hal	0.8758	5.00 *)	2.0567	0.8957	5.00 *)	2.0576

*) concentration was set. **) calculation indicates the formation of $7.2 \cdot 10^{-11}$ mol portlandite, the concentration of H^+ was $1.5 \cdot 10^{-10}$ mol/ kg H_2O.

Table 3.2: Comparison of calculated saturation concentrations (mol/kgw) according to the previous data set [VOI2020] and the updated one of this work (reciprocal systems).

Na^+, Ca^{2+} // Cl, SO_4 - H_2O				
	previous data set		this work	
	Na^+	Ca^{2+}	Na^+	Ca^{2+}
***T* = 0 °C, 1 bar**				
hal / gyp	6.0749	$4.098 \cdot 10^{-2}$	6.0576	$4.085 \cdot 10^{-2}$
***T* = 25 °C, 1 bar**				
gyp / anh	3.8633	$5.666 \cdot 10^{-2}$	3.8547	$5.658 \cdot 10^{-2}$
hal / anh	6.1351	$3.791 \cdot 10^{-2}$	6.1245	$3.781 \cdot 10^{-2}$
***T* = 100 °C, 2 bar**				
hal / anh	6.6403	$2.914 \cdot 10^{-2}$	6.6944	$2.906 \cdot 10^{-2}$

Na^+, K^+ // Cl^-, SO_4^{2-} - H_2O						
	previous data set			this work		
	Na^+	K^+	SO_4^{2-}	Na^+	K^+	SO_4^{2-}
***T* = 25 °C**						
hal / then / glas	6.549	1.118	0.8643	6.517	1.120	0.8483
hal / syl / glas	5.364	2.259	0.2829	5.357	2.242	0.282
***T* = 100 °C**						
hal / then / glas	6.499	3.059	0.8074	6.506	3.102	0.787

Table 3.3 (continued)

Na^+, Mg^{2+} // Cl^-, SO_4^{2-} - H_2O						
	previous data set			this work		
	Na^+	Mg^{2+}	SO_4^{2-}	Na^+	Mg^{2+}	SO_4^{2-}
***T* = 0 °C**						
hal / eps / mir	3.032	2.055	0.7292	3.008	2.065	0.7229
***T* = 25 °C**						
hal / eps / bloed	1.564	3.283	0.938	1.536	3.304	0.929
hal / then / bloed	5.453	0.956	1.027	5.419	0.962	1.013
***T* = 100 °C**						
hal / dans / vant	6.462	0.547	0.492	6.436	0.582	0.480

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