

## **Binary Pitzer Model Parameters for Predicting the Solubility of Key Electrolytes in Hanford Waste – 14215**

Robert Carter\*, Kayla L. Pierson\*\*, and Jacob G. Reynolds\*\*

\* Energy Solutions, 2345 Stevens Dr.#240, Richland, WA 99354

\*\* Washington River Protection Solutions, LLC, P.O. Box 850 MSIN H6-04,  
Richland, WA 99352

### **ABSTRACT**

Predicting the solubility of salts in Hanford waste is important for a number of waste treatment options. The two most important parameters for predicting solubility are the temperature-dependent Gibbs free energies of the solids, and a solution phase activity coefficient for the major electrolytes. The present study develops these for the key Hanford electrolytes  $\text{Na}_2\text{C}_2\text{O}_4$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaHCO}_3$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{NaCl}$ , and  $\text{NaF}$ . The Pitzer model is a widely used liquid phase activity model for concentrated electrolytes and is employed in the present study. The Pitzer model has a number of interaction parameters that determine the impact of one electrolyte on the activity coefficient of another. The most influential ion pair parameters are the  $B_0$ ,  $B_1$ , and  $C$  parameters for the interaction with a given cation ( $\text{Na}^+$ ) and a given anion (the anions in the electrolytes above). These three parameters are denoted the Binary Pitzer parameters by the scientific community. The present study develops temperature-dependent Binary Pitzer parameters for  $\text{Na}^+\text{-C}_2\text{O}_4^{2-}$ ,  $\text{Na}^+\text{-CO}_3^{2-}$ ,  $\text{Na}^+\text{-HCO}_3^-$ ,  $\text{Na}^+\text{-SO}_4^{2-}$ ,  $\text{Na}^+\text{-Cl}^-$ , and  $\text{Na}^+\text{-F}^-$  by regressing osmotic coefficient data. These Pitzer coefficients are then employed to predict the temperature dependence of the solubility of these electrolytes in water. The results demonstrate that the parameters determined here provide an excellent prediction of the solubility of these electrolytes. Thus, these binary Pitzer model parameters provide the backbone of a model for predicting the solubility of salts in Hanford waste.

### **INTRODUCTION**

The Hanford tank farm contractor uses the Hanford Tank Waste Operations Simulator (HTWOS) to simulate mission performance and assist in system planning. The phase distribution of major species in the waste during waste treatment is an important parameter to mission planning. Therefore, the HTWOS model must predict the phase distribution for Hanford waste. The solubility of major waste constituents has historically been modeled using wash and leach factors in HTWOS [1]. Wash and leach factors are effective as long as the process being modeled is run under the exact same conditions in which the experimental data was collected to generate the wash and leach factors. When conditions change, however, the effectiveness of wash and leach factors is reduced drastically unless new factors are developed for the new operating conditions. Another disadvantage of wash and leach factors is that they are one-directional (solids being dissolved). They are incapable of predicting when solids precipitate. Solids precipitation has been identified as a complicating factor for Hanford waste processing [2, 3]. Many saltcakes have formed in the staged feed that were not predicted to form by wash and leach factors [4]. Given these issues with wash and leach factors, several outside review groups have recommended that solubility models replace wash and leach factors in process flowsheets [5-8].

Solubility is frequently calculated using thermodynamics. Thermodynamic-based solubility models predict liquid-solid phase equilibria by choosing solid and liquid phase species that minimize the total Gibbs free energy of the system. The present study follows the convention of Weber et al. [9] and Steel et al. [10], to employ the maximum amount of information already developed by them. This convention defines a reduced chemical potential ( $\mu$ ) for each species 'j', which is a function of the Gibbs free energy of each species at standard state ( $\mu^\circ$ ) per Equation 1 [9]:

$$\mu_j = \mu^\circ / RT \quad (\text{Eq. 1})$$

where T is temperature and R is the Universal Gas constant. The  $\mu_j$  values are functions of temperature, modeled using Equation 2.

$$\text{Parameter at } T = A + B(T - T_r) + C \left( \frac{1}{T} - \frac{1}{T_r} \right) + D \ln \left( \frac{T}{T_r} \right) + E(T^2 - T_r^2) \quad (\text{Eq. 2})$$

In Equation 2, the parameter is either the  $\mu_j$  of a species or a binary Pitzer parameter (explained below),  $T_r$  is a reference temperature (the standard state of 298.15 K), and A through E are empirically determined parameters. Equation 2 can frequently be truncated and still adequately represent the data. Consequently, Coefficients C, D, or E are often statistically indistinguishable from zero, and zero is retained for the parameter value in those cases.

The  $\mu_j$  values in Equation 1 are only representative of the Gibbs free energy at standard state conditions for dissolved species. Therefore, activity coefficients are required for real concentrations. This study uses the Pitzer model to calculate activity coefficients. The Pitzer model is given by [11]

$$\ln \gamma_i = \ln \gamma_i^{DH} + \sum B_{ij}(I)m_j + \sum_j \sum_k C_{ijk} m_j m_k + \dots \quad (\text{Eq. 3})$$

where

$$B_{ij} = B_0 + B_1 \exp(-\alpha I^{0.5}) \quad (\text{Eq. 4})$$

Here, m is the molality of ion 'i',  $\gamma_i$  is the activity coefficient,  $\gamma_i^{DH}$  is the modified form of the Debye-Huckel activity coefficient, I is ionic strength,  $B_0$  and  $B_1$  are Binary Pitzer parameters for each pair of ions, and  $C_{ijk}$  is another Binary Pitzer parameter that is usually taken to be independent of ionic strength. The  $\alpha$  parameter is a universal constant [11].

The Pitzer parameters are required for each cation-anion pair in the electrolyte solutions. The Pitzer parameters are assumed to be independent of solution ionic strength, but they are temperature-dependent. The temperature dependence of the Binary Pitzer parameters are expressed using Equation 2 [9]. The  $B_0$ ,  $B_1$ , and C parameters described in Equations 3 and 4 are known as the binary Pitzer parameters [11] because they are parameters that reflect the interaction between a single cation and anion pair. Modeling complex Hanford waste likely

requires ternary parameters for interactions between other major anions like nitrate and nitrite. Development of the binary Pitzer parameters, however, is a necessary first step to the development of these more complicated models. For a more detailed description of the Pitzer model, see reference [11].

The binary Pitzer parameters to be developed in the present study are for  $\text{Na}^+\text{-C}_2\text{O}_4^{2-}$ ,  $\text{Na}^+\text{-CO}_3^{2-}$ ,  $\text{Na}^+\text{-HCO}_3^-$ ,  $\text{Na}^+\text{-SO}_4^{2-}$ ,  $\text{Na}^+\text{-Cl}^-$ , and  $\text{Na}^+\text{-F}^-$ . Sodium is the dominant cation in the liquid phase of Hanford waste. The anions  $\text{C}_2\text{O}_4^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{F}^-$  are components of salts that have been reported in Hanford waste [4, 12]. Chloride, although not a solid salt seen in Hanford waste, was included in this study because it is a component in the liquid phase, and therefore affects the water activity of Hanford liquids. Additionally, NaCl is the dominant electrolyte in the gibbsite solubility study reported by Wesolowski [13]. Wesolowski's [13] data will be used in a future study to determine the model parameters for aluminum solubility in Hanford waste, and the  $\text{Na}^+\text{-Cl}^-$  binary parameters developed here will be an input to that study.

Other major anions of interest that are not covered in the present study are nitrite, nitrate, hydroxide, and the aluminate ion. Modeling nitrite, nitrate, and hydroxide solutions are complicated by the formation of contact ion-pairs [14]. Consequently, the Pitzer parameters for these electrolytes will be developed in a more focused study [15]. The solubility of aluminate in Hanford waste exhibits unusual behavior [16, 17]. Thus, aluminum solubility will also be the subject of a more focused modeling effort in the future.

## **MODEL DEVELOPMENT**

### **Model Parameter Overview**

The next section describes how the temperature-dependent binary Pitzer parameters and reduced chemical potentials described by Equation 2 are determined. Table I and Table II provide these parameters determined here, or taken from the literature. The parameters for Equation 2 for the reduced chemical potentials of all dissolved ions were taken from Weber et al. [9] or Steele et al. [10], to ensure consistency of the  $\text{Na}^+$  ion parameters across all of the sodium-electrolyte solutions and to ensure consistency with other data from this same research group. Thus, the reduced chemical potentials developed below are for the solid salt species.

### **NaCl**

Sodium chloride is not a major constituent in tanks, but is required to evaluate parameters for other species, for example gibbsite from Wesolowski's data [13].

The binary Pitzer parameters were determined by fitting osmotic coefficient data [18, 19]. The reduced chemical potentials of solid NaCl were determined by fitting the Pitzer model to the NaCl solubility data from Seidell [20]. The resulting parameters are listed in Tables I and II. The accuracy of the solubility predictions, shown in Figure 1, has a standard deviation of 0.004 over the temperature range.

TABLE I. Coefficients for Gibbs energy of formation

$$\mu_0/RT = A + B(T - T_0) + C(1/T_0 - 1/T) + D \ln(T/T_0) + E(T^2 - T_0^2)$$

Constituent	A	B	C	D	E	Reference
H <sub>2</sub> O	-95.665	-1.0029	0	324.04	0.000508	[10]
Na+	-105.73	0.85194	0	0	-0.000883	[10]
H+	0	0	0	0	0	[10]
OH-	-63.534	0.75606	0	0	-0.000747	[10]
Cl-	-52.928	0.367999	0	0	-0.000358	[10]
F-	-112.59	1.1322	0	0	-0.001143	[10]
CO <sub>3</sub> <sup>-2</sup>	-213.14	2.28402	0	0	-0.002298	[9]
HCO <sub>3</sub> <sup>-</sup>	-236.948	2.40768	0	0	-0.002471	[10]
SO <sub>4</sub> <sup>-2</sup>	-300.531	3.11291	0	0	-0.003155	[10]
C <sub>2</sub> O <sub>4</sub> <sup>-2</sup>	-272.165	2.782581	0	0	-0.002792	[10]
Na <sub>2</sub> CO <sub>3</sub> ·H <sub>2</sub> O	-519.2349	2.707537	0	443.1349	-0.003707	[10]
Na <sub>2</sub> CO <sub>3</sub> ·7H <sub>2</sub> O	-1095.284	-0.305245	0	1862.046	-0.002667	This Study
Na <sub>2</sub> CO <sub>3</sub> ·10H <sub>2</sub> O	-1383.078	-3.021157	0	2800.334	-0.001406	This Study
NaCl	-155.0132	1.019301	0	39.13024	-0.001117	This Study
NaF	-219.391	2.022907	0	0	-0.002087	This Study
Na <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	-489.4015	5.041464	37072.55	-247.939	-0.004768	This Study
Na <sub>2</sub> SO <sub>4</sub>	-513.202	5.605164	-1.13987	-126.817	-0.005555	This Study
Na <sub>2</sub> SO <sub>4</sub> ·10H <sub>2</sub> O	-1471.994	-9.562487	40.0842	3900.05	0.003914	This Study
NaHCO <sub>3</sub>	-343.561	4.737928	28198.59	-347.771	-0.004361	This Study

TABLE II. Binary Pitzer parameters

$$P(T) = A + B(T - T_0) + C(1/T_0 - 1/T) + D \ln(T/T_0)$$

Label	Anion	Param	A	B	C	D	Temp.	Reference
Na-OH-B0	OH <sup>-</sup>	β <sup>0</sup>	0.091763	-0.07308	-7118.75	45.78472	0-100	[15]
Na-OH-B1	OH <sup>-</sup>	β <sup>1</sup>	0.212694	0.414149	46598	-279.171		[15]
Na-OH-C	OH <sup>-</sup>	C	0.001748	0.002725	267.9999	-1.7259		[15]
Na-Cl-B0	Cl <sup>-</sup>	β <sup>0</sup>	0.075318	0.006943	1042.211	-5.34011	0-100	This Study
Na-Cl-B1	Cl <sup>-</sup>	β <sup>1</sup>	0.276964	0.016939	1843.033	-10.9493		This Study
Na-Cl-C	Cl <sup>-</sup>	C	0.000703	-0.00052	-72.0357	0.379806		This Study
Na-F-B0	F <sup>-</sup>	β <sup>0</sup>	0.033	0	246.8	-0.6728	0-100	[9]
Na-F-B1	F <sup>-</sup>	β <sup>1</sup>	0.2456	0	2833	-9.451		[9]

Na-F-C	F <sup>-</sup>	C	0.00281	0	12.25	-0.0436		[9]
Na-CO <sub>3</sub> -B0	CO <sub>3</sub> <sup>-2</sup>	β <sup>0</sup>	0.03623	-0.0233	-1108.38	11.19856	0-90	This Study
Na-CO <sub>3</sub> -B1	CO <sub>3</sub> <sup>-2</sup>	β <sup>1</sup>	1.50975	-0.09784	-4412.51	44.58207		This Study
Na-CO <sub>3</sub> -C	CO <sub>3</sub> <sup>-2</sup>	C	0.00184	0	0	0		This Study
Na-HCO <sub>3</sub> -B0	HCO <sub>3</sub> <sup>-</sup>	β <sup>0</sup>	0.028	-0.01446	-682.886	6.899586	0-90	This Study
Na-HCO <sub>3</sub> -B1	HCO <sub>3</sub> <sup>-</sup>	β <sup>1</sup>	0.044	-0.02447	-1129.39	11.41086		This Study
Na-HCO <sub>3</sub> -C	HCO <sub>3</sub> <sup>-</sup>	C	0	0	0	0		This Study
Na-SO <sub>4</sub> -B0	SO <sub>4</sub> <sup>-2</sup>	β <sup>0</sup>	0.017271	0	758.5359	-2.00966	0-100	This Study
Na-SO <sub>4</sub> -B1	SO <sub>4</sub> <sup>-2</sup>	β <sup>1</sup>	1.147943	0	-6174.03	22.67425		This Study
Na-SO <sub>4</sub> -C	SO <sub>4</sub> <sup>-2</sup>	C	0.001957	0	-34.5971	0.085673		This Study
Na-C <sub>2</sub> O <sub>4</sub> -B0	C <sub>2</sub> O <sub>4</sub> <sup>-2</sup>	β <sup>0</sup>	0.3249	0	17.36		0-110	[10]
Na-C <sub>2</sub> O <sub>4</sub> -B1	C <sub>2</sub> O <sub>4</sub> <sup>-2</sup>	β <sup>1</sup>	-0.0288	0	0.1478			[10]
Na-C <sub>2</sub> O <sub>4</sub> -C	C <sub>2</sub> O <sub>4</sub> <sup>-2</sup>	C	-0.0483	0	4.58			[10]

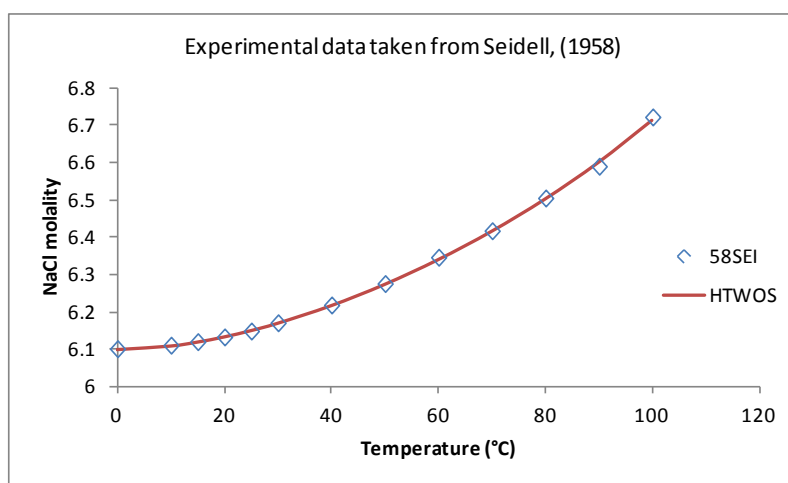


Fig. 1. Solubility of NaCl in H<sub>2</sub>O from 0 to 100 °C.

## Na<sub>2</sub>SO<sub>4</sub>

The experimental osmotic coefficient data in Table III was regressed to provide coefficients for the binary Pitzer parameters for Na<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O. The results of predictions with the new coefficients are plotted in Figures 2a through 2f. The figure captions for the experimental data are defined in Table III. The fit to the experimental data had a standard deviation of 0.003 osmotic coefficients for all the data over the temperature range.

TABLE III. Data sources for osmotic coefficients for Na<sub>2</sub>SO<sub>4</sub>.

Reference (Legend Entry)	Temperature Range (°C)	Concentration Range (mol/kg)	Number of Points
[21] Kangro and Groeneveld, 1962 (62KAN/GRO)	20, 25	0.5 – 3.0	12
[22] Robinson, Wilson and Stokes, 1941 (41ROB/WIL)	25	0.09 – 4.20	23
[23] Hellams et al., 1965 (65HEL/PAT)	45	0.7 – 3.5	13
[24] Humphries, Kohrt and Patterson, 1968 (68HUM/KOH)	60	0.9 – 3.5	13
[25] Moore, Humphries and Patterson, 1972 (72MOO/HUM)	80	0.93 – 2.98	30
[26] Patterson, Gilpatrick and Soldano, 1960 (60PAT/GIL)	99.6	0.89 – 3.18	5

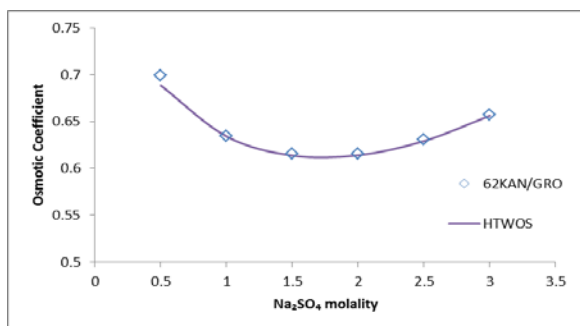


Fig. 2a.  $\text{Na}_2\text{SO}_4$  Osmotic Coefficients at 20 °C.

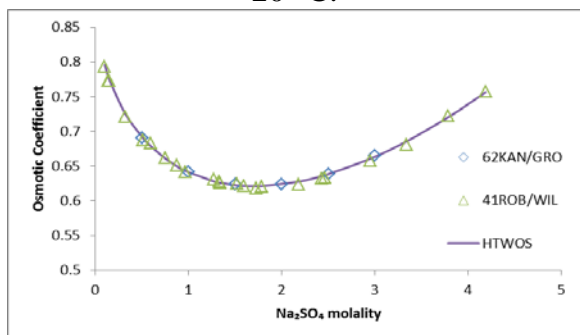


Fig. 2b.  $\text{Na}_2\text{SO}_4$  Osmotic Coefficients at 25 °C.

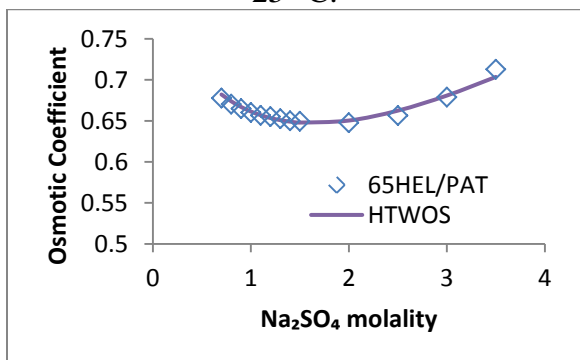


Fig. 2c.  $\text{Na}_2\text{SO}_4$  Osmotic Coefficients at 45 °C.

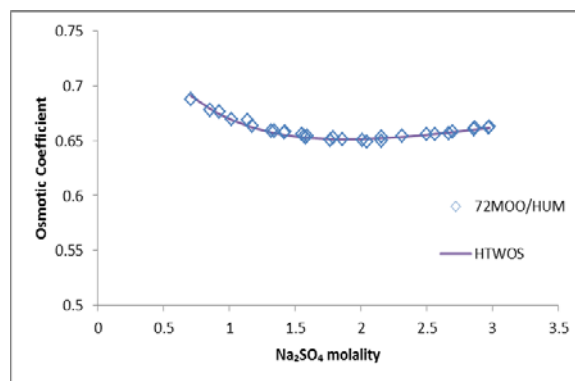


Fig. 2e.  $\text{Na}_2\text{SO}_4$  Osmotic Coefficients at 80 °C.

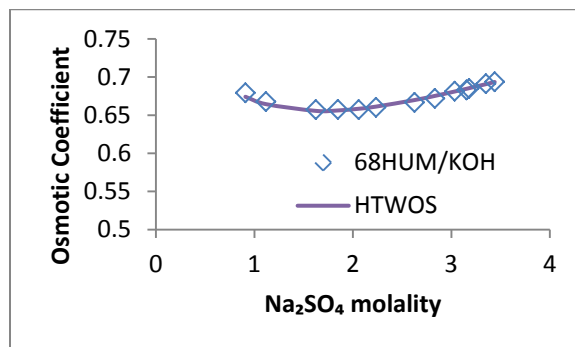


Fig. 2d.  $\text{Na}_2\text{SO}_4$  Osmotic Coefficients at 60 °C.

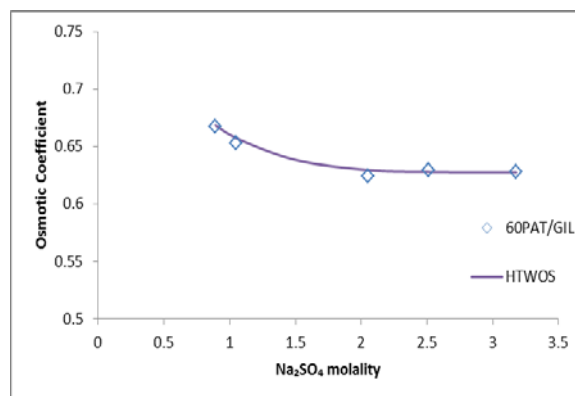


Fig. 2f.  $\text{Na}_2\text{SO}_4$  Osmotic Coefficients at 99.6 °C.

The parameters for the reduced chemical potentials were determined by regressing the solubility data reported by Seidell [20]. Prediction of the solubility from the complete HTWOS model is

shown in Figure 3 also, where the standard deviation of fit is 0.007 over the temperature range from 0 to 100 °C.

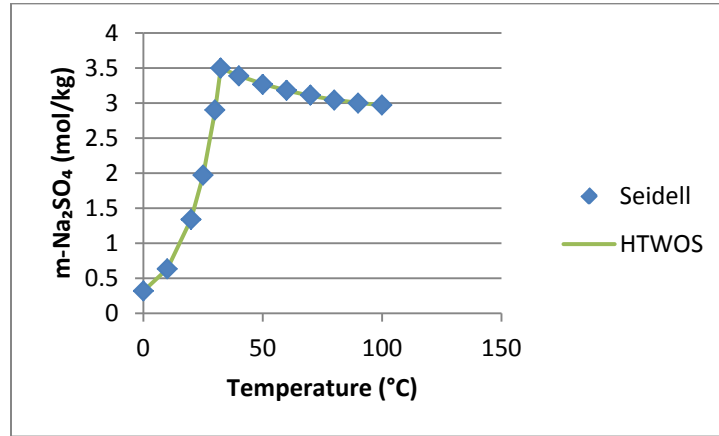
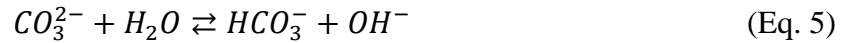


Fig. 3. Solubility of Na<sub>2</sub>SO<sub>4</sub> in H<sub>2</sub>O from 0 to 100 °C.

### Na<sub>2</sub>CO<sub>3</sub> and NaHCO<sub>3</sub>

The thermodynamics of sodium carbonate cannot be studied as a simple binary system due to the hydrolysis of carbonate ions leading to bicarbonate and hydroxide ions. Therefore, the system has to be treated as a mixture of sodium carbonate, sodium bicarbonate and sodium hydroxide. The hydrolysis of the carbonate ion can be described by:



The equilibrium constant for this reaction is given by:

$$K_h = \frac{a_{HCO_3^-} \times a_{OH^-}}{a_{CO_3^{2-}} \times a_{H_2O}} = \frac{K_w}{K_2} \quad (\text{Eq. 6})$$

or

$$\ln K_h = \ln K_w - \ln K_2 \quad (\text{Eq. 7})$$

Where  $K_h$  is the hydrolysis constant,  $K_2$  is the second ionization constant of carbonic acid, and  $K_w$  is the self-ionization constant of water. The carbonate and bicarbonate ion differ by a proton, so the equilibrium between the two depend on pH. In terms of chemical potentials of the ions, this equilibrium can be written as:

$$RT \ln K_h = \mu_{CO_3^{2-}}^0 + \mu_{H_2O}^0 - \mu_{HCO_3^-}^0 - \mu_{OH^-}^0 \quad (\text{Eq. 8})$$

The temperature-dependent coefficients of Steele et al. [10] for the reduced chemical potentials of the ions were used together with their coefficients for the Pitzer parameters, except for NaOH which were taken from Reynolds et al. [15]. To test the consistency and accuracy of Steele's coefficients, the predictions of osmotic coefficients from the model developed by Peiper and

Pitzer [27] in the temperature range of 5 to 45 °C were employed because experimentally determined osmotic coefficients at temperatures other than 25 °C could not be found in the literature. The results of this analysis, which included the hydrolysis reaction, are given in Table IV.

This analysis shows that the Steele model parameters lead to predictions of osmotic coefficient that compare very favorably with Peiper's model predictions [10, 27]. During this analysis, the B coefficient for  $\beta_1$  of Na-CO<sub>3</sub> was adjusted from Steele's original value of 0.09989 to 0.09784 so that the first temperature derivative ( $\partial\beta_1/\partial T$ ) value at 25 °C matched that given by Peiper and Pitzer [27]. With this change included, the remaining parameter coefficients from Steele et al. [10] were accepted and shown in Tables I and II.

Table IV. Comparison of Osmotic Coefficients for Na<sub>2</sub>CO<sub>3</sub> from 5 to 45 °C.

t (°C)	5.0			15.0			25.0			35.0			45.0		
m	P&P <sup>a</sup>	Steele <sup>b</sup>	$\delta^c$	P&P	Steele	$\delta$	P&P	Steele	$\delta$	P&P	Steele	$\delta$	P&P	Steele	$\delta$
0.001	0.968	0.968	0.000	0.970	0.970	0.000	0.971	0.971	0.000	0.972	0.973	-0.001	0.974	0.974	0.000
0.002	0.955	0.955	0.000	0.956	0.957	-0.001	0.957	0.958	-0.001	0.959	0.959	0.000	0.960	0.961	-0.001
0.005	0.931	0.932	-0.001	0.932	0.933	-0.001	0.933	0.934	-0.001	0.934	0.935	-0.001	0.936	0.936	0.000
0.010	0.909	0.909	0.000	0.910	0.910	0.000	0.910	0.911	-0.001	0.911	0.912	-0.001	0.912	0.912	0.000
0.020	0.883	0.883	0.000	0.884	0.884	0.000	0.884	0.885	-0.001	0.884	0.885	-0.001	0.884	0.885	-0.001
0.050	0.846	0.846	0.000	0.847	0.847	0.000	0.847	0.848	-0.001	0.846	0.847	-0.001	0.845	0.845	0.000
0.100	0.814	0.815	-0.001	0.817	0.817	0.000	0.817	0.818	-0.001	0.817	0.818	-0.001	0.815	0.815	0.000
0.200	0.777	0.777	0.000	0.782	0.782	0.000	0.784	0.785	-0.001	0.785	0.786	-0.001	0.783	0.784	-0.001
0.400	0.725	0.726	-0.001	0.736	0.737	-0.001	0.743	0.744	-0.001	0.746	0.747	-0.001	0.746	0.747	-0.001
0.600	0.687	0.687	0.000	0.703	0.704	-0.001	0.715	0.716	-0.001	0.722	0.723	-0.001	0.724	0.725	-0.001
0.800	0.657	0.657	0.000	0.679	0.680	-0.001	0.696	0.696	0.000	0.706	0.707	-0.001	0.711	0.711	0.000
1.000	0.634	0.634	0.000	0.662	0.662	0.000	0.683	0.683	0.000	0.697	0.698	-0.001	0.704	0.705	-0.001
	S.D. <sup>d</sup>	0.00044		S.D.	0.00053		S.D.	0.00087		S.D.	0.00085		S.D.	0.00065	

<sup>a</sup> P&P = osmotic coefficient from the model of Peiper and Pitzer 1982 [27].

<sup>b</sup> Steele = Osmotic coefficient from the model in ORNL/TM-2000/348 [10].

<sup>c</sup>  $\delta = \varphi(\text{P\&P}) - \varphi(\text{Steele})$ .

<sup>d</sup>  $S.D. = \sqrt{\{(\sum\delta^2)/(N - 1)\}}$  where S.D. = standard deviation and N = number of data points.

As Steele et al. [10] does not report reduced chemical potential coefficients for the solid sodium carbonate species, they were determined here for Na<sub>2</sub>CO<sub>3</sub>·10H<sub>2</sub>O, Na<sub>2</sub>CO<sub>3</sub>·7H<sub>2</sub>O, and Na<sub>2</sub>CO<sub>3</sub>·1H<sub>2</sub>O. The solubility data listed in Seidell [20] was employed for this determination. The solid reduced chemical potentials were fit using the value of the ion activity product at the saturated concentration as the target  $K_{sp}$  for each temperature. The ions and water reduced chemical potentials were calculated as before from Steele's coefficients (Table I). The expressions for the solid carbonates chemical potentials were calculated at each temperature as follows:

for Na<sub>2</sub>CO<sub>3</sub>·10H<sub>2</sub>O:

$$\mu_{Na_2CO_3 \cdot 10H_2O}^0 = 2\mu_{Na^+}^0 + \mu_{CO_3^{2-}}^0 + 10\mu_{H_2O}^0 + RT \ln K_{sp, Na_2CO_3 \cdot 10H_2O} \quad (\text{Eq. 9})$$



for  $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$ :

$$\mu_{\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}}^0 = 2\mu_{\text{Na}^+}^0 + \mu_{\text{CO}_3^{2-}}^0 + 7\mu_{\text{H}_2\text{O}}^0 + RT \ln K_{sp, \text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}} \quad (\text{Eq. 10})$$

for  $\text{Na}_2\text{CO}_3 \cdot 1\text{H}_2\text{O}$ :

$$\mu_{\text{Na}_2\text{CO}_3 \cdot 1\text{H}_2\text{O}}^0 = 2\mu_{\text{Na}^+}^0 + \mu_{\text{CO}_3^{2-}}^0 + \mu_{\text{H}_2\text{O}}^0 + RT \ln K_{sp, \text{Na}_2\text{CO}_3 \cdot 1\text{H}_2\text{O}} \quad (\text{Eq. 11})$$

The ion activity products are calculated from the values using standard methods [28]. For temperatures less than 32 °C the solid phase is the decahydrate, between 32 and 35.37 °C the solid phase is the heptahydrate, and above 35.37 °C the solid is the monohydrate. The reduced chemical potential values were then regressed to calculate the coefficients of the temperature dependency of Equation 2. The predictions using these revised coefficients are also shown in Figure 4, where the standard deviation of fit is 0.033 over the temperature range from 0 to 100 °C. Given that there are three different salt hydrates in the  $\text{Na}_2\text{CO}_3\text{-H}_2\text{O}$  system, the solubility of all three hydrates as a function of temperature is shown in Figure 4 (with c.# indicating the number of waters of hydration in the salt), showing the excellent fit of the present model to all of the data. The reduced chemical potential coefficients determined are displayed in Table I.

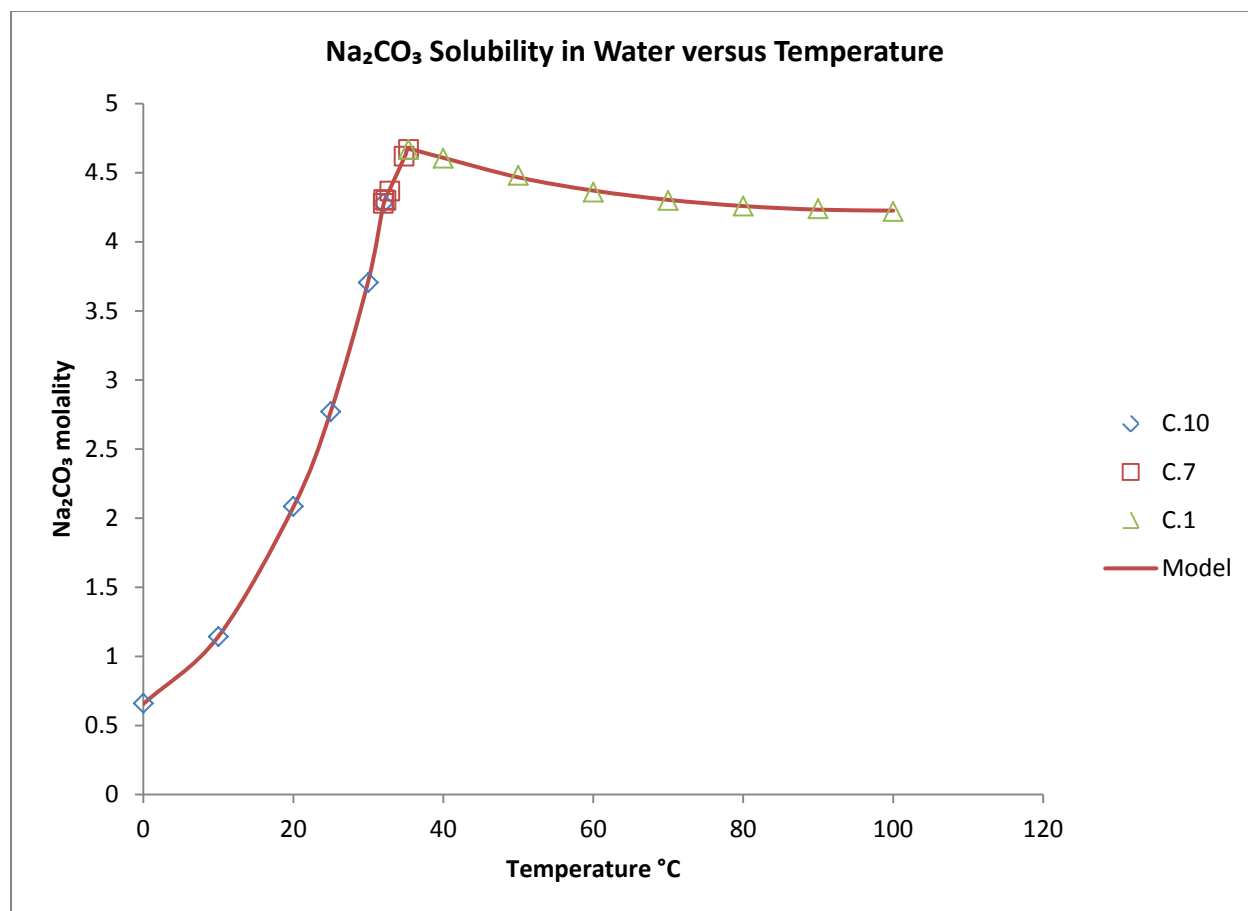


Fig. 4. Solubility of  $\text{Na}_2\text{CO}_3$  in  $\text{H}_2\text{O}$  from 0 to 100 °C.

## Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>

Qafoku and Felmy [29] provided binary Pitzer parameters and Gibbs free energies for the Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>-H<sub>2</sub>O system at 25 °C, but not at other temperatures. Therefore, temperature-dependent parameters are needed and developed here. There is no osmotic coefficient data for the Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> system for use in model fitting. Thus, solubility data is employed for this system. The binary Pitzer model parameters and reduced chemical potentials for the dissolved oxalate species reported by Steel et al. [10] were used in this study. The solid-phase reduced chemical potentials for Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> were determined by regressing available solubility data [30, 31]. The solubility isotherm predicted from this analysis is shown in Figure 5, which has a standard deviation of 0.002 molal over the fitted temperature range. The coefficients thus obtained are shown in Tables I and II.

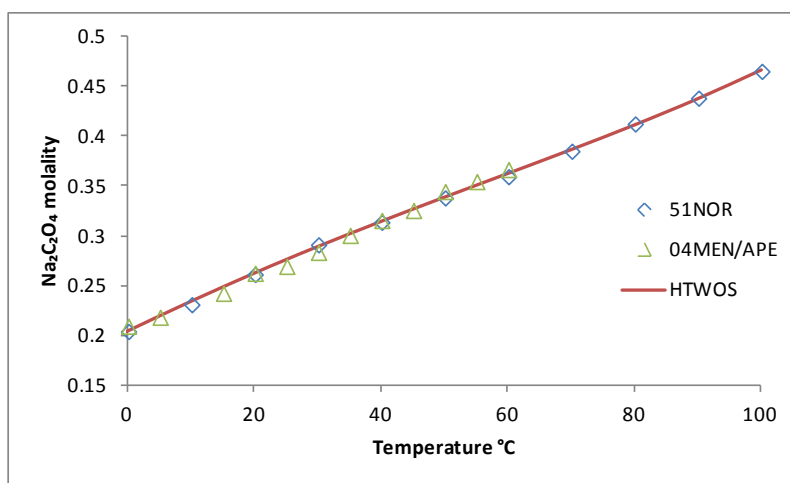


Fig. 5. Solubility of Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> in H<sub>2</sub>O from 0 to 100 °C.

## NaF

Weber et al. [9] provide both temperature-dependent binary Pitzer parameters and reduced chemical potentials for the NaF-H<sub>2</sub>O system. The solubility of NaF in water as a function of temperature available in the literature [20, 32, 33] are extremely scattered, and thus not particularly diagnostic regarding the accuracy of Weber et al.'s [9] model parameters. An analysis (data not shown) indicated that their model parameters provided a reasonable representation of the central tendency of the scattered data. Thus, Weber et al.'s [9] model parameters are used here, and included in Tables I and II.

## CONCLUSION

This study has determined the Gibbs free energies (via reduced chemical potentials) and the binary Pitzer model parameters for the important electrolytes Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, Na<sub>2</sub>CO<sub>3</sub>, NaHCO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, NaCl, and NaF. These parameters are not the only ones needed to model the solubility of these salts in multi-component Hanford nuclear waste, but they do provide the necessary backbone for the complete model.

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