The Component Slope Linear Model for Calculating Intensive Partial Molar Properties: Application to Waste Glasses and Aluminate Solutions - 13099

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ABSTRACT

Partial molar properties are the changes occurring when the fraction of one component is varied while the fractions of all other component mole fractions change proportionally. They have many practical and theoretical applications in chemical thermodynamics. Partial molar properties of chemical mixtures are difficult to measure because the component mole fractions must sum to one, so a change in fraction of one component must be offset with a change in one or more other components. Given that more than one component fraction is changing at a time, it is difficult to assign a change in measured response to a change in a single component. In this study, the Component Slope Linear Model (CSLM), a model previously published in the statistics literature, is shown to have coefficients that correspond to the intensive partial molar properties. If a measured property is plotted against the mole fraction of a component while keeping the proportions of all other components constant, the slope at any given point on a graph of this curve is the partial molar property for that constituent. Actually plotting this graph has been used to determine partial molar properties for many years. The CSLM directly includes this slope in a model that predicts properties as a function of the component mole fractions. This model is demonstrated by applying it to the constant pressure heat capacity data from the NaOH-NaAl(OH)$_4$-H$_2$O system, a system that simplifies Hanford nuclear waste. The partial molar properties of H$_2$O, NaOH, and NaAl(OH)$_4$ are determined. The equivalence of the CSLM and the graphical method is verified by comparing results determined by the two methods. The CSLM model has been previously used to predict the liquidus temperature of spinel crystals precipitated from Hanford waste glass. Those model coefficients are re-interpreted here as the partial molar spinel liquidus temperature of the glass components.

INTRODUCTION

Hanford nuclear wastes are mixtures of many chemicals. Many waste properties of interest, particularly thermodynamic properties, are a function of the waste composition. Statisticians often denote models of these properties as "mixture models," which are models where the independent variables are fractions that must sum to one.[1] Hrma [2] noted that the coefficients of these empirical mixture models often have physical meaning to scientists, but the different vocabulary set of the statistical and physical science communities can sometimes hide these facts.[2] In this light, the present study shows that the coefficients of the empirical mixture model of Piepel [3] has physical meaning (partial molar properties) when applied to thermodynamic properties of mixtures.[3] In this study, the Component Slope Linear Model (CSLM) from Piepel [3] is used to predict the heat capacity of concentrated NaOH-NaAl(OH)$_4$-H$_2$O, which can be thought of as a simplified Hanford waste caustic leaching solutions product.[4] In the process, the partial molar heat capacity of the systems components will be

determined. Furthermore, Piepel's [3] application of this model to spinel liquidus temperature in nuclear waste glass is shown to provide the partial molar properties of the waste glass components.

Chemical properties are functions of composition, described mathematically by Walas:[5]

$$P = \sum B_i x_i \qquad \text{(Eq. 1)}$$

where P is the value of the property for the solution at the mixture composition, x_i is the moles or mole fraction of component 'i' and B_i is the partial molar property of the component. Note that B_i does not have to be a constant; B_i may itself be a rather complex function of composition. A recent example of this would be the electrolyte solution heat capacity model of Laliberte.[6] Laliberte's model has the same functional form of Equation 1, but a sub-model is used to predict the B_i coefficients as a function of water content.[6]

Chemists call properties "extensive" if they depend on the total quantity of solution, with volume, enthalpy, and free energy being examples.[5] Extensive partial molar properties use the units of moles for x_i in Equation 1. Properties are said to be "intensive" if they are independent of the total quantity of solution, depending only on the composition of solution at constant temperature and pressure.[5] Examples of intensive properties include density, viscosity, heat capacity, and chemical potential. They have units of mole fraction for x_i in Equation 1. Extensive properties can be converted to intensive properties by dividing by the size of the system.

Common thermodynamic textbooks describe extensive partial molar properties as the change in property when one mole of component 'i' is added to an infinitely large system.[5] While it is not possible to create an infinitely large system, it is possible to add a small quantity of a component to a very large quantity of solution and experimentally observe the property change. Consequently, evaluating extensive partial molar properties are relatively straightforward, and methods to do so have been available for about 100 years.[7, 8]

In comparison to extensive properties, evaluation of the intensive properties of solutions is more difficult because it is impossible to change the concentration of one component without concomitantly changing the concentration of another component. This is caused by the constraint that solution mole fractions must sum to one (the mixture constraint). This restriction confounds the interpretation of component effects on the property because it is not clear if the change in property is from the increase in the first component or the decrease in other components.[1] The confounding of intensive partial molar properties has been known for many years, but has not always been widely understood by the scientific community.[7, 9]

Lewis and Randall suggest using a graphical method to determine intensive partial molar properties.[7] In the graphical method, the property value is plotted as a function of mole fraction of one component, keeping all other components in the same relative proportion. The slope of the curve is then estimated from the graph for any desired mole fraction. This process is repeated for each component and composition of interest. Piepel suggested the graphical method could be employed more efficiently by using models to create the plot rather than actual

data.[10] The Piepel method requires less experimental data, and allows for more efficient experimental design.[10]

Application of the CSLM to the thermodynamic properties of mixtures is described in the next section. That section will show that the CSLM has coefficients corresponding to what will be recognized as partial molar properties. Thus, the CSLM is a new method to determine intensive partial molar properties. This model is subsequently demonstrated for the partial molar heat capacity of the $NaOH-NaAl(OH)_4-H_2O$ system. This system can be thought of as a simplified nuclear waste caustic leaching system.[4] The $NaOH-NaAl(OH)_4-H_2O$ system is employed because the constant pressure heat capacity of this system is an approximately linear function of composition over a large concentration range, at least sufficiently linear to demonstrate the CSLM. Aqueous electrolyte solution heat capacities become highly non-linear functions of composition as the electrolytes are diluted out by water, so only data from the more concentrated composition region is explored in this study.[6, 11]

Piepel demonstrated the CSLM by using it to predict the liquidus temperature of spinel crystals (AB_2O_4, where A and B are metal ions) in nuclear waste glasses.[3] His model results are re-interpreted in terms of the partial molar liquidus temperature of the glass components in the final section of this paper.

REVIEW OF PIEPEL'S COMPONENT SLOPE LINEAR MODEL

This section provides a review of the CSLM. Piepel has reviewed the derivation of the CSLM previously.[3, 12] The present description aspires to make it evident that these empirical model coefficients are the partial molar properties of the solution components. Note that the CSLM is only applicable to intensive properties that have a first order response function with respect to composition.

The most common first order empirical models of mixture properties employed by statisticians are Scheffe's [13] canonical polynomials:[1]

$$P = \sum_{i=1}^{q} \beta_i x_i \qquad \text{(Eq. 2)}$$

Here, P is the property of interest, x_i is the component mole fraction, β_i is a coefficient empirically determined by regression, and q is the number of components in the solution. Hrma has noted that Equation 2 has the same functional form as Equation 1, and thus β_i represents an estimate of the partial molar property.[2] Piepel noted that β_i is an estimate of the value of P for pure component 'i'.[12] Putting these two observations together concludes that β_i is an estimate of the partial molar property for the pure component 'i'. Thus, β_i is only the partial molar property for 'i' at pure component end-member composition despite having the same functional form as Equation 1. Note that B_i in Equation 1 is not equal to β_i in Equation 2 because B_i can change with solution composition whereas β_i is constant. Thus, β_i is only a fair estimate of the partial molar property of component 'i' for a system with a first order response function.

In order to investigate the change in property response relative to a specific mixture composition, Cox [14] introduced a reference composition 's' into the Scheffe polynomials. The Cox model is: [14]

$$P = \alpha_o + \sum_{i=1}^{q} \alpha_i x_i \qquad\qquad \text{(Eq. 3a)}$$

where the Cox model component coefficients, α_i, are subject to the constraint:

$$0 = \sum_{i=1}^{q} \alpha_i s_i \qquad\qquad \text{(Eq. 3b)}$$

Here, α_o represents the value of the property at the reference composition 's', and s_i is the fraction of component 'i' at that reference composition. The result within the summation symbol of Equation 3a is the change in the property with respect to the reference composition. The α_i coefficient is the change in the property that occurs between the reference mixture and the pure component 'i'. The reference composition concept used in Equation 3 is identical to the concept of a standard state used in thermodynamic modeling.[15]

Like the β_i coefficients, the α_i coefficients in Equation 3 are not the partial molar property of component 'i' in the solution. The partial molar property of 'i' at the reference composition is the slope of the property versus composition line made when component 'i' is added to the reference mixture at the expense of the other mixture components.[5] For instance, imagine a property is calculated or measured at both a reference composition 's' and at another composition that differs only in the mole fraction of component 'i', with the mole fraction of the rest of the components reduced or increased proportionally to ensure the sum of mole fractions equals one. The plot of the property versus mole fraction of component 'i' between these two data points forms a line. The slope of the line is the partial molar property for 'i'. Piepel (2007) noted a mathematical relationship between the α_i value in Equation 3 and the slope of this line, where the slope is the brackets in Equation 4.[3]

$$\alpha_i = (1 - s_i) \left[\frac{P_i - P_s}{\Delta_i} \right] \qquad\qquad \text{(Eq. 4)}$$

In Equation 4, P_s is the value of the property at the reference composition 's' ($P_s = \alpha_o$), P_x is the value of the property for the pure component ($P_i = \beta_i$ in Equation 2), and Δ_i is the change in the fraction of 'i' between the pure component and reference mixture. Indeed, actually plotting measured data along this line is the graphical method of determining partial molar properties that has been used for many years.[7] Therefore, the slope of this line (the brackets in Equation 4) is the true partial molar property for component 'i' at the reference composition 's'.

Piepel proposed a first order model that directly includes the slope (Equation 5).[3]

$$P = \gamma_o + \sum_{i=1}^{q} \gamma_i (1 - s_i) x_i \qquad \text{(Eq. 5a)}$$

Equation 5a is subject to the constraint

$$0 = \sum_{j=1}^{q} \gamma_j (1 - s_j) s_j \qquad \text{(Eq. 5b)}$$

where $\gamma_o = \alpha_o$ = the property at the reference composition 's', and $\gamma_i = \alpha_i/(1-s_i)$ = the slope along the Cox effect direction. As stated previously, the slope of the line along the Cox effect direction is the true partial molar property for component 'i' with respect to reference composition 's'. Thus, γ_i = the partial molar property of component 'i' at 's'. Therefore, the partial molar property for every component of any system with a first order response surface can be determined for any reference composition by fitting Equation 5 to data for that system. Equation 5 is known as the CSLM.[3]

APPLICATION TO AQUEOUS SODIUM HYDROXIDE-SODIUM ALUMINATE SOLUTIONS

Piepel originally applied the CSLM to the liquidus temperature of spinel crystallized from nuclear waste glasses.[3] This study uses constant pressure heat capacity as an example, because of its familiarity with a wide audience.

This study applies the CSLM to the heat capacity of the $NaOH$-$NaAl(OH)_4$-H_2O system, as an example. The 25 °C data published by Mal'tsev and Mashovets [16] is used. The data published by Magalhaes et al. [17] for this system was not used because it covers a more dilute solute concentration region where the heat capacity response is non-linear. As stated above, the CSLM is not applicable to highly non-linear systems. Table I provides some descriptive statistics for the dataset.

TABLE I. Descriptive Statistics of the Mal'tsev and Mashovets [16] Data at 25 °C.

Number of Data Points	H_2O Mole Fraction Range (Minimum, Mean, Maximum)	NaOH Mole Fraction Range (Minimum, Mean, Maximum)	$NaAl(OH)_4$ Mole Fraction Range (Minimum, Mean, Maximum)	NaOH-$NaAl(OH)_4$ Concentration Correlation Coefficient (r)
23	0.7772, 0.8500, 0.9500	0.0466, 0.1190, 0.2139	0.0029, 0.0031, 0.1065	0.16

Equation 5 was fit to the Mal'tsev and Mashovets [16] dataset by numerically optimizing the γ_i and γ_o values that produce the minimum square difference between the measured and predicted values, subject to the constraint in Equation 5b. The i's used in this example were the mole fractions of H_2O, NaOH, and $NaAl(OH)_4$, which were the three components in the matrix studied by Mal'tsev and Mashovets.[16] The standard reference composition 's', from which the partial molar properties (γ_i) are referenced to, was chosen to be the mean composition in the Mal'tsev and Mashovets [16] dataset at 25 ºC. Hence, s_{H2O} = 0.8500, s_{NaOH} = 0.1190, and $s_{NaAl(OH)4}$ = 0.0031 (Table I). This value was arbitrarily chosen for this example, and the user could choose any value of s that they are interested in.

The values determined for each partial molar heat capacity at the reference mixture (γ_i) as well as the value of γ_o are shown in Table II. The R^2 and R^2_{adj} statistics (calculated per reference [18]) came to be 0.985 and 0.983, indicating a good fit to the data. Figure 1 compares the measured versus predicted heat capacities for the dataset. The measured and predicted values are essentially indistinguishable on the plot (Figure 1), demonstrating the goodness of the fit.

TABLE II. Composition at 's', and Coefficients Determined from Fitting
Mal'tsev and Mashovets [16] Data to Equation 5 at 25 °C.

Component	Mole Fraction at Reference Composition (s)	γ_i	Value (KJ/K/Kg/mole)
H_2O	0.850009	γ_{H2O}	2.727265
NaOH	0.118981	γ_{NaOH}	-1.69695
$NaAl(OH)_4$	0.031009	$\gamma_{NaAl(OH)4}$	-5.65188
Sum	1	γ_o	3.452108

These results indicate that composition dependence of the heat capacity of NaOH-NaAl(OH)$_4$-H_2O solutions are sufficiently close to first order in the composition range of the data studied by Mal'tsev and Mashovets [16] to be represented by Equation 5. Therefore, Equation 5, along with the coefficients in Table II, can be used to calculate the heat capacity of NaOH-NaAl(OH)$_4$-H_2O within this composition range at 25 ºC. The γ_i values in Table II are only the partial molar heat capacity of the components at the selected reference composition. Nonetheless, given the success of the model within this region, it can be assumed that the model could be re-fit using any reference composition within the region to provide the partial molar heat capacity for each component at that reference composition.

Another way to show that the coefficients in the CSLM are the partial molar heat capacities of the components is to check the γ_i values against the graphical method. Here, a model is used to generate the graph, as suggested by Piepel [10]. Equation 2 was fit to the same data as the CSLM, the resulting coefficients shown in Table III. The R^2 and R^2_{adj} statistics of this fit came to be 0.985 and 0.983, the same as the CSLM, as expected.[12] The heat capacity of a NaOH-NaAl(OH)$_4$-H_2O solution was then calculated at several different water mole fractions, keeping the ratio of NaOH and NaAl(OH)$_4$ constant and equal to the ratio at composition 's' [NaOH: NaAl(OH)$_4$ mole ratio = 3.837]. These values were then plotted in Figure 2, the slope of the line

in the figure being the partial molar heat capacity of H_2O. As can be seen in Figure 2, the slope of this line is 2.7273, the same value as the coefficient for water in Equation 5 (see Table II). Thus, this graphical test demonstrates that the coefficients returned by the CSLM are the partial molar heat capacities of the components at composition 's', as evidenced by the consistency with the graphical method. Of note is that the value of β_{H2O} does not exactly match the heat capacity of pure water, because this value is only applicable to this mixture composition.
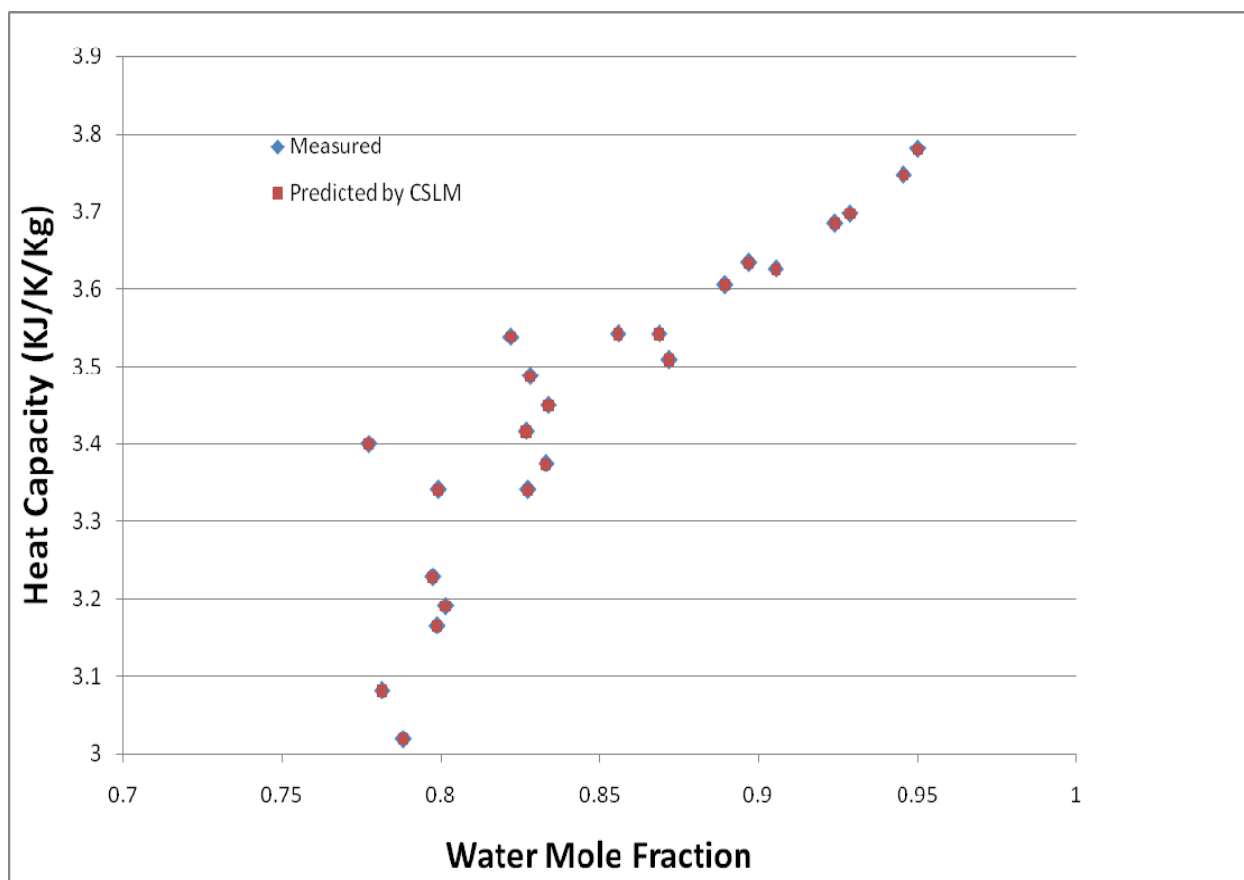

Fig 1. Comparison of the Heat Capacities from Mal'tsev and Mashovets [16] Against those Predicted by the CSLM.[16]

TABLE III. Coefficients Determined by Fitting Equation 2 to
Fitting Mal'tsev and Mashovets [16] 25 °C Data.

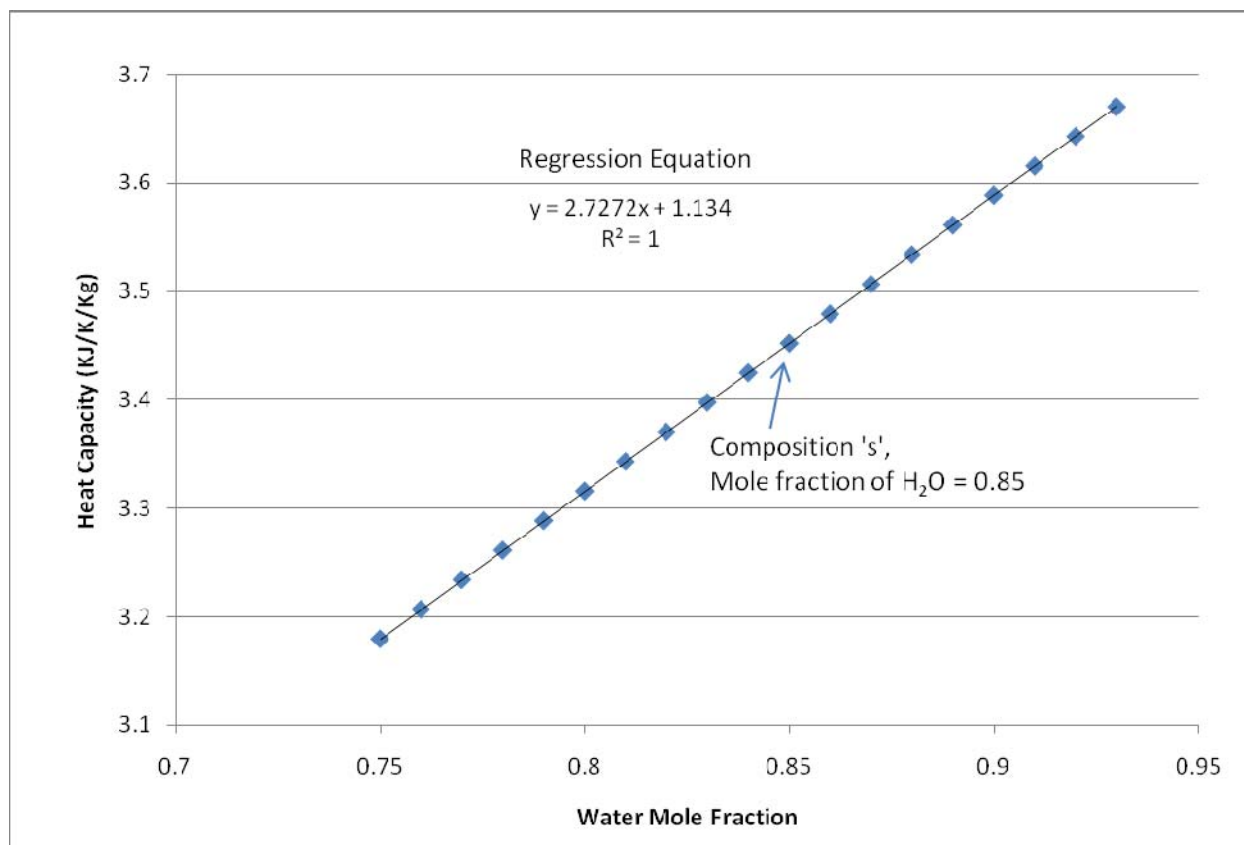| Component	β_i Value (Equation 2)
H_2O	3.86116
NaOH	1.957148
$NaAl(OH)_4$	-2.02449

Fig 2. Change in Heat Capacity with Change in Water Mole Fraction at Constant NaOH:NaAl(OH)₄ Ratio (Ratio = 3.837, Same as Composition 's').

The results show that water has a positive partial molar heat capacity (2.7 KJ/K/Kg/mole) whereas NaOH and NaAl(OH)₄ had negative partial molar heat capacities. This is consistent with the observation that water has a high heat capacity and that the heat capacity of an aqueous solution has a lower heat capacity than pure water at the same temperature. At the reference composition 's', substituting NaAl(OH)₄ for NaOH and H₂O lowers the heat capacity more than substituting NaOH for NaAl(OH)₄ and H₂O. These relationships have practical applicability. For instance, the Hanford Site is currently planning to leach the mineral boehmite (γ-AlOOH) in aqueous NaOH solutions.[4] When the mineral Boehmite is dissolved at high-pH, the chemical reaction is:

$$AlOOH_{(s)} + NaOH_{(aq)} + H_2O \leftrightarrow NaAl(OH)_{4(aq)} \qquad \text{(Eq. 6)}$$
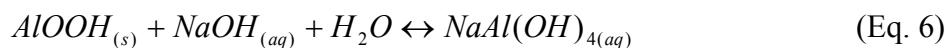
As can be seen in this reaction stoichiometry, equal molar amounts of water and hydroxide are replaced in the liquid phase by NaAl(OH)₄. If the starting solution composition were at composition 's' prior to boehmite dissolution, the heat capacity of the liquid phase would decrease by 5.65 KJ/K/Kg per mole of boehmite dissolved, the value of -5.65 KJ/K/Kg being the partial molar heat capacity of NaAl(OH)₄ at composition 's' (Table II). Conversely, the heat capacity of the liquid phase would increase by 5.65 KJ/K/Kg/mole by the precipitation of boehmite from composition 's'. Similarly, the change in the heat capacity of the liquid can be

determined when the solution evaporates. The heat capacity of a solution with a starting composition of 's' would decrease by 2.73 KJ/K/Kg/mol as water is evaporated from it, Figure 2 being an example of a change in solution heat capacity with evaporation.

IMPLICATIONS FOR SPINEL LIQUIDUS TEMPERATURE MODELS

When Piepel developed the CSLM, he applied the model to predict the liquidus temperature of Fe-Mn-Ni-Cr-bearing spinel crystals in nuclear waste glasses.[3] Models of the Scheffe type (Equation 2) have frequently been used to model the liquidus temperature of these spinels as a function of glass composition so that glasses could be formulated for waste vitrification.[19, 20, 21, 22] Piepel developed the CSLM as an alternative to Equation 2, noting that the two equations have identical regression statistics and predictive ability but differ in the interpretation of the coefficients.[3, 12]

The liquidus temperature is the highest temperature that a crystal can be stable in a melt. Liquidus temperature has not been widely discussed as a partial molar property. Nonetheless, Hrma has started describing the coefficients in Equation 2 as the "partial molar liquidus temperature" for the glass components.[2, 23] He did this in order to argue that the coefficients in Equation 2 have physical meaning, and are more than just empirically determined coefficients.[2] As stated above in the present work, β_i coefficients in Equation 2 are estimates of the partial molar properties of the pure components; in this case they would represent the "partial molar spinel liquidus temperature" of the pure components.

Piepel believed that the CSLM had more favorable interpretation of the liquidus temperature model coefficients than Equation 2.[3, 12] He argued that CSLM γ_i coefficients were more meaningful than Equation 2 because liquidus temperature of spinel does not have a physical meaning for the pure glass components.[3] For instance, a pure molten Cr_2O_3 liquid cannot crystallize a mixed Fe-Mn-Cr-Ni-bearing spinel crystal because there is no Fe, Mn or Ni in Cr_2O_3. Thus, the partial molar liquidus temperature of spinel in a pure Cr_2O_3 melt is meaningless. Piepel, however, did not describe these CSLM coefficients as the "partial molar liquidus temperature" of the glass components at the reference composition 's'.[3] Above, it is shown that the γ_i coefficients are the partial molar properties of the constituents at the reference composition 's'. Therefore, it can be concluded that the empirically determined CSLM coefficients for spinel liquidus temperature presented by Piepel [3] do have thermodynamic meaning, which is consistent with the argument Hrma [2] applied to Equation 2.

WHEN THE CSLM SHOULD BE USED TO DETERMINE PARTIAL MOLAR PROPERTIES

In a previous section of this report, we compared the CSLM with the graphical method for determining partial molar properties because this provides both a visual and numerical equivalence of the two methods. Some modern thermodynamics textbooks endorse using

derivatives with respect to mole fractions to obtain partial molar properties.[5] Section 2.5 of the book by Walas [5] describes this methodology in detail. First, the property is fit by a simple polynomial of the response as a function of the mole fraction such as

$$P = ax_1^2 + bx_2^2 + cx_2^3 + dx_1 + ex_2 + fx_3 \qquad \text{(Eq. 7)}$$

for a three-component mixture. This equation is then converted to an extensive property, by treating the total size of the system as one mole. Three versions of this equation are then written (or j versions for a j-component mixture), eliminating one component each time. A component is eliminated in Equation 7 by equating that component to the sum of all of the other components (x_j = 1- sum of the other components; see Example 2.4 of Walas, [5]). In the vocabulary of statisticians, this would be to create j component slack variable models for a j-component mixture (one slack variable equation with each component as the slack variable). Each of these equations is used to calculate the partial molar property for one component. The derivative with respect to each component is taken in the original property equation, and then substituted into each slack variable model in place of the remaining variables. This means that six derivatives must be taken for a three-component mixture, like the NaOH-NaAl(OH)$_4$-H$_2$O study discussed earlier. For the thirteen-component Spinel liquidus temperature study of Piepel [3], 156 derivatives would need to be taken (13 equations times 12 derivatives per equation = 156 derivatives).[3] Modelers who are working with many-component systems (like Hanford waste) may find it easier to fit the CSLM than to take 156 derivatives. This is especially true given the fact that fitting the CSLM is not appreciably more difficult than fitting Equation 7.

One of the disadvantages of the CSLM, however, is the partial molar properties of each component can only be determined at one reference composition at a time. The model would have to be re-fit each time the partial molar properties are needed with respect to an additional reference composition. Thus, a modeler who needs the partial molar properties at many reference compositions may prefer the partial derivative method over the CSLM, even if it requires taking many derivatives.

Another disadvantage of the CSLM is that it is only valid for systems with a first order response surface as a function of composition over the range of interest. Many chemical properties are non-linear functions of composition. Hrma has noted that responses are often linear for systems with many components (like waste glass) because limited miscibility restricts the composition to a small range.[24] The liquidus temperature study of Piepel is a great example of such a system, being restricted to waste glass melts in the Fe-Cr-Mn-Ni-Spinel primary phase field.[3] Thus, for many component systems where the CSLM is easier to apply than the partial derivative method, the response will often be first order.

CONCLUSION

This study has shown that the γ_i coefficients in the CSLM represent the partial molar properties at the reference composition 's' of a solution fit by the model. Thus, the CSLM can be used to calculate partial molar properties of solutions that have a first order response function. This model is equivalent to the graphical method endorsed by Lewis and Randall [7] years ago.

The CSLM was applied to the heat capacity of NaOH-NaAl(OH)$_4$-H$_2$O solutions, with the reference composition set to the mean composition in the Mal'tsev and Mashovets [16] dataset. The partial molar properties (at the mean concentration within the Mal'tsev and Mashovets [16] dataset) are shown in Table II.

Piepel originally applied the CSLM to the liquidus temperature of spinel crystals in molten waste glass as a function of composition.[3] Here, his coefficients were re-interpreted as being the "partial molar liquidus temperature of spinel" for the glass components at the reference composition chosen by Piepel [3]. This interpretation is consistent with Hrma's [2, 23] interpretation of the Scheffe model coefficients (Equation 2); a model that is mathematically equivalent to the CSLM. The important distinction between the two models is that the partial property is referenced to the pure solution component in the Scheffe model but referenced to a standard reference mixture composition in the CSLM.[12]

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