Correlational Approach to Predict the Enthalpy of Mixing for Chloride Melt Systems

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ABSTRACT: A methodology to estimate the heat of mixing ($\Delta_{\text{mix}}H$) for salt liquids in unexplored AkCl−AnCl$_3$/LnCl$_x$ (Ak = alkali, An = actinide, Ln = lanthanide) systems is developed. It improves upon previous empirical approaches by eliminating the need for arbitrarily choosing the required composition at maximum short-range ordering, the minimum $\Delta_{\text{mix}}H$ prior to performing the estimation, which avoids the intrinsic ambiguity of that approach. This semiempirical method has computationally reproduced the behavior of NaCl−UCl$_3$ and KCl−UCl$_3$ systems, providing $\Delta_{\text{mix}}H$ values that agree well with the reported measurements within a propagated two standard deviations (2σ). The capability of the approach is demonstrated in its application to the entirety of the AkCl−UCl$_3$ and AkCl−PuCl$_3$ systems, the results from which have facilitated the accurate thermodynamic modeling of these and other AkCl−AnCl$_3$/LnCl$_x$ systems. The resultant assessed Gibbs energy functions and models have been incorporated in the Molten Salt Thermal Properties Database—Thermochemical (MSTDB-TC).

1. INTRODUCTION

Research in molten salt systems has increased significantly in the last decade due to their application as solvents for metals, particularly for extraction processes, and in recycling and reprocessing of rare-earth elements used in electronics and magnets. Salt systems are also being developed as heat transfer media for solar-thermal systems and in molten salt reactors (MSRs), which use salts as a coolant for solid fuel or as a solvent for a liquid fuel containing actinides.

The newfound interest in MSRs, in particular, has led to a need for molten salt thermodynamic data to aid in modeling and simulation of the fuel/coolant, which is a central issue for material design and system optimization, reactor operation, and regulatory efforts. An important thermodynamic value is the heat of mixing or mixing enthalpy ($\Delta_{\text{mix}}H$), which represents interactions between system components and can be used to inform the development of thermodynamic descriptions through the CALculation of PHAse Diagram (CALPHAD) approach. Yet, there is a lack of information on the $\Delta_{\text{mix}}H$ for many lanthanide and other important salt systems because of the experimental challenge in measuring these values, and thus, a straightforward methodology for predicting $\Delta_{\text{mix}}H$ would be of great value. In principle, ab initio calculations can provide mixing enthalpies, but these are computationally expensive for salt melt systems and resultant values retain significant error. Thus, a more practical approach to predicting $\Delta_{\text{mix}}H$ for such salt systems is needed.

This work presents a significantly improved semiempirical approach to calculating $\Delta_{\text{mix}}H$ for AkCl−AnCl$_3$/LnCl$_x$ systems (Ak = alkali, An = actinide, Ln = lanthanide). It utilizes a unique method for determining the salt composition at maximum short-range order (SRO), which is associated with the most negative mixing enthalpy for the system, through
correlations of ionic charge and radius among similar cations. The ultimate goal of this effort is to provide support for the further development of the Molten Salt Thermal Properties Database—Thermochemical (MSTDB-TC), where predicted \( \Delta_{mix}H \) values are key information used for determining the overall thermodynamic models for salt systems. While the technique finds application with MSR-related salts, the approach is generally applicable to any family of salts and will find utility in many areas where thermodynamic descriptions of molten salts are needed.

**1.1. Background.** The enthalpy of mixing is defined as the energy released or absorbed upon mixing of pure components to obtain a single phase in an equilibrium state. This quantity is measured as the change in enthalpy upon mixing components at constant pressure, temperature, and composition such that

\[
\Delta_{mix}H(P, T, x_1, x_2, ..., x_n) = H(P, T, x_1, x_2, ..., x_n) - \sum x_i H_i^e(P, T)
\]

where \( H \) is the molar enthalpy of the mixture, \( x_i \) is the mole fraction of component \( i \) in the final mixture, and \( H_i^e \) is the molar enthalpy of pure liquid component \( i \). It should be noted that \( \Delta_{mix}H \) is generally calculated as the difference between two large quantities so relatively large errors can be introduced if \( H_i \) values are not well known or \( \Delta_{mix}H \) is small (near ideal mixing), i.e., on the order of a few hundred joules or less.

1.1.1. Influence of Alkali Ionic Radius on \( \Delta_{mix}H \). For some alkali mixed salts, \( \Delta_{mix}H \) is asymmetric with respect to composition. For example, as seen in Figure 1a, the most negative \( \Delta_{mix}H \) for alkali chlorides with CeCl\(_3\) occurs with \( x_{CeCl3} < 0.5 \). According to the conformal solution theory of Reiss, Katz, and Kleppa (RKK),

\( \lambda_{M} = \Delta_{mix}H x_{ACL3}^{23} \)

where \( x_{ACL3} \) is the mole fraction of \( ACL3 \). According to the conformal solution theory of Davis, the model parameters vary quadratically with \( \delta_{12} \)

\( \delta_{12} = \frac{(r_{Ak}^2 + r_{Cl}^2) - (r_{Ak}^{2+} + r_{Cl}^{-})}{(r_{Ak}^{2+} + r_{Cl}^{-})} \)

where \( r_{Ak}^{2+} \) and \( r_{Cl} \) are the ionic radii of the alkali (Figure 1b), lanthanide/actinide, and a chlorine atom, respectively, which are octahedral Shannon radii. Measurements on binary halides carried out by Papatheodorou et al. and Dienstbach and Blachnik have shown that the \( \lambda_{M} \) description of Davis is improved using a quadratic function for \( \delta_{12} \). In the Flengas and Kucharski theory of \( \Delta_{mix}H \), the model parameters vary quadratically with \( \delta_{12} \) within a family of metal dichlorides.

Fitting \( \Delta_{mix}H \) data usually uses eq 2 in a polynomial form,

\( \lambda_{M} = a_0 + a_1 x + a_2 x^2 + a_3 x^3 \)

where \( x \) is the mole fraction of \( ACL3 \). This model is adequate for charge symmetric systems that exhibit minima near the equimolar composition. However, it is not well adapted to represent charge-asymmetric systems. To address this issue, Hatem and co-workers developed an approach referred to as the surrounded ion model (SIM) (eqs 4 and 5), which takes into account the charge on the ions. In this work, we utilized the SIM

\[
\Delta_{mix}H = [(1 - x)pq + xrs](1 + x')(f_1 + f_2 x' + f_3 x'^2)
\]

where \( p = q = s = 1, r = 3, \) and \( f_i \) are fitting coefficients.

1.1.2. Temperature Dependence of \( \Delta_{mix}H \). Papatheodorou and Kleppa used calorimetry to study the influence of temperature on \( \Delta_{mix}H \) for the charge-asymmetric systems AkCl–MnCl\(_2\) and AkCl–FeCl\(_3\) (Ak = Li, Cs) at 1083 and 963 K, reporting an estimated maximum experimental error of 6%. A later study on KCl–YCl\(_3\) at 1143 and 1053 K was reported, although no values for experimental error were indicated. The \( \Delta_{mix}H \) values for the melts of CsCl–FeCl\(_3\) and KCl–YCl\(_3\) are shown in Figure 2a,b for two different temperatures, with their error limits propagated to obtain values for two standard deviations (2\( \sigma \)).
temperature dependence of their diversity. For instance, the KCl–BiCl₃ system studied at 690 K; however, they do not contain lanthanides or actinides and are also considered at relatively low temperatures compared with those for the systems of this study.

1.2. Regression Analysis. In the current work, the relations for Δₘₑ₈H were computed using a Python version 3.8-developed code for regression analysis with calculations carried out using NumPy version 1.19.5. The Levenberg–Marquardt algorithm (LMA) in SciPy version 1.4.1 was used in a χ²-minimization to fit the coefficients of the SIM using Δₘₑ₈H values

\[ χ^2 = \sum \left( \frac{r_i}{\sigma_i} \right)^2 \]  

where rᵢ is the calculated residual and σᵢ is the error in the measurement.

Experimental errors are usually reported in the literature thanks to extensive work published in the 1960s on mixtures of alkali chlorides and actinide trichlorides, as it is demonstrated in the plots of Figure 3 for three pseudobinary systems.

For CsCl–FeCl₃ at 1083 and 963 K, the most negative Δₘₑ₈H values are −23610 ± 425 and −23700 ± 467 J/mol, respectively, both at x₉FeCl₃ = 0.43. Similarly, the KCl–YCl₃ system has minima at x₉YCl₃ = 0.35 of −22770 ± 283 J/mol at 1143 K and −22180 ± 580 J/mol at 1053 K. We note that the difference in values due to temperature for each set is within 2σ, as is only a maximum difference of 2.6%, and thus the temperature dependence of Δₘₑ₈H can be disregarded for a ΔT of ≤120 K. The result is not surprising as the enthalpy of molten salts is understood to change slowly with temperature, as is defined as the integral of the heat capacity, which are reported with small or no temperature dependence.

1.1.3. Alkali–Lanthanide/Actinide Chloride Systems. The experimental Δₘₑ₈H data for alkali chloride mixtures with lanthanide and yttrium trichlorides are abundant in the literature, thanks to extensive work published in the 1960s–1970s by Kleppa and co-workers, and in the last few decades by Gaune-Escard’s group. However, work on mixtures of alkali chlorides and actinide trichlorides appears to be nonexistent with the exception of that for the NaCl–UCl₃ and KCl–UCl₃ systems. The Δₘₑ₈H of the 48 sets of data available for these systems were extracted for our analysis and are listed in Table 1.

Other alkali chloride mixtures with the trichlorides have been reported, e.g., the KCl–AlCl₃ system studied at 543 K, the KCl–FeCl₃ system studied at 970–1000 K, and the KCl–BiCl₃ system studied at 690 K; however, they do not contain lanthanides or actinides and are also considered at relatively low temperatures compared with those for the systems of this study.
estimating $\Delta_{\text{mix}}H$. Unfortunately, estimation of $\Delta_{\text{mix}}H$ at any composition other than the composition of maximum SRO creates ambiguity (see Figure 4). Therefore, an unambiguous application of the Davis's,$^{22,23}$ method to charge-asymmetric salt systems requires a means for selecting the composition of maximum SRO.$^{59,60}$ We will now address this problem by correlating the composition of maximum SRO with a previously described property of the salt structure, $\delta_{12}$. The composition at maximum SRO, i.e., where $\Delta_{\text{mix}}H$ is most negative, was determined for each system of Table 1 by

Table 1. Alkali and Actinide Pseudobinary Systems for Which $\Delta_{\text{mix}}H$ Values Are Available and Considered in the Current Analysis Together with the Nonalkali Metal Shannon Radius, Compositional Range, Number of Data Points, and Reported Error Limits$^2$.

| system | Ln. & An | exp. temp. | radius (non-Ak)$^4$ | $x$ (non-Ak) range | data points | error | reference |
|--------|---------|------------|---------------------|-------------------|------------|-------|-----------|
| LiCl   | LaCl$_3$ | 1173       | 1.032               | [0.196–0.787]     | 7          | 5.0   | Papatheodorou and Ostvold$^{25}$ |
| CeCl$_3$ | 1130   | 0.010      | 0.15–0.92           | 6                 | 5.0        | Papatheodorou and Kleppa$^{26}$ |
| PrCl$_3$ | 1044   | 0.990      | 0.014–0.942         | 20                | 6.0        | Rycerz et al.$^{27}$ |
| NdCl$_3$ | 1044   | 0.983      | 0.031–0.958         | 13                | 6.0        | Rycerz et al.$^{27}$ |
| GdCl$_3$ | 1263   | 0.938      | 0.15–0.68           | 6                 | 5.0        | Dienstbach and Blachnik$^{26}$ |
| TbCl$_3$ | 1109   | 0.923      | [0.0286–0.9017]     | 15                | 6.0        | Rycerz and Gaune-Escard$^{41}$ |
| YCl$_3$ | 1143   | 0.900      | [0.056–0.907]       | 6                 | 5.0        | Papatheodorou et al.$^{24}$ |
| TmCl$_3$ | 1130   | 0.880      | [0.098–0.912]       | 9                 | 6–8        | Chojnacka et al.$^{28}$ |
| NaCl   | LaCl$_3$ | 1173       | 1.032               | [0.046–0.852]     | 10         | 5.0   | Papatheodorou and Ostvold$^{25}$ |
| CsCl   | LaCl$_3$ | 1173       | 1.032               | [0.09–0.72]       | 11         | 5.0   | Dienstbach and Blachnik$^{26}$ |
| UCl$_3$ | 1113   | 1.025      | [0.0048–0.949]      | 23                | 6.0        | Matsuura et al.$^{69}$ |
| CeCl$_3$ | 1153   | 1.010      | 0.04–0.81           | 9                 | 5.0        | Dienstbach and Blachnik$^{26}$ |
| CeCl$_3$ | 1118   | 1.010      | 0.05–0.90           | 11                | 5.0        | Papatheodorou and Kleppa$^{26}$ |
| PrCl$_3$ | 1122   | 0.990      | [0.104–0.953]       | 14                | 6.0        | Gaune-Escard et al.$^{44}$ |
| NdCl$_3$ | 1124   | 0.983      | [0.0511–0.9500]     | 16                | 6.0        | Gaune-Escard et al.$^{44}$ |
| SmCl$_3$ | 1153   | 0.958      | 0.04–0.80           | 9                 | 5.0        | Dienstbach and Blachnik$^{26}$ |
| GdCl$_3$ | 1263   | 0.938      | [0.08–0.82]         | 9                 | 5.0        | Dienstbach and Blachnik$^{26}$ |
| TbCl$_3$ | 1109   | 0.923      | [0.0472–0.9007]     | 19                | 6.0        | Rycerz and Gaune-Escard$^{41}$ |
| DyCl$_3$ | 1153   | 0.912      | [0.03–0.79]         | 9                 | 5.0        | Dienstbach and Blachnik$^{26}$ |
| DyCl$_3$ | 1100   | 0.912      | 0.05–0.95           | 20                | 6.0        | Gaune-Escard et al.$^{44}$ |
| YCl$_3$ | 1143   | 0.900      | [0.047–0.890]       | 10                | 5.0        | Papatheodorou et al.$^{24}$ |
| ErCl$_3$ | 1153   | 0.890      | [0.03–0.79]         | 9                 | 5.0        | Dienstbach and Blachnik$^{26}$ |
| TbCl$_3$ | 1130   | 0.880      | [0.02–0.891]        | 21                | 6–8        | Chojnacka et al.$^{28}$ |
| YbCl$_3$ | 1153   | 0.866      | [0.10–0.79]         | 11                | 5.0        | Dienstbach and Blachnik$^{26}$ |
| KCl    | LaCl$_3$ | 1173       | 1.032               | [0.043–0.899]     | 14         | 5.0   | Papatheodorou and Ostvold$^{25}$ |
| CsCl   | LaCl$_3$ | 1173       | 1.032               | [0.0502–0.9048]   | 12         | 6–8   | Rycerz et al.$^{47}$ |
| CsCl   | 1113   | 1.025      | [0.05–0.90]         | 17                | 5.0        | Papatheodorou and Kleppa$^{10}$ |
| CsCl   | 1118   | 1.010      | 0.05–0.90           | 17                | 5.0        | Papatheodorou and Kleppa$^{10}$ |
| CsCl   | 1122   | 0.990      | [0.0101–0.9470]     | 20                | 6.0        | Gaune-Escard et al.$^{44}$ |
| CsCl   | 1065   | 0.983      | [0.0899–0.9430]     | 28                | 6.0        | Gaune-Escard et al.$^{44}$ |
| CsCl   | 1263   | 0.938      | [0.10–0.79]         | 8                 | 5.0        | Dienstbach and Blachnik$^{26}$ |
| CsCl   | 1109   | 0.923      | [0.0240–0.9532]     | 28                | 6.0        | Rycerz and Gaune-Escard$^{41}$ |
| CsCl   | 1143   | 0.900      | [0.045–0.901]       | 13                | 5.0        | Papatheodorou et al.$^{24}$ |
| CsCl   | 1053   | 0.900      | [0.048–0.917]       | 9                 | 5.0        | Papatheodorou et al.$^{24}$ |

“Ionic radius in the octahedral geometry from Shannon.$^{19}$
smaller than that for the \( \Delta_{\text{mix}}H \) measurements, they are assumed to be error-free. The linear behavior seen in Figure 5 within a relatively narrow 2\( \sigma \) band allows reasonably accurate interpolation of the composition at maximum SRO for systems lacking such values. As that is the case for uranium- and plutonium-containing systems, they were used to find their compositions at maximum SRO, which are reported in Table 2 along with their respective 2\( \sigma \) values.

2.2. Demonstration of Methodology via Application to NaCl–UCl\(_3\). The two alkali–actinide metal chloride systems with available experimental data for the heat of mixing are the NaCl–UCl\(_3\) system, which was studied by Matsuura et al.\(^{40}\) who measured 23 mixtures at 1113 K; and the KCl–UCl\(_3\) system recently reported by Rycerz et al.\(^ {47}\) in which 12 mixtures were also studied at 1113 K. These \( \Delta_{\text{mix}}H \) values were used to test our correlational approach, where we intentionally omitted those values in generating the linear fit of Figure 5b. The predicted \( \Delta_{\text{mix}}H \) value for the composition of maximum SRO of \( x_{\text{UCl}_3} = 0.459 \) interpolated from Figure 5b is obtained from the curve of Figure 6a. From the comparison with the measurements of \( \Delta_{\text{mix}}H \) for the NaCl–UCl\(_3\) system seen in Figure 6b, it is clear that our predictions (\( x_{\text{UCl}_3} = 0.459 \pm 0.017 \) and \( \Delta_{\text{mix}}H = -7299 \pm 350 \text{ J/mol} \)) are in good agreement with the observations of Matsuura et al.\(^{40}\) within their reported 6\% experimental error (SIM-calculated \( x_{\text{UCl}_3} = 0.447 \) and \( \Delta_{\text{mix}}H = -7290 \pm 437 \text{ J/mol} \)). Further, a similar estimation for the KCl–UCl\(_3\) system (\( x_{\text{UCl}_3} = 0.432 \pm 0.028 \) and \( \Delta_{\text{mix}}H = -15851 \pm 1003 \text{ J/mol} \)) agrees with the measurements of Rycerz et al.\(^ {47}\) within their reported 8\% uncertainty range (SIM-calculated \( x_{\text{UCl}_3} = 0.440 \) and \( \Delta_{\text{mix}}H = -18270 \pm 1462 \text{ J/mol} \)).

2.3. Determining \( \Delta_{\text{mix}}H \) for UCl\(_3\) or PuCl\(_3\) with AkCl. Encouraged by the comparative results for the NaCl–UCl\(_3\) and KCl–UCl\(_3\) systems, our methodology was applied to the remaining alkali–uranium and alkali–plutonium chloride systems. The \( \Delta_{\text{mix}}H \) calculated for each system at the predicted maximum SRO and with related \( \delta_{12} \) values were fit to a quadratic polynomial with 2\( \sigma \) intervals produced as previously described by propagating the errors calculated from the \( \Delta_{\text{mix}}H \) SIM regression at the composition of maximum SRO (Figure 7). Thus, the \( \Delta_{\text{mix}}H \) predictions incorporate the calculated errors from fitting the experimental \( \Delta_{\text{mix}}H \) values as well as the relative dispersion around the nominal fit (Figure 7 and Table 3).

Figure 3. Typical pseudobinary \( \Delta_{\text{mix}}H \) results from the SIM: (a) LiCl–CeCl\(_3\) at 1130 K; (b) LiCl–PrCl\(_3\) at 1044 K; and (c) KCl–TbCl\(_3\) at 1109 K.

Figure 4. Example of the potential for ambiguity in \( \Delta_{\text{mix}}H \) solutions, here showing a selection of the equimolar composition for asymmetric halide salts.
The methodology for determining $\Delta_{\text{mix}}H$ is used in CALPHAD modeling of the NaCl−PuCl$_3$ system to provide an example of its utility. Limited experimental data are available for this system, consisting of only end-member values and phase equilibria (Figure 8a). The excess enthalpy (Figure 8b) for the melt was obtained from our estimation of the $\Delta_{\text{mix}}H$ at 1123 K, which is near the average temperature of the $\Delta_{\text{mix}}H$ data set (1142 K), and identification of the composition at maximum SRO. In the development of the set of consistent thermodynamic models of the system, the melt was represented by the modified quasichemical model in the quadruplet approximation (MQMQA), which takes into account SRO between first- and second-nearest neighbors on a lattice or sublattice.

For the MQMQA, the first-nearest-neighbor (FNN) coordination numbers, $z_{ij}$, were specified as:

$$z_{\text{Na}/\text{Cl}} = z_{\text{Pu}/\text{Cl}} = 6; z_{\text{Pu}/\text{Cl}} = 2$$

### Table 2. Composition at Maximum SRO for AkCl−UCl$_3$ and AkCl−PuCl$_3$ Systems with Their 2σ Values

| alkali | $x_{\text{UCl}_3}$ | 2σ interval | $x_{\text{PuCl}_3}$ | 2σ interval |
|--------|-------------------|-------------|-------------------|-------------|
| LiCl   | 0.455             | 0.503       | 0.420             | 0.458       |
|        | 0.407             | 0.477       | 0.436             | 0.450       |
| NaCl   | 0.459             | 0.442       | 0.415             | 0.440       |
| KCl    | 0.432             | 0.404       | 0.393             | 0.439       |
| RbCl   | 0.431             | 0.417       | 0.417             | 0.428       |
| CsCl   | 0.425             | 0.414       | 0.399             | 0.428       |

### 2.4. Use of Computed $\Delta_{\text{mix}}H$ in CALPHAD Modeling.

The methodology for determining $\Delta_{\text{mix}}H$ is used in CALPHAD modeling of the NaCl−PuCl$_3$ system to provide an example of its utility. Limited experimental data are available for this system, consisting of only end-member values and phase equilibria (Figure 8a). The excess enthalpy (Figure 8b) for the melt was obtained from our estimation of the $\Delta_{\text{mix}}H$ at 1123 K, which is near the average temperature of the $\Delta_{\text{mix}}H$ data set (1142 K), and identification of the composition at maximum SRO. In the development of the set of consistent thermodynamic models of the system, the melt was represented by the modified quasichemical model in the quadruplet approximation (MQMQA), which takes into account SRO between first- and second-nearest neighbors on a lattice or sublattice.

For the MQMQA, the first-nearest-neighbor (FNN) coordination numbers, $z_{ij}$, were specified as:

$$z_{\text{Na}/\text{Cl}} = z_{\text{Pu}/\text{Cl}} = 6; z_{\text{Pu}/\text{Cl}} = 2$$

### Figure 5. Maximum SRO vs $\delta_{12}$ plots with interpolated values for uranium and plutonium alkali chlorides: (a) LiCl−MCl$_3$ series; (b) NaCl−MCl$_3$ series; (c) KCl−MCl$_3$ series; (d) RbCl−MCl$_3$; and (e) CsCl−MCl$_3$ series. The fitted coefficients $b$ and $m$ were determined from the relation $x_{\text{SRO}} = m\delta_{12} + b$.
The values of cation−cation, i.e., the second-nearest-neighbor (SNN) coordination numbers, $Z_i$, that best represent the phase equilibria were found to be $Z_{36}, 2.4$. A value of 0.333 was used for the required ratio $Z_{\text{NaPu/Cl}}/(Z_{\text{NaPu/Cl}} + Z_{\text{PuCl}})$ to represent the average coordination number of plutonium complex species $\text{PuCl}_6^{3−}$. The presence of the $\text{PuCl}_6^{3−}$ is seen as the reason why the composition at maximum SRO is skewed toward lower $\text{PuCl}_3$ compositions.

The excess Gibbs free energy for the NaCl–PuCl$_3$ melt was determined by optimizing the known system phase equilibria, the predicted $\Delta_{\text{mix}}H$, and the thermodynamic values for the compounds in Table 4, and is expressed as

$$\Delta g_{\text{NaPu/Cl}}(\text{J/mol}) = -8685.7 - 0.993T - 4079.8\chi_{\text{NaPu}} - 6004.6\chi_{\text{PuNa}}$$

where $\chi_{\text{NaPu}}$ and $\chi_{\text{PuNa}}$ represent the cation pair fractions as defined in the MQMQA. The system has a eutectic composition as described by Benes and Konings, and Yin et al., each describing a similar calculated phase diagram with their models differing by values of $\Delta_{\text{mix}}H$ (Figure 8b). Yin et al. predicted $\Delta_{\text{mix}}H$ assumed a minimum at an equimolar composition. Consequently, our predicted $\Delta_{\text{mix}}H$ is over 10% more negative than theirs (Figure 8b).

### 3. CONCLUSIONS

We have developed a correlational approach to estimate the composition of maximum SRO, which is the point at which $\Delta_{\text{mix}}H$ is most negative. Additionally, the correlation can propagate the errors reported for experimental measurements to ultimate $\Delta_{\text{mix}}H$ values. As experimental measurements of $\Delta_{\text{mix}}H$ are often unavailable or difficult to obtain, the demonstrated relations and developed methodology meet a critical need for efficiently generating thermodynamic properties of molten salts.
Along with propagated errors from the underlying experimental data, our method provides valuable information for the development of unambiguous thermodynamic models for halide salts. Hence, we have produced a complete set of heretofore unknown values for the thermodynamic properties of the AkCl–UCl₃ and AkCl–PuCl₃ salt systems at potential MSR temperatures. The results reported here are being used to provide models for systems that are being integrated into the Melted Salt Thermal Properties Database—Thermochemical (MSTDB-TC)¹⁵ to serve as a resource for the MSR and related communities. Although we focused on the application of molten salt melts for MSRs, the approach to determine $\Delta_{\text{mix}} H$ solution can be used for a wide variety of technologically interesting halide salt systems that require thermodynamic models for their effective implementation.

### Table 4. Thermodynamic Properties of Compounds Used in the NaCl–PuCl₃ Optimization

| Compound   | $T$ range (K) | $H_{298.15}$ (J/mol) | $S_{298.15}$ (J/mol.K) | $c_p$ (J/mol.K) | ref |
|------------|---------------|----------------------|------------------------|-----------------|-----|
| NaCl (s)   | 298.15–15000  | −411120              | 72.132                 | 45.94 + 0.016318(T/K) | 66  |
| NaCl (l)   | 298.15–1500   | −394956              | 76.076                 | 77.7638 – 0.0075312 (T/K) | 66  |
|            | 1500–2000     | 66.944               |                        |                  |     |
| PuCl₃ (s)  | 298.15–2000   | −959600              | 161.4                  | 91.412 + 0.03716(T/K) – 27400(T/K)² | 65  |
| PuCl₃ (l)  | 298.15–2000   | −931116              | 170.463                | 144              | 65  |

**Figure 8.** (a) Computed phase diagram for NaCl–PuCl₃ from this work as well as those of Beneš and Konings⁶⁵ and Yin et al.⁵⁴, together with phase equilibria measurements.⁶¹ (b) $\Delta_{\text{mix}} H$ values from this work and those of Beneš and Konings⁶⁵ and Yin et al.⁵⁴

Our analysis of 48 charge-asymmetric actinide/lanthanide systems indicates that the previously observed quadratic (or nearly linear) relationship of $\delta_{12}$ to $\Delta_{\text{mix}} H$ applies within families of alkali chlorides mixed with lanthanide and actinide trichloride salts. We have uniquely observed that there appears to be a linear correlation between $\delta_{12}$ and the pseudobinary composition at maximum SRO, which represents the most negative $\Delta_{\text{mix}} H$ values. This correlation has allowed the development of a novel, simple, and yet accurate method to predict such values for the pseudobinary systems of interest. When coupled with the Davis’¹²,²³ approach, the methodology provides a new means for well-predicting $\Delta_{\text{mix}} H$ at the composition of maximum SRO, the value for which no longer needs to be assumed a priori. Additional $\Delta_{\text{mix}} H$ predictions of unmeasured AkCl–LnCl₃ systems are provided in the Supporting Information.

### ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c04755.

Predictions of enthalpy of mixing for 27 unexplored AkCl–LnCl₃ systems: LiCl–PmCl₃, LiCl–SmCl₃, LiCl–EuCl₃, LiCl–DyCl₃, LiCl–HoCl₃, LiCl–ErCl₃, NaCl–PmCl₃, NaCl–EuCl₃, NaCl–HoCl₃, KCl–PmCl₃, KCl–SmCl₃, KCl–EuCl₃, KCl–HoCl₃, KCl–ErCl₃, RbCl–PrCl₃, RbCl–PmCl₃, RbCl–SmCl₃, RbCl–EuCl₃, RbCl–DyCl₃, RbCl–HoCl₃, RbCl–ErCl₃, CsCl–PrCl₃, CsCl–PmCl₃, CsCl–SmCl₃, CsCl–EuCl₃, CsCl–DyCl₃, and CsCl–HoCl₃ (PDF)

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Author Contributions

J.S.P. and J.A.Y. were responsible for the writing and development of ideas for the manuscript with feedback given by all authors. J.S.P. compiled and critically evaluated the available data. J.A.Y. performed the statistical analysis and error propagation. M.S.C., M.A.A.A., and A.M.M. advised J.S.P. and J.A.Y. in various matters including graphical design, document structure, methodology, and statistical analysis. T.M.B directed the research.

Notes

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ABBREVIATIONS

Ak, alkali; An, actinide; Ln, lanthanide; MSTDB-TC, Molten Salt Thermal Properties Database—Thermochemical; MSRs, molten salt reactors; CALPHAD, CALculation of PHase diagrams; SIM, surrounded ion model; SRO, short-range order; MQMAQ, the modified quaasichemical model in the quadruplet approximation; FNN, first-nearest neighbor; SNN, second-nearest neighbor

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