Production and Chemical Analysis of NaCl-KCl-UCl₃ Salts

Chemical and Fuel Cycle Technologies Division
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by
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February 26, 2021
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1. Introduction

Thermochemical and thermophysical properties of several molten salt systems of interest to molten salt reactor (MSR) developers are being measured at Argonne National Laboratory. These properties are needed by developers to design, license, and operate their reactors. Thermochemical properties being measured at Argonne include thermal transitions, phase behavior, and heat capacity. Thermophysical properties being measured at Argonne include liquid density, surface tension, volumetric thermal expansion of the liquid phase, thermal diffusivity, thermal conductivity, and viscosity.

Properties of the ternary NaCl-KCl-UCl₃ system that may be used as a fuel bearing salt are being measured. Low-melting eutectic salt compositions are of interest to developers owing to the thermal efficiency. Using salts with low melting temperatures allow reactors to be operated at a lower temperature to improve operation and decrease safety concerns. Confirming low melting behaviors are maintained during composition changes that occur during fission is also an important factor. It is essential to any molten salt reactor developer utilizing a fuel bearing salt to have a complete understanding of the behavior of that fuel salt at a variety of compositions near the eutectic composition they plan to use. This kind of stability is indicated on a phase diagram by low liquidus slopes at compositions bordering the eutectic. Therefore, a thermodynamic model was constructed to determine what compositions of the ternary NaCl, KCl, and UCl₃ system should be studied to support MSR developers.

2. Description of the thermochemical model

A thermodynamic model for the NaCl-KCl-UCl₃ ternary system was created using the Computer Coupling of Phase Diagrams and Thermochemistry (CALPHAD) approach. In this method, unknown thermodynamic property values of a system are estimated by fitting solution models to experimental data. A full thermodynamic description of a multicomponent system is obtained using thermodynamic assessments of all binary subsystems and application of standard interpolation methods. Models of binary subsystems are created using Gibbs energy functions for all pure compounds, solid solutions, and liquid solutions of that system.

The Gibbs energy as a function of temperature for pure compounds is defined as:

\[
G(T) = \Delta_f H^0(298) - S^0(298)T + \int_{298}^{T} C_p(T')dT' - T \int_{298}^{T} \frac{C_p(T')}{T}dT'
\]

where \(G(T)\) is the Gibbs energy at temperature \(T\), \(\Delta_f H^0(298)\) and \(S^0(298)\) are the standard enthalpy of formation and the standard absolute entropy at 298.15 K, respectively. The \(C_p(T')\) term is the heat capacity as a function of temperature at constant pressure. The thermochemical properties of pure compounds relevant to the NaCl-KCl-UCl₃ ternary system are provided in Table 1.
Table 1: The ΔfH°(298.15) (kJ mol⁻¹), S°(298.15) (J K⁻¹ mol⁻¹) and Cp (J K⁻¹ mol⁻¹) data of pure compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>ΔfH°</th>
<th>S°</th>
<th>C° = a + bT + cT² + dT⁵ + eT⁰.₅</th>
<th>Temp. (K) range for Cp</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl(s)</td>
<td>-411120</td>
<td>72.132</td>
<td>56.304 -0.01303 -342570 2.1875E-5 -</td>
<td>298 – 900</td>
<td>1</td>
</tr>
<tr>
<td>NaCl(l)</td>
<td>-382962</td>
<td>98.355</td>
<td>56.304 -0.01303 -342570 2.1875E⁻5 -</td>
<td>298 – 900</td>
<td>1</td>
</tr>
<tr>
<td>KCl(s)</td>
<td>-436684.1</td>
<td>82.555</td>
<td>50.477 0.00592 -144174 7.4967E⁻6 -</td>
<td>298 – 700</td>
<td>1</td>
</tr>
<tr>
<td>KCl(l)</td>
<td>-410400.2</td>
<td>107.731</td>
<td>50.477 0.00592 -144174 7.4967E⁻6 -</td>
<td>298 – 700</td>
<td>1</td>
</tr>
<tr>
<td>UCl₃(s)</td>
<td>-861904</td>
<td>158.992</td>
<td>136.3 - 993200 -776.9</td>
<td>298 – 600</td>
<td>FactPS</td>
</tr>
<tr>
<td>UCl₃(l)</td>
<td>-817588.7</td>
<td>198.685</td>
<td>90.03 0.0294</td>
<td>600 – 1110</td>
<td>FactPS</td>
</tr>
<tr>
<td>K₂UCl₅(s)</td>
<td>-1785272.2</td>
<td>324.102</td>
<td>129.704 -</td>
<td>600 – 2000</td>
<td>Estimated</td>
</tr>
</tbody>
</table>

The molar Gibbs energy of a solution is described by the following expression:

\[ G_m = G_m^o + G_m^{id} + G_m^{xs} \]  

(2)

where \( G_m^o \) is the weighted molar Gibbs energy of the pure end-member solution components, \( G_m^{id} \) is an entropy of mixing term that accounts for ideal mixing effects, and \( G_m^{xs} \) is the excess Gibbs free energy that accounts for non-ideal mixing effects. Model development of the three binary subsystems of the NaCl-KCl-UCl₃ ternary involved optimizing the parameters of Gibbs excess energy functions for the liquid solution of each binary as well as the solid solution for the NaCl-KCl binary.

The (Na,K)Cl solid solution was modeled using the Redlich-Kister mixing model, following the approach of Sergeev et al. [1]. In this model, the molar Gibbs excess energy \( (G_m^{xs}) \) is defined as:

\[ G_m^{xs} = x_i x_j \sum_{\nu=0}^{n} L_{ij}^{(\nu)} (x_i - x_j)^\nu \]  

(3)

where \( x_i \) and \( x_j \) are the mole fractions of end member species \( i \) and \( j \), respectively, and \( L_{ij}^{(\nu)} \) is a temperature-dependent polynomial:

\[ L_{ij}^{(\nu)} = A + BT + CT \ln T + DT^2 \ldots \]  

(4)

The \( L_{ij}^{(\nu)} \) interaction terms for the (Na,K)Cl solid solution are provided in Table 2. A solution database was created for this solid solution using the “one-lattice polynomial model” (QKTO) in FactSage.
Table 2: The Gibbs excess energy functions of the (Na,K)Cl solid solution

<table>
<thead>
<tr>
<th>Binary system</th>
<th>Interaction term</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl-KCl</td>
<td>$L^{[0]} = 15975.6 + 33.08 \cdot T - 5.593 \cdot T \cdot \ln(T)$</td>
</tr>
<tr>
<td></td>
<td>$L^{[1]} = 1650.4$</td>
</tr>
</tbody>
</table>

The modified quasi-chemical model in the quadruplet approximation (MQMQA) described by Pelton et al. [2] was applied to optimize the excess Gibbs free energy functions of the liquid solutions. The MQMQA accounts for first-nearest-neighbor (FNN) and second-nearest-neighbor (SNN) short-range ordering in solutions and is the recommended method for modeling molten salt solutions because it best describes the configurational entropy [3]. The MQMQA considers the system of interest to be a series of quadruplets (sets of 4 ions) that contain two cations and two anions. If the system of interest has three cations (A, B, and C) and one anion (X), it is considered as six quadruplets. These quadruplets consist of three unary sets ([A2X2]quad, [B2X2]quad, and [C2X2]quad) that represent the three end members and three binary sets ([ABX2]quad, [ACX2]quad, and [BCX2]quad). Each ion within a quadruplet has a SNN coordination number. For example, the SNN coordination number of A in quadruplet A2X2 is denoted $Z_{\text{A2X2}}^A$ and represents the number of A cations neighboring a single A cation (i.e., the cation-cation coordination number). The cation-cation coordination numbers selected for the NaCl-KCl-UCl3 system are shown in Table 3. The anion-anion coordination numbers are determined by satisfying electroneutrality. For example, the anion-anion coordination number for anion X in the ABX2 quadruplet ($Z_{\text{ABX2}}^X$) is defined as follows:

$$\frac{q_A}{Z_{\text{ABX2}}^A} + \frac{q_B}{Z_{\text{ABX2}}^B} = \frac{q_X}{Z_{\text{ABX2}}^X} + \frac{q_X}{Z_{\text{ABX2}}^X}$$

where $q_A$, $q_B$, and $q_X$ are the absolute charges of cations A and B and anion X, respectively.

Table 3: Cation-cation coordination numbers of liquid solutions

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>$Z_{\text{AB}}^A$</th>
<th>$Z_{\text{AB}}^B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na+</td>
<td>Na+</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Na+</td>
<td>U3+</td>
<td>3</td>
<td>6</td>
</tr>
<tr>
<td>U3+</td>
<td>U3+</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>K+</td>
<td>U3+</td>
<td>3</td>
<td>6</td>
</tr>
<tr>
<td>K+</td>
<td>K+</td>
<td>6</td>
<td>6</td>
</tr>
</tbody>
</table>

A liquid solution database incorporating the Gibbs excess energy parameters for the binary subsystems was created in FactSage using the “two-lattice modified quasichemical model revised” (SUBQ) model. In this model, two sublattices were defined: sublattice A for the cations and sublattice B for the anion. In addition to the cation-cation coordination number, the ratio of the FNN to the SNN ($\zeta$) is also required as input in the model for each solution end member. The ratio for the AX end member of the A2X2 quadruplet is defined as:

$$\zeta_{\text{AX}} = \frac{2Z_{\text{A2X2}}^A Z_{\text{A2X2}}^X}{Z_{\text{A2X2}}^A Z_{\text{A2X2}}^X + Z_{\text{A2X2}}^X}$$
where \( Z_{A2/X2}^A \) and \( Z_{A2/X2}^X \) are the previously defined SNN coordination numbers of A and X in the \( A_2X_2 \) quadruplet. Table 4 reports the \( \zeta \) value for each end member species (i.e., each unary quadruplet).

<table>
<thead>
<tr>
<th>End member species</th>
<th>Quadruplet</th>
<th>( \zeta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>Na(_2)Cl(_2)</td>
<td>6</td>
</tr>
<tr>
<td>KCl</td>
<td>K(_2)Cl(_2)</td>
<td>6</td>
</tr>
<tr>
<td>UCl(_3)</td>
<td>U(_2)Cl(_2)</td>
<td>3</td>
</tr>
</tbody>
</table>

The Gibbs excess energy function of the liquid solution for an AX-BX binary system is defined as the Gibbs energy change for the second-nearest-neighbor pair-exchange reaction (\( \Delta g_{AB/X} \)):

\[
(A - X - A) + (B - X - B) = 2(A - X - B), \quad \Delta g_{AB/X}
\]

(7)

The Gibbs energy change parameter for a binary AX-BX system (\( \Delta g_{AB/X} \)) can be expanded into the following polynomial:

\[
\Delta g_{AB/X} = \Delta g_{0}^{AB/X} + \sum_{(i+j \geq 1)} g_{ij}^{AB/X} \chi_{AB/X}^i \chi_{BA/X}^j
\]

(8)

where \( \Delta g_{0}^{AB/X} \) and \( g_{ij}^{AB/X} \) are composition-independent (but potentially temperature dependent) coefficients that are obtained by fits to experimental data. The composition-dependent \( \chi_{AB/X} \) term is defined as:

\[
\chi_{AB/X} = \left( \frac{x_{AA}}{x_{AA} + x_{AB} + x_{BB}} \right)
\]

(9)

where \( x_{AA}, x_{AB}, \) and \( x_{BB} \) are the mole fractions of the cation-cation pairs. The Gibbs excess energy functions that were determined for the binary subsystems of the NaCl-KCl-UCl\(_3\) system are provided in Table 5. The Gibbs excess energy functions were obtained from optimizations of experimentally determined liquidus and solidus temperatures using the OptiSage module in FactSage. The references to the experimental data are provided in Table 5.

<table>
<thead>
<tr>
<th>Binary system</th>
<th>( \Delta G^m ) (J mol(^{-1}))</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl-UCl(_3)</td>
<td>( \Delta G_{NaU/ClCl} = -7847.15 + 1.138T + \chi_{NaU}(-4880.95 + 2.383T) + \chi_{Una}(-20.29 - 2.505T) )</td>
<td>[4, 5]</td>
</tr>
<tr>
<td>NaCl-KCl</td>
<td>( \Delta G_{NaK/ClCl} = 1592.1 - 2.291T + \chi_{NaK}(-1205.2) ) + ( \chi_{KNa}(531.73) + \chi_{NaK}^2(247.56) )</td>
<td>[1, 6-8]</td>
</tr>
<tr>
<td>KCl-UCl(_3)</td>
<td>( \Delta G_{KU/ClCl} = -23031.1 + 7.84T + \chi_{UK}(-13319.4) + \chi_{KU}(-8866.68) )</td>
<td>[9-10]</td>
</tr>
</tbody>
</table>

A thermodynamic model for the ternary system was extrapolated from the binary subsystems using the Kohler or Toop methods depending on whether the subsystem was treated as symmetric or asymmetric, respectively. System components were grouped into two categories: one category for
the components with monovalent cations (i.e., NaCl and KCl) and the other category for components with polyvalent cations (i.e., UCl₃). Component pairs within the category (e.g., NaCl and KCl) were modeled as symmetric while those between different categories (e.g., NaCl and UCl₃) were modeled as asymmetric. The data interpolation models for the higher order system were assigned in the FactSage solution database.

3. Optimization results of the NaCl-KCl-UCl₃ system

Phase diagrams of the optimized NaCl-KCl, NaCl-UCl₃, and KCl-UCl₃ binary subsystems are provided in Figures 1 – 3, respectively. The calculated liquidus projection for the ternary system is provided in Figure 4. The calculated invariant equilibria from the thermochemical model developed in this work and those obtained from the literature for the ternary NaCl-KCl-UCl₃ system are provided in Table 6 for comparison. The ternary system has a single eutectic at 470 °C with a composition of 42.9 mol% NaCl, 20.3 mol% KCl, and 36.8 mol% UCl₃.

![Figure 1: Calculated phase diagram for the NaCl-KCl system. The data points are measured values from the literature that were used in the optimizations: (+) Vesnin and Zakovrjashin, 1979 (●) Pelton et al., 1985, and (○) Coleman and Lacy, 1967.](image-url)
Figure 2: Calculated phase diagram for the NaCl-UCl₃ system. The data points are measured values from the literature that were used in the optimizations: (●) Kraus, 1943 and (▲) Sooby et al., 2015.
Figure 3: Calculated phase diagram for the KCl-UCl₃ system. The data points are measured values from the literature that were used in the optimizations: (●) Thoma et al., 1965 and (○) Hames et al., 2018.
Figure 4: Calculated liquidus projection for the NaCl-KCl-UCl3 system.

![Liquidus projection for the NaCl-KCl-UCl3 system](image.png)

**Table 6: Invariant equilibria in the NaCl-KCl-UCl3 system**

<table>
<thead>
<tr>
<th>Phases present</th>
<th>Type</th>
<th>Temp (°C)</th>
<th>$X_{NaCl}$</th>
<th>$X_{KCl}$</th>
<th>$X_{UCl3}$</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_2UCl_5$, (Na,K)Cl, UCl3, liquid</td>
<td>Eutectic</td>
<td>470.15</td>
<td>0.429</td>
<td>0.203</td>
<td>0.368</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td></td>
<td>489.6</td>
<td>0.493</td>
<td>0.135</td>
<td>0.372</td>
<td>[11]</td>
</tr>
</tbody>
</table>

An isopleth of the pseudo binary system $UCl_3$ - (68% NaCl-32% KCl) is shown in Figure 5 and the stable phases present in the isopleth are listed in Table 7. The liquidus curve of the pseudo binary passes through the eutectic composition for the ternary system (36.8% UCl3 at 470 °C) and indicates how the liquidus temperature is affected as the UCl3 concentration varies while the ratio of the NaCl and KCl concentrations is held constant.
Figure 5: An isopleth of the pseudo binary system UCl₃ - (68% NaCl-32% KCl). The stable phases are identified in Table 7.

Table 7: Phases present in isopleth of UCl₃ - (68% NaCl-32% KCl) pseudo-binary

<table>
<thead>
<tr>
<th>Label</th>
<th>Phases present</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Liquid + (Na,K)Cl</td>
</tr>
<tr>
<td>b</td>
<td>Liquid + K₂UCl₅ + (Na,K)Cl</td>
</tr>
<tr>
<td>c</td>
<td>K₂UCl₅ + (Na,K)Cl</td>
</tr>
<tr>
<td>d</td>
<td>K₂UCl₅ + (Na,K)Cl₁ + (Na,K)Cl₂</td>
</tr>
<tr>
<td>e</td>
<td>Liquid + K₂UCl₅ + (Na,K)Cl</td>
</tr>
<tr>
<td>f</td>
<td>UCl₃ + K₂UCl₅ + (Na,K)Cl</td>
</tr>
<tr>
<td>g</td>
<td>Liquid + UCl₃</td>
</tr>
<tr>
<td>h</td>
<td>Liquid</td>
</tr>
</tbody>
</table>
4. Conclusions

The first composition for which thermophysical and thermochemical properties will be measured is the eutectic composition identified by the model as 42.9 % NaCl, 20.3 % KCl and 36.8 %UCl$_3$ molar. This composition has the lowest melting point in the ternary system and will be of most interest to MSR developers. The second composition will have less uranium than the eutectic to represent depletion by fission. Based on the isopleth, the 51 % NaCl - 24 % KCl - 25 % UCl$_3$ molar composition will be used to represent the salt at a lower uranium concentration. It is expected that this composition will have a higher melting temperature and additional solid solutions.

Salts of the compositions identified here will be synthesized and their thermophysical and thermochemical properties will be measured to support the development of MSRs. The properties to be measured include melting temperatures, identify any additional phases or phase transitions, and heat capacity. The density, thermal diffusivity and viscosity will be measured at several temperatures to determine the temperature dependencies. Additional properties calculated from the measurements will include surface tension, volumetric thermal expansion of the liquid phase, and thermal conductivity. The measured values and calculations will support the design, licensing and operation of reactors utilizing this salt system. Additionally, these measurements will demonstrate the level of quality presently achievable using state-of-the-art techniques.
References


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