Thermodynamic evaluation of LiCl-KCl-PuCl₃ system

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Abstract

The present study focuses on developing the phase diagram of LiCl-KCl-PuCl₃ system based on the CALPHAD (CALculation of PHase Diagram) method. Sub-binary systems of LiCl-KCl, LiCl-PuCl₃, and KCl-PuCl₃ were developed first by optimizing the Gibbs energy parameters according to the experimental data from literature using the two-sublattice model. Then the enthalpy of mixing of the LiCl-KCl-PuCl₃ system was estimated, to explore the ternary interactions, using an empirical correlation derived from the surrounded-ion model for the asymmetric salt system due to the scarcity of available data for the ternary system. Based on the phase diagram developed, the solubility of PuCl₃ in the eutectic LiCl-KCl melt at different temperatures was obtained, as well as the Gibbs energy of formation of PuCl₃ in the salt as a function of PuCl₃ concentration. The present study extends the experimental data for dilutions to concentrated solutions for which no experimental data have been well reported.

Keywords: LiCl-KCl-PuCl₃, Phase diagram, CALPHAD, Two-sublattice model

1. Introduction

Pyroprocessing in LiCl-KCl molten salt has been developed as an alternative to the PUREX process to separate the uranium and other actinides from used nuclear fuels [1,2,3], which will reduce the volume of radioactive waste and recycle the useful fuel. Electrorefiner is the key step in pyroprocessing, where uranium electrodeposits onto a solid cathode selectively by controlling the applied current, then the residual uranium, plutonium, and other minor actinides are collected from the salt as a group [4]. As more and more fuel is reprocessed, the composition of molten salt changes, which will alter the thermodynamic properties of the system and cause adjustments to the operation conditions to be needed [5,6,7]. In order to optimize the system design and operate it safely, thermodynamic assessment of actinides and lanthanides in LiCl-KCl molten salt is significantly needed. Even though several systems have been assessed, such as LiCl-KCl-CeCl₃ [8,9] and LiCl-KCl-UCl₃ [10], as one of the major actinides in pyroprocessing, PuCl₃ in LiCl-KCl has not been evaluated.

In the present work, thermodynamic properties of LiCl-KCl-PuCl₃ are being considered and evaluated. Two-sublattice model for ionic liquid was applied to LiCl-KCl, LiCl-PuCl₃, and KCl-

PuCl₃ binary systems primarily to model their Gibbs energies. The experimental data used includes the phase information and enthalpy of mixing from literature. However, for the LiCl-KCl-PuCl₃ ternary system, previous studies are limited in electrochemical measurements with dilute solution. These data could be used but not enough to evaluate the ternary interactions in the system. As a supplementary, an empirical correlation to estimate the enthalpy of mixing for asymmetric salt system that has been successfully used in the LiCl-KCl-UCl₃ system [10] was applied to calculate the enthalpy of mixing of the LiCl-KCl-PuCl₃. These data combined with the results from binary systems were used as input to assess the thermodynamic equilibria of the LiCl-KCl-PuCl₃ system. After that, the solubility and Gibbs energy of formation of PuCl₃ in the typical molten LiCl-KCl used in pyroprocessing were derived from the optimized results.

2. Thermodynamic modelling

Phase diagram development is the process to find the stable or metastable phases and phase boundaries. All these properties could be reflected by the Gibbs energy of the system [11]. For example, the global minimum Gibbs energy corresponds to stable phase and local minimum Gibbs energy to the metastable phase. Also, when two phases coexist, the chemical potential of a species in these two phases should be the same

$$\mu_i^{\varphi 1} = \left(\frac{\partial G_t^{\varphi 1}}{\partial n_i^{\varphi 1}} \right)_{n_{j \neq i}, p, T} = \mu_i^{\varphi 2} = \left(\frac{\partial G_t^{\varphi 2}}{\partial n_i^{\varphi 2}} \right)_{n_{j \neq i}, p, T} \quad \text{Eq. 1}$$

where $\mu_i^{\varphi j}$ and $n_i^{\varphi j}$ are the chemical potential and mole number of i in phase φj , respectively. $G_t^{\varphi j}$ is the total Gibbs energy of phase φj . p and T are the pressure and absolute temperature, respectively. Generally, for the solution phase of a ternary system with components of 1-2-3, the molar Gibbs energy could be expressed by [12]

$$\begin{aligned} G_m &= \sum_{i=1}^3 x_i G_i^0 + RT \sum_{j=1}^3 x_j \ln x_j + G_m^{ex} \\ &= \sum_{i=1}^3 x_i G_i^0 + RT \sum_{j=1}^3 x_j \ln x_j + (G_{m,12}^{ex} + G_{m,23}^{ex} + G_{m,13}^{ex} + G_{m,123}^{ex}) \end{aligned} \quad \text{Eq. 2}$$

where G_i^0 is the standard molar Gibbs energy of i . G_m^{ex} is the molar excess Gibbs energy including the contributions from all sub-binary systems 1-2, 2-3, and 1-3 as well as the ternary system 1-2-3 in the solution. x_i is the mole fraction of i in the solution phase, R is the gas constant, and T is the temperature in kelvin. Therefore, in order to calculate the phase diagram, a Gibbs energy model to describe the solution of the system should be built first.

In the present work, a two-sublattice model [13][14] was applied to describe the excess Gibbs energy of liquid. The model separates anions and cations into different sublattices. There are two intermediate compounds in LiCl-KCl-PuCl₃ system, K₂PuCl₅ and K₃PuCl₆ [15] and a previous study shows PuCl₆³⁻ prevails in Pu(III)-containing molten salt [16]. Accordingly, here K₃PuCl₆ is treated as a neutral species in anionic sublattice to deal with the short-range ordering. Now the model is indicated by

The parenthesis represents different lattices and the colon is used to separate them. In every parenthesis, there is a constituent array resided in the sub-lattice. p and q are the site numbers in the corresponding lattice and given by

$$p = y_{Cl^-} \quad \text{Eq. 3}$$

And

$$q = y_{K^+} + y_{Li^+} + 3y_{Pu^{3+}} \quad \text{Eq. 4}$$

where y_i is the site fraction of a particular species i on the corresponding sublattice. The molar Gibbs energy of liquid phase now is

$$\begin{aligned} G_m^{Liq.} = & y_{Li^+} y_{Cl^-} {}^0G_{Li^+:Cl^-}^{Liq.} + y_{K^+} y_{Cl^-} {}^0G_{K^+:Cl^-}^{Liq.} + y_{Pu^{3+}} y_{Cl^-} {}^0G_{Pu^{3+}:Cl^-}^{Liq.} \\ & + {}^0G_{K_3PuCl_6}^{Liq.} + RT[p(y_{Li^+} \ln y_{Li^+} + y_{K^+} \ln y_{K^+} + y_{Pu^{3+}} \ln y_{Pu^{3+}}) \\ & q(y_{Cl^-} \ln y_{Cl^-} + y_{K_3PuCl_6} \ln y_{K_3PuCl_6})] + {}^E G_m^{Liq.} \end{aligned} \quad \text{Eq. 5}$$

where ${}^0G_{Li^+:Cl^-}^{Liq.}$, ${}^0G_{K^+:Cl^-}^{Liq.}$, ${}^0G_{Pu^{3+}:Cl^-}^{Liq.}$, ${}^0G_{K_3PuCl_6}^{Liq.}$ are the standard molar Gibbs energy of LiCl, KCl, PuCl₃, and K₃PuCl₆ in liquid status, respectively. ${}^E G_m^{Liq.}$ is the molar excess Gibbs energy. In the manner of Muggianu formalism [17], it was given by

$$\begin{aligned} {}^E G_m^{Liq.} = & y_{Cl^-} (y_{K^+} y_{Li^+} L_{K^+,Li^+:Cl^-}^{Liq.} + y_{K^+} y_{Pu^{3+}} L_{K^+,Pu^{3+}:Cl^-}^{Liq.} + y_{Li^+} y_{Pu^{3+}} L_{Li^+,Pu^{3+}:Cl^-}^{Liq.}) \\ & + y_{Cl^-} y_{K_3PuCl_6} (y_{K^+} L_{K^+:Cl^-,K_3PuCl_6}^{Liq.} + y_{Li^+} L_{Li^+:Cl^-,K_3PuCl_6}^{Liq.} + y_{Pu^{3+}} y_{K_3PuCl_6} L_{Pu^{3+}:Cl^-,K_3PuCl_6}^{Liq.}) \\ & + y_{Cl^-} y_{K_3PuCl_6} (y_{K^+} y_{Li^+} L_{K^+,Li^+:Cl^-,K_3PuCl_6}^{Liq.} + y_{K^+} y_{Pu^{3+}} L_{K^+,Pu^{3+}:Cl^-,K_3PuCl_6}^{Liq.} \\ & + y_{Li^+} y_{Pu^{3+}} L_{Li^+,Pu^{3+}:Cl^-,K_3PuCl_6}^{Liq.}) + y_{K^+} y_{Li^+} y_{Pu^{3+}} y_{Cl^-} (L_{K^+,Li^+,Pu^{3+}:Cl^-}^{Liq.} \\ & + y_{K_3PuCl_6} L_{K^+,Li^+,Pu^{3+}:Cl^-,K_3PuCl_6}^{Liq.}) \end{aligned} \quad \text{Eq. 6}$$

These interaction parameters L for both binary and ternary interactions could be expressed as concentration and temperature dependent. For example, binary interaction parameter $L_{K^+,Pu^{3+}:Cl^-}^{Liq.}$ can be expanded as a Redlich-Kister polynomial [18]

$$L_{K^+,Pu^{3+}:Cl^-}^{Liq.} = \sum_{v=0}^n L_{K^+,Pu^{3+}:Cl^-}^{Liq.} (y_{K^+} - y_{Pu^{3+}})^v \quad \text{Eq. 7}$$

And ternary one, for example, can be

$$L_{Li^+,K^+,Pu^{3+}:Cl^-}^{Liq.} = y_{Li^+} L_{Li^+:Cl^-} + y_{K^+} L_{K^+:Cl^-} + y_{Pu^{3+}} L_{Pu^{3+}:Cl^-} \quad \text{Eq. 8}$$

Then linear dependence on temperature is applied to these parameters like

$${}^v L = a_v + b_v T \quad \text{Eq. 9}$$

a_v and b_v are the parameters that will be optimized during the calculation. Since there are no heat capacity data for the intermediate compounds K_2PuCl_5 and K_3PuCl_6 , their standard Gibbs energies are written according to Neumann–Kopp rule [19] as

$${}^0 G_{K_m Pu_n Cl_{m+3n}}^{state} = m {}^0 G_{KCl}^{state} + n {}^0 G_{PuCl_3}^{state} + A + BT \quad \text{Eq. 10}$$

where “state” stands for liquid or solid. A and B are variables related to the enthalpy and entropy of formation of the intermediate compound $K_m Pu_n Cl_{m+3n}$, respectively. These values were optimized according to experimental data.

The only solid solution considered in the $LiCl$ - KCl - $PuCl_3$ system is the $LiCl$ - KCl mutual terminal solution that is less than 5 at% reported by Ghosh [10]. The solid solution is also described by two-sublattice model as

The molar Gibbs energy is

$$G_m^S = y_{K^+} {}^0 G_{K^+:Cl^-}^S + y_{Li^+} {}^0 G_{Li^+:Cl^-}^S + RT(y_{K^+} \ln y_{K^+} + y_{Li^+} \ln y_{Li^+}) + {}^E G_m^S \quad \text{Eq. 11}$$

And excess Gibbs energy is

$${}^E G_m^S = y_{Li^+} y_{K^+} {}^v L_{Li^+, K^+, Cl^-}^S = y_{Li^+} y_{K^+} \sum_{v=0}^n L_{Li^+, K^+, Cl^-}^S (y_{Li^+} - y_{K^+})^v \quad \text{Eq. 12}$$

3. Database for the LiCl-KCl-PuCl₃ system

For developing the ternary phase diagram based on CALPHAD, experimental data for all the binary systems (LiCl-KCl, LiCl-PuCl₃, KCl-PuCl₃) and the ternary system are needed. In this section, the database was developed based on previous experimental data.

3.1. Binary systems

The LiCl-KCl system has been widely studied. Phase boundary information was investigated by Richards [20], Aukrust [21], Korin [22], and Basin [23] with the methods of heating curves, cooling curves, calorimetric measurements and oscillation phase analysis. Hersh [24] studied the enthalpy of mixing at the temperature of 1013 K. Recently Ghosh [10] evaluated the LiCl-KCl system with terminal solubility and demonstrated by experiments that the mutual solubility is less than 5 at%. However, there are only a few studies on LiCl-PuCl₃ and KCl-PuCl₃. Bjorklund and co-workers [25] studied the phase equilibria of the LiCl-PuCl₃ binary system and reported it to be a simple eutectic system without any solid solution or intermediate compounds. The eutectic point occurs at 28% PuCl₃ with a temperature of 734 K. The phase diagram of KCl-PuCl₃ is a little more complex compared to the other two binary systems since two intermediate compounds were reported [15]: K₃PuCl₆ and K₂PuCl₅. K₃PuCl₆ melts congruently at 685°C and the peritectic point related to K₂PuCl₅ melting appears at 35% PuCl₃ with a temperature of 611°C.

3.2. Ternary system

Even though no reports about the phase diagram or enthalpy have been found about the LiCl-KCl-PuCl₃ system, a variety of experimental measurements have been done to explore the electrochemical behaviors of PuCl₃ in LiCl-KCl eutectic salt. By emf (electromotive force) measurement, Roy [26] studied the Gibbs energy of formation of PuCl₃ in a temperature range of 673 K to 773 K. This study was carried out using many different PuCl₃ mole fractions from $x_{PuCl_3} = 1.91 \times 10^{-5}$ to $x_{PuCl_3} = 1.58 \times 10^{-3}$. Sakamura [27] reported the standard potential of PuCl₃ at 723 K against Ag/AgCl with 1 wt% AgCl by varying the composition from $x_{PuCl_3} = 3.54 \times 10^{-5}$ to $x_{PuCl_3} = 1.03 \times 10^{-3}$ using cyclic voltammetry. Another study [28] was also carried out by them using emf method with $x_{PuCl_3} = 2.9 \times 10^{-4} - 2.35 \times 10^{-3}$ at the temperatures from 673-773 K. Shirai [29] conducted experiments by cyclic voltammetry with temperatures from 723 K to 823 K to explore the redox potential of Pu³⁺/Pu. Both Mo solid electrode and Bi liquid electrode were applied into the weight percent of $w_{PuCl_3} = 0.46\% - 0.87\%$. They concluded the redox potential is

more positive with the liquid Bi electrode than with the solid electrode. Shirai [30] also investigated the Gibbs energy of formation of PuCl_3 at the temperature range between 723 K and 823 K but only at one composition of $x_{\text{PuCl}_3} = 1.4 \times 10^{-3}$. Serp [31] measured the apparent standard potential and Gibbs energy of formation of PuCl_3 in the range of $x_{\text{PuCl}_3} = 1.662 - 3.03 \times 10^{-3}$ by cyclic voltammetry and chronopotentiometry method and then derived the activity coefficient at temperatures of 733, 773, and 823 K. They found the values are sensitive to the supercooled data. They obtained activity coefficient of $\gamma_{\text{PuCl}_3} = 3.5 - 7.9 \times 10^{-3}$ under UEA-TDP data source [32] but $\gamma_{\text{PuCl}_3} = 9.5 - 16 \times 10^{-3}$ under f-MPD data source [33] when other conditions were kept the same. Using the similar method, Masset [34] studied the Gibbs energy of formation of PuCl_3 and calculated the activity coefficient with the values of $\gamma_{\text{PuCl}_3} = 3.5 - 7.9 \times 10^{-3}$ at the temperature range from 733 K to 823 K. These review data were inputted to the Gibbs energy model to evaluate the ternary interactions.

4. Results and discussion

The parameter optimization was carried out in the PARROT module of CALPHAD software Thermo-Calc [35] by minimizing the sum of squares of errors through iterations. Data collected in Table 1 were edited into an experimental data file to be used as the input. After obtaining the Gibbs energy expressions for different phases in the system, phase diagrams were calculated and plotted accordingly in the POLY module of the same software.

4.1. Binary phase diagrams

4.1.1. *LiCl-KCl*

Figure 1 plots the calculated phase diagram of LiCl-KCl. The eutectic point calculated occurs at 58.6 at% LiCl and 626 K. Also, due to the similarity of K and Li, a small portion of K atoms could be substituted for Li atoms in LiCl crystal. Then K atoms act as the solute in the matrix of LiCl while LiCl would still keep its structure. The same rule applies to KCl as well. So the two solid solution phases marked as LiCl and KCl at two terminals of the phase diagram in Figure 1 are not pure LiCl and KCl but LiCl-structure crystal and KCl-structure crystal, respectively. Or it could be said these two solid solution phases are two different halite structure crystals.

4.1.2. *LiCl-PuCl₃*

LiCl- PuCl_3 was reported as a simple eutectic system with the eutectic point at 28 at% PuCl_3 and 734 K [25]. Figure 2 shows our calculated phase diagram. And the eutectic point obtained in this work is at 26.8 at% and 731 K, which agrees very well with experimental data

4.1.3. KCl-PuCl₃

KCl-PuCl₃ has two intermediate components K₂PuCl₅ and K₃PuCl₆. The calculated phase is shown in Figure 3. Calculated melting point of K₃PuCl₆ is at 958 K, compared to the value of 958 K reported by Benz [15]. The peritectic point calculated for K₂PuCl₅ is at 35 at% KCl and 884 K, while the values of 35 at% KCl and 884 K reported by Benz [15] as well. Table 2 shows the optimized parameters for these binary systems and Table 4 is the comparison between the calculated results and the literature data.

4.2. Ternary phase diagram

There are extensive studies about the electrochemical behaviors of PuCl₃ in LiCl-KCl eutectic melt for dilution but no studies reported on the enthalpy or phase information of the LiCl-KCl-PuCl₃ ternary system. Here an empirical correlation derived from the surrounded-ion model, which has been employed in a LiCl-KCl-UCl₃ system [10], was used to estimate the enthalpy of mixing of the current ternary system. On the basis of this model, the enthalpy of mixing is described by

$$\begin{aligned} \Delta_{mix} H = & \frac{3x_{PuCl_3}x_{LiCl}}{1+2x_{PuCl_3}} \left[\frac{1}{3} \left(\frac{x_{LiCl}}{1+2x_{PuCl_3}} \right) \Delta \overline{H}_{PuCl_3(LiCl)}^\infty + \left(1 - \frac{x_{LiCl}}{1+2x_{PuCl_3}} \right) \Delta \overline{H}_{LiCl(PuCl_3)}^\infty \right] \\ & + \frac{x_{LiCl}x_{KCl}}{1+2x_{PuCl_3}} \left[\frac{x_{KCl}}{1+2x_{PuCl_3}} \Delta \overline{H}_{LiCl(KCl)}^\infty + \left(1 - \frac{x_{KCl}}{1+2x_{PuCl_3}} \right) \Delta \overline{H}_{KCl(LiCl)}^\infty \right] \\ & + \frac{3x_{KCl}x_{PuCl_3}}{1+2x_{PuCl_3}} \left[\frac{3x_{PuCl_3}}{1+2x_{PuCl_3}} \Delta \overline{H}_{KCl(PuCl_3)}^\infty + \left(1 - \frac{3x_{PuCl_3}}{1+2x_{PuCl_3}} \right) \frac{1}{3} \Delta \overline{H}_{PuCl_3(KCl)}^\infty \right] \end{aligned} \quad \text{Eq. 13}$$

where x_i is the mole fraction of species i and $\Delta \overline{H}_{i(j)}^\infty$ represents partial enthalpy of mixing at infinite dilution for component i in the i - j binary system. Figure 4 shows the calculated enthalpy of mixing for these three binary systems at 1200 K. The similar structure of the LiCl and KCl is indicated by the pretty symmetric curve. What should attract one's attention mostly is that the minimum value of enthalpy of mixing of KCl-PuCl₃ system presents at PuCl₃-rich side with around 0.63 mole fraction of PuCl₃. This is unexpected because the only two compounds existing in the system are K₂PuCl₅ and K₃PuCl₆, which are both KCl-rich. This phenomenon could be due to the effects of some local ordering [36,37]. But further experiments, for example, by X-ray diffraction method, are merited to investigate it and provide more insightful information. Then based on the plot of enthalpy of mixing, these $\Delta \overline{H}_{i(j)}^\infty$ in Eq. 13 can be obtained, which are shown in Table 5. Based the model, the enthalpy of mixing of LiCl-KCl-PuCl₃ system at 1200 K

with $x(\text{LiCl}):x(\text{KCl})=0.586:0.414$ is estimated and also indicated in Figure 4, which was used as the input to extrapolate the binary systems to ternary one based on the Muggianu formalism with ternary interactions described by Eq. 5 to 9 [17].

The optimized parameters are shown in Table 2. The obtained results for A and B in Eq. 10 indicates that the enthalpy and entropy of formation are -48155.48 J/mol and 23.92 J/mol/K, respectively, for K_2PuCl_5 crystal and -21250.17 J/mol and 78.80 J/mol/K for K_3PuCl_6 crystal. Based on the equilibrium information, the apparent potential of PuCl_3 ($E_{\text{PuCl}_3}^{ap}$ vs Cl_2/Cl^-) in LiCl-KCl eutectic was calculated at a typical dilute solution with $x_{\text{PuCl}_3}=1.25\times10^{-3}$ to compare with the data from the literature reviewed in 3.2. The reported values in literature and calculated results are plotted in Figure 5. The fitted correlations are listed in Table 3. As seen from the comparison, present work is in a good agreement with the literature. It demonstrates the correctness of our optimization. The maximum difference of 9% should be reasonable when considering the difference of PuCl_3 mole fraction in the salt, electrode reference, and electrochemical methods used in experiments [10].

Figure 6 is the calculated isothermal section at 773 K, which is the general temperature pyroprocessing operates at. Figure 7 shows the calculated liquidus projection. It indicates two eutectics and one quasi-peritectic. One eutectic (E1) involving LiCl, PuCl_3 , and K_2PuCl_5 occurs at 616 K and another one (E2) involving LiCl, KCl, and K_3PuCl_6 at 589 K. The quasi-peritectic involving K_2PuCl_5 , K_3PuCl_6 , and LiCl appears at 658 K. There is also a monovariant eutectic involving LiCl and K_2PuCl_5 at 690 K. All these phase reactions have been presented in Table 4.

Three temperatures of 723, 773, and 823 K are taken to be analyzed in detail. Figure 8 shows the calculated liquidus projection of these three temperatures. The dashed line stands for the compositions with $x(\text{LiCl}):x(\text{KCl})=0.586:0.414$. The squares represent where solid first appears and the circles represent where PuCl_3 starts to become solid, which should be the limit of solubility of PuCl_3 in LiCl-KCl eutectic salt at different temperatures. The mole fractions of PuCl_3 at these positions are list in Table 6. Generally, the solubility S_{PuCl_3} in the unit of mole fraction can be expressed by [38]

$$\log S_{\text{PuCl}_3} = a + \frac{b}{T} \quad \text{Eq. 14}$$

which is used to fit the calculated data in Table 6. Figure 9 shows the fitting result, which gives the correlation of

$$\log S_{\text{PuCl}_3} = 0.2415 - \frac{478.37}{T} \quad \text{Eq. 15}$$

Figure 10 shows the Gibbs energy of formation of PuCl_3 in LiCl-KCl eutectic up to 5 at% at different temperatures. The Gibbs energy change at 4.3 at% PuCl_3 at 723 K is due to the precipitation of LiCl in the liquid. It shows that the Gibbs energy is dependent on the concentration and increases with it, which should be noted but is not well reported in the literature.

Conclusions

Thermodynamic assessment for the LiCl-KCl-PuCl_3 ternary system has been carried out by CALPHAD method using two-sublattice model. Binary systems of LiCl-KCl , LiCl-PuCl_3 , and KCl-PuCl_3 are primarily evaluated based on available phase information and enthalpy of mixing. The calculation shows consistency with experimental data. The enthalpy of mixing of LiCl-KCl-PuCl_3 was estimated by an empirical correlation for the asymmetric ionic salt system. The estimation combined with the output from binary systems and previous electrochemical studies were used as the input to extrapolate to ternary system.

The solubility and Gibbs energy of formation of PuCl_3 in LiCl-KCl eutectic were obtained from the optimized results. Other interesting thermodynamic properties could be derived from it as well. This study will help to evaluate the salt status and PuCl_3 properties during pyroprocessing and will also contribute to evaluating other salt systems with more components. Also, the properties of PuCl_3 with a full range of composition may benefit the safeguards of pyroprocessing of detecting the concentration of PuCl_3 in the electrorefining batch.

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Figure 1. Calculated LiCl-KCl phase diagram (solid lines)

Figure 2. Calculated LiCl-PuCl₃ phase diagram (solid lines)

Figure 3. Calculated KCl-PuCl₃ phase diagram (solid lines)

Figure 4. Calculated enthalpy of mixing for LiCl-KCl, LiCl-PuCl₃, KCl-PuCl₃, and LiCl-KCl-PuCl₃ ternary system with $x(\text{LiCl}):x(\text{KCl})=0.586:0.414$ at 1200 K

Figure 5. Comparison of apparent potential for PuCl_3 in LiCl-KCl eutectic

Figure 6. Calculated isothermal section of LiCl-KCl-PuCl_3 at 773 K

Figure 7. Calculated liquidus projection for LiCl-KCl-PuCl_3 system

Figure 8. Calculated liquidus projection for LiCl-KCl-PuCl_3 system at 723, 773, and 823 K

Figure 9. Calculated solubility of PuCl_3 in LiCl-KCl eutectic and the fitting curve

Figure 10. Calculated Gibbs energy of formation of PuCl_3 in LiCl-KCl eutectic at 723, 773, and 823 K

Table 1. Gibbs energy database input for the LiCl-KCl-PuCl₃ system

Parameters	Functions	Reference
Liquid	${}^0G_{Li:Cl}^{Liq.} = -395043.11 - 16.124629T - 4.0793198T \ln(T) - 0.071486773T^2$ $+1.4175712 \times 10^{-5}T^3 - 394814T^{-1}$, 298.15 K < T < 883 K $= -417132.497 + 421.76137T - 73.3062T \ln(T)$ $+0.004715055T^2 - 16535T^{-1}$, 883 K < T < 2000 K	[10]
	${}^0G_{K:Cl}^{Liq.} = -427035.9 + 247.546026T - 52.801T \ln(T) + 0.93665 \times 10^{-3}T^2$ $-2.409027 \times 10^{-6}T^3 + 97730T^{-1}$, 298.15 K < T < 750 K $-648588.535 + 3031.321656T - 469.507T \ln(T) + 350.0937 \times 10^{-3}T^2$ $-57.429763 \times 10^{-6}T^3 + 22222816T^{-1}$, 750 K < T < 1045 K $-443361.737 + 404.765951T - 73.3994T \ln(T)$, 1045 K < T < 2000 K	[10]
	${}^0G_{Pu:Cl}^{Liq.} = -1037967.35 + 479.21511T - 94.12701T \ln(T) - 0.0135962T^2$ $-6.25 \times 10^{-10}T^3 - 28380T^{-1} + 63579 - 61.5653437T$, 298.15 K < T < 1033 K $-1064596.34 + 766.881722T - 133.888T \ln(T) + 63597$ $-61.5653437T$, 1033 K < T < 1500 K	[39]
	${}^0G_{K_3PuCl_6}^{Liq.} = 3{}^0G_{KCl}^{Liq.} + {}^0G_{PuCl_3}^{Liq.} - 6700 - 66.7T$	[40]
Solid	${}^0G_{Li:Cl}^S = 423060.237 + 246.636632T - 44.7048T \ln(T) - 0.0089638T^2$ $-3.1058 \times 10^{-7}T^3 + 97229T^{-1}$, 289.15 K < T < 883 K $= 490131.802 + 821.73726T - 124.44483T \ln(T) + 0.025420461T^2$ $-1.523016 \times 10^{-6}T^3 + 9722242T^{-1}$, 883 K < T < 2000 K	[10]
	${}^0G_{K:Cl}^S = -452489.937 + 263.149637T - 51.2948T \ln(T) - 1.40523 \times 10^{-3}$ $-1731001 \times 10^{-6}T^3 + 76732T^{-1}$, 298.15 K < T < 700 K $-487176.143 + 762.308381T - 127.7773T \ln(T)$ $+72.96818 \times 10^{-3}T^2 - 15.190909 \times 10^{-6}T^3 + 3002008T^{-1}$, 700 K < T < 800 K $-729641.417 + 3635.724945T - 553.3953T \ln(T)$ $+406.611005 \times 10^{-3}T^2 - 63.587069 \times 10^{-6}T^3$ $+28867854T^{-1}$, 800 K < T < 1045 K $-9292757.859 + 83732.64789T - 11945.8623451T \ln(T)$ $+7098.951923 \times 10^{-3}T^2 - 795.735427 \times 10^{-6}T^3$ $+1229243789T^{-1}$, 1045 K < T < 1100 K $-469544.033 + 429.820456 - 73.3994T \ln(T)$, 1100 K < T < 2000 K	[10]

${}^0G_{PuCl_3}^s$	$-1.37967.35 + 479.21511T - 94.12701T \ln(T) - 0.0135862T^2$ $-6.25 \times 10^{-10}T^3 - 28380T^{-1}, 298.15 \text{ K} < T < 1033 \text{ K}$ $-1064596.34 + 766.881722T - 133.888T \ln(T), 1033 \text{ K} < T < 1500 \text{ K}$	[39]
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Table 2. Optimized parameters for the LiCl-KCl-PuCl₃ system

Phase	Parameters
Solid	${}^0L_{Li^+,K^+:Cl^-} = 17467.15$ ${}^0G_{K_2PuCl_5}^s = 2{}^0G_{KCl}^s + {}^0G_{PuCl_3}^s - 48155.48 - 23.92T$ ${}^0G_{K_3PuCl_6}^s = 3{}^0G_{KCl}^s + {}^0G_{PuCl_3}^s - 21250.17 - 78.80T$
Liquid	${}^0L_{Li^+,K^+:Cl^-} = -17523.74$ ${}^0L_{Pu^{3+},Li^+:Cl^-} = -41287.45 + 29.33T$ ${}^1L_{Pu^{3+},Li^+:Cl^-} = 4617.38 - 6.59T$ ${}^0L_{K^+,Pu^{3+}:Cl^-} = -125404.78 + 40.40T$ ${}^1L_{K^+,Pu^{3+}:Cl^-} = -18196.78$ ${}^0L_{K^+:Cl^-,K_3PuCl_6} = -37469.98$ ${}^0L_{Pu^{3+}:Cl^-,K_3PuCl_6} = -107125.88$ ${}^0L_{Li^+,K^+,Pu^{3+}:Cl^-} = -316741.85$ ${}^1L_{Li^+,K^+,Pu^{3+}:Cl^-} = 5046.88$ ${}^2L_{Li^+,K^+,Pu^{3+}:Cl^-} = 61450.10$

Table 3. Comparison of apparent potential for PuCl₃ in LiCl-KCl eutectic

Apparent potential/V vs. Cl ₂ /Cl ⁻	Temperature/K	Reference
$E_{PuCl_3}^{ap} = -3.3187 + 7.044 \times 10^{-4} T$	673-773	[26]
$E_{PuCl_3}^{ap} = -3.2950 + 6.594 \times 10^{-4} T$	673-773	[28]
$E_{PuCl_3}^{ap} = -3.2904 + 7.500 \times 10^{-4} T$	723-823	[29]
$E_{PuCl_3}^{ap} = -3.2980 + 7.600 \times 10^{-4} T$	723-823	[30]
$E_{PuCl_3}^{ap} = -3.3048 + 6.910 \times 10^{-4} T$	733-823	[31]
$E_{PuCl_3}^{ap} = -3.3048 + 6.910 \times 10^{-4} T$	733-823	[34]
$E_{PuCl_3}^{ap} = -3.4727 + 7.058 \times 10^{-4} T$	673-823	Present work

Table 4. Phase reactions in LiCl-KCl-PuCl₃ system

Phase reaction	Reaction type	Composition of liquid		T/K	Reference
		x_{LiCl}	x_{PuCl_3}		
Binary					
Liquid $\rightleftharpoons$ LiCl + KCl	Eutectic	0.586	-	626	This work
		0.585±0.003	-	628±3	[10, 20-23]
Liquid $\rightleftharpoons$ LiCl + PuCl ₃	Eutectic	-	0.268	731	This work
		-	0.28	734	[25]
Liquid $\rightleftharpoons$ KCl + K ₃ PuCl ₆	Eutectic	-	0.161	895	This work
		-	0.17	894	[15]
Liquid $\rightleftharpoons$ K ₃ PuCl ₆	Congruent	-	0.250	958	This work
		-	0.250	958	[15]
Liquid + K ₃ PuCl ₆ $\rightleftharpoons$ K ₂ PuCl ₅	Peritectic	-	0.350	884	This work
		-	0.35	884	[15]
Liquid $\rightleftharpoons$ PuCl ₃ + K ₂ PuCl ₅	Eutectic	-	0.564	759	This work
		-	0.57	759	[15]
Ternary					
Liquid $\rightleftharpoons$ LiCl + KCl + K ₃ PuCl ₆	Eutectic	0.350	0.089	589	This work
Liquid + K ₂ PuCl ₅ $\rightleftharpoons$ K ₃ PuCl ₆ + LiCl	Quasi-peritectic	0.338	0.155	658	This work
Liquid $\rightleftharpoons$ LiCl + PuCl ₃ + K ₂ PuCl ₅	Eutectic	0.279	0.359	616	This work
Liquid $\rightleftharpoons$ LiCl + K ₂ PuCl ₅	Eutectic	0.324	0.225	690	This work

Table 5. Partial enthalpies at infinite dilution at 1200 K

i	j	$\Delta \bar{H}_{i(j)}^{\infty}$ (kJ/mol)	$\Delta \bar{H}_{j(i)}^{\infty}$ (kJ/mol)
LiCl	KCl	-15.33	-15.77
LiCl	PuCl ₃	-40.48	-33.84

KCl	PuCl ₃	-99.66	-53.86
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Table 6. Mole fraction of PuCl₃ at the squares and circles in Figure 8

	723 K	773 K	823 K
Squares	0.043	0.076	0.137
Circles	0.382	0.415	0.460

References

- [1] M. Misra, K.S. Raja, A.V. Jaques, and S. Baral. "Effect of Addition of Multi-Component Lanthanides to LiCl-KCl Eutectic on Thermal and Electrochemical Properties." *ECS Transactions* 33.7 (2010): 351-360.
- [2] M. Li, Q. Gu, W. Han, X. Zhang, Y. Sun, M. Zhang and Y. Yan. "Electrochemical behavior of La (III) on liquid Bi electrode in LiCl-KCl melts.-Determination of thermodynamic properties of La-Bi and Li-Bi intermetallic compounds." *RSC Advances* (2015).
- [3] Y. Wang, M. Li, W. Han, M. Zhang, Y. Yang, Y. Sun, Y. Zhao and Y. Yan. "Electrochemical extraction and separation of praseodymium and erbium on reactive magnesium electrode in molten salts." *Journal of Solid State Electrochemistry* (2015): 1-10.
- [4] T. Koyama, M. Iizuka, Y. Shoji, R. Fujita, H. Tanaka, T. Kobayashi and M. Tokiwai. "An experimental study of molten salt electrorefining of uranium using solid iron cathode and liquid cadmium cathode for development of pyrometallurgical reprocessing." *Journal of nuclear science and technology* 34.4 (1997): 384-393.
- [5] W. Zhou and J. Zhang. "Direct Calculation of Concentration-Dependent Activity Coefficient of UCl_3 in Molten LiCl-KCl." *Journal of The Electrochemical Society* 162.10 (2015): E199-E204.
- [6] W. Zhou and J. Zhang. "Chemical diffusion coefficient calculation of U^{3+} in LiCl-KCl molten salt." *Progress in Nuclear Energy* 91 (2016): 170-174.
- [7] Y. Wang, W. Zhou and J. Zhang. "Investigation of concentration-dependence of thermodynamic properties of lanthanum, yttrium, scandium and terbium in eutectic LiCl-KCl molten salt." *Journal of Nuclear Materials* 478 (2016): 61-73.
- [8] M. He, G. Lu, Z. Kang and Y. Zhang. "Thermodynamic assessment of the LiCl-KCl-CeCl₃ system." *Calphad* 49 (2015): 1-7.
- [9] T. Shujian, L. Qingfan, L. Shixiang and Z. Chaogui. "Phase diagram of the ternary system CeCl₃-KCl-LiCl." *Journal of alloys and compounds* 274.1 (1998): 142-147.
- [10] S. Ghosh, B.P. Reddy, K. Nagarajan and K.H. Kumar. "Experimental investigations and thermodynamic modelling of KCl-LiCl- UCl_3 system." *Calphad* 45 (2014): 11-26.
- [11] H.L. Lukas, S.G. Fries and B. Sundman. *Computational thermodynamics: the Calphad method*. Vol. 131. Cambridge: Cambridge university press, 2007.
- [12] U.R. Kattner. "The thermodynamic modeling of multicomponent phase equilibria." *JOM* 49.12 (1997): 14-19.
- [13] M. Hillert, B. Jansson, B. Sundman. "A two-sublattice model for molten solutions with different tendency for ionization." *Metallurgical Transactions A* 16.1 (1985): 261-266.
- [14] B. Sundman. "Modification of the two-sublattice model for liquids." *Calphad* 15.2 (1991): 109-119.
- [15] R. Benz, M. Kahn and J.A. Leary. "Phase Equilibria of the Binary System PuCl_3 -KCl." *The Journal of Physical Chemistry* 63.11 (1959): 1983-1984.

-
- [16] V.Y. Buz'ko, G.Y. Chuiko and K.B. Kushkhov. "DFT study of the structure and stability of Pu (III) and Pu (IV) chloro complexes." *Russian Journal of Inorganic Chemistry* 57.1 (2012): 62-67.
- [17] Y. M. Muggianu, M. Gambino, J. P. Bros, Enthalpies of formation of liquid alloys, *J. Chim. Phys.*, 72 (1975): 83–88
- [18] O. Redlich and A.T. Kister. "Algebraic representation of thermodynamic properties and the classification of solutions." *Industrial & Engineering Chemistry* 40.2 (1948): 345-348.
- [19] H. Kopp. "Investigations of the specific heat of solid bodies." *Philosophical Transactions of the Royal Society of London* (1865): 71-202.
- [20] T.W. Richards and W.B. Meldrum. "THE MELTING POINTS OF THE CHLORIDES OF LITHIUM, RUBIDIUM AND CAESIUM, AND THE FREEZING POINTS OF BINARY AND TERNARY MIXTURES OF THESE SALTS, INCLUDING ALSO POTASSIUM AND SODIUM CHLORIDE." *Journal of the American Chemical Society* 39.9 (1917): 1816-1828.
- [21] E. Aukrust, B. Björge, H. Flood and T. Førland. "ACTIVITIES IN MOLTEN SALT MIXTURES OF POTASSIUM-LITHIUM-HALIDE MIXTURES: A PRELIMINARY REPORT." *Annals of the New York Academy of Sciences* 79.11 (1960): 830-837.
- [22] E. Korin and L. Soifer. "Thermal analysis of the system KCl-LiCl by differential scanning calorimetry." *Journal of thermal analysis* 50.3 (1997): 347-354.
- [23] A.S. Basin, A.B. Kaplun, A.B. Meshalkin and N.F. Uvarov. "The LiCl-KCl binary system." *Russian Journal of Inorganic Chemistry* 53.9 (2008): 1509-1511.
- [24] L.S. Hersh and O.J. Kleppa. "Enthalpies of mixing in some binary liquid halide mixtures." *The Journal of Chemical Physics* 42.4 (1965): 1309-1322.
- [25] C.W. Bjorklund, J.G. Reavis, J.A. Leary and K.A. Walsh. "Phase Equilibria in the Binary Systems PuCl₃-NaCl and PuCl₃-LiCl." *The Journal of Physical Chemistry* 63.10 (1959): 1774-1777.
- [26] J.J. Roy, L.F. Grantham, D.L. Grimmer, S.P. Fusselman, C.L. Krueger, T.S. Storvick, T. Inoue, Y. Sakamura and N. Takahashi. "Thermodynamic Properties of U, Np, Pu, and Am in Molten LiCl-KCl Eutectic and Liquid Cadmium." *Journal of the Electrochemical Society* 143.8 (1996): 2487-2492.
- [27] Y. Sakamura, T. Hijikata, K. Kinoshita, T. Inoue, T.S. Storvick, C.L. Krueger, J.J. Roy, D.L. Grimmer, S.P. Fusselman and R.L. Gay. "Measurement of standard potentials of actinides (U, Np, Pu, Am) in LiCl-KCl eutectic salt and separation of actinides from rare earths by electrorefining." *Journal of alloys and compounds* 271 (1998): 592-596.
- [28] Y. Sakamura, O. Shirai, T. Iwai and Y. Suzuki. "Distribution behavior of plutonium and americium in LiCl-KCl eutectic/liquid cadmium systems." *Journal of Alloys and Compounds* 321.1 (2001): 76-83.
- [29] O. Shirai, M. IIZUKA, T. IWAI and Y. ARAI. "Electrode reaction of Pu³⁺/Pu couple in LiCl-KCl eutectic melts: comparison of the electrode reaction at the surface of liquid Bi with that at a solid Mo electrode." *Analytical sciences* 17.1 (2001): 51-57.

-
- [30] O. Shirai, H. Yamana and Y. Arai. "Electrochemical behavior of actinides and actinide nitrides in LiCl–KCl eutectic melts." *Journal of alloys and compounds* 408 (2006): 1267-1273.
- [31] J. Serp, R.J.M. Konings, R. Malmbeck, J. Rebizant, C. Scheppeler and J.P. Glatz. "Electrochemical behaviour of plutonium ion in LiCl–KCl eutectic melts." *Journal of Electroanalytical Chemistry* 561 (2004): 143-148.
- [32] R.J. Lemire. *Chemical thermodynamics of neptunium and plutonium*. Vol. 4. Elsevier, 2001.
- [33] R.J.M. Konings. "The ITU Material Property Data Base for f-elements and compounds, f-MPD, Available from <http://www.f-elements.net> (2002).
- [34] P. Masset, R.J. Konings, R. Malmbeck, J. Serp and J.P. Glatz. "Thermochemical properties of lanthanides (Ln= La, Nd) and actinides (An=U, Np, Pu, Am) in the molten LiCl–KCl eutectic." *Journal of Nuclear Materials* 344.1 (2005): 173-179.
- [35] J.O. Andersson, T. Helander, L. Höglund, P. Shi and B. Sundman. "Thermo-Calc & DICTRA, computational tools for materials science." *Calphad* 26.2 (2002): 273-312.
- [36] Mallett, J. J., et al. "Underpotential codeposition of Cu–Au alloys." *Electrochemical and solid-state letters* 12.8 (2009): D57-D60.
- [37] Alkire, R. C., Philip N. Bartlett, and Jacek Lipkowski. "Electrochemical engineering across scales: from molecules to processes." *Advances in electrochemical science and engineering* 15 (2015), p.86-87.
- [38] J. Zhang. "Kinetic model for electrowinning, part II: Model applications and case studies." *Progress in Nuclear Energy* 70 (2014): 287-297.
- [39] Thermo-Calc Software Database SSUB5, (Accessed 3/20/2016)
- [40] R. Benz. "Thermodynamic properties of the system PuCl₃-KCl", Dissertation, The University of New Mexico, 1958.