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Thermodynamic optimization of the NaCl–PrCl$_3$ system and the LiCl–NaCl–PrCl$_3$ system

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ABSTRACT

The NaCl–PrCl$_3$ system and the LiCl–NaCl–PrCl$_3$ system were critically optimized using the CALPHAD technique. The liquid phase was described by a two-sublattice model (Li$^+$, Na$^+$)$_p$(Cl$^-$, PrCl$_6^{3-}$, PrCl$_3$)$_q$. The end-member-based compounds NaCl and LiCl with the same NaCl-type structure were treated as one phase and described by a two-sublattice model (Li, Na)Cl. The end-member PrCl$_3$ was treated as stochiometric compound. On the basis of experimental phase diagram and thermodynamic data, the phase diagram and the mixing enthalpy of liquid at 1122 K in the NaCl–PrCl$_3$ system and six vertical sections in the LiCl–NaCl–PrCl$_3$ system were optimized using Thermo-Calc software, and a set of self-consistent thermodynamic parameters of the LiCl–NaCl–PrCl$_3$ system was obtained.

1. Introduction

Molten salt electrolysis is widely used for the production of rare earth metals and their alloys. Molten salts are being considered for use as fluid targets in the nuclear incineration of transuranium elements with proton accelerators [1]. The phase diagrams of rare-earth metal halides in combination with alkali or alkali-earth metal halide systems are of prime importance when considering those salt systems for possible use in this reprocessing application; specifically, the temperature and liquid composition at the eutectic reaction need to be known [2].

This work aims to optimize the phase diagram and thermodynamic properties of the NaCl–PrCl$_3$ system and the LiCl–NaCl–PrCl$_3$ system.

2. Literature review

2.1. LiCl–NaCl system

In the LiCl–NaCl system, some researchers [3–11] reported the presence of an eutectic reaction and intermediate compounds, while some other researchers [12–14] reported it as an isomorphous system with a minimum on the liquidus. Due to the existence of the contradiction in experimental data obtained by different researchers, Tian et al. [15] reexamined this binary system by means of XRD and came to a conclusion that it was an isomorphous system with a minimum on the liquidus. The optimizing results in the SGTE (Scientific Group Thermochemistry Europe) database [16] were right consistent with the experimental data of Tian et al. [15]. So, the thermodynamic parameters of the binary LiCl–NaCl system [16] were accepted in the present work, and Fig. 1 shows the calculated LiCl–NaCl phase diagram.

2.2. LiCl–PrCl$_3$ system

On the basis of the experimental phase diagram [11,17] and the enthalpies of mixing in the liquid [18], Gong et al. [19] optimized the LiCl–PrCl$_3$ system. Fig. 2 shows the calculated LiCl–PrCl$_3$ phase diagram using the thermodynamic parameters [19].

2.3. NaCl–PrCl$_3$ system

The NaCl–PrCl$_3$ phase diagram was reported to be a simple eutectic system [20–22], while Hattori et al. [23] found a compound 3PrCl$_3$·NaCl. Qiao et al. [11] reexamined the NaCl–PrCl$_3$ system by means of DTA, and found that it was a simple eutectic one with an eutectic point of 751 K at 38 at% PrCl$_3$.

Gaune-Escard et al. [24] measured the enthalpies of mixing of liquid at 1122 K in the NaCl–PrCl$_3$ system using a Calvet-type high-temperature microcalorimeter. Calibration of the calorimeter was performed with NIST-alumina, and known amounts of alumina were dropped directly into the melt. The surface of the thermograms was automatically integrated by a computer.

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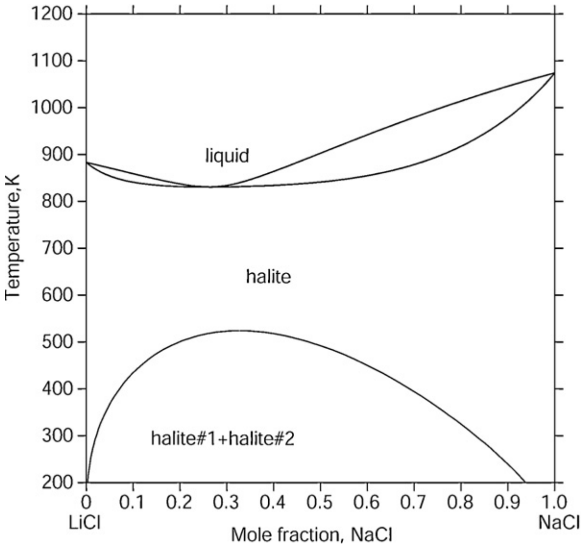

Fig. 1. Calculated LiCl–NaCl phase diagram using the thermodynamic parameters from Ref. [16].

2.4. LiCl–NaCl–$PrCl_3$ system

Qiao et al. [11] investigated the LiCl–NaCl–$PrCl_3$ system using DTA method, and six vertical sections and one liquidus surface projection were reported. No ternary compound was found.

2.5. Thermodynamic model

The Gibbs energy function $G_i^{\phi}(T) = {}^0G_i^{\phi}(T) - H_i^{SER}$ (298.15 K) of the end-member component i (i = LiCl, NaCl, $PrCl_3$) was described by an equation of the following form:

$$G_i^{\phi}(T) = a + bT + cT \ \ln T + dT^2 + eT^3 + fT^{-1} + gT^7 + hT^{-9} \tag{1}$$

In the present work, the Gibbs energy functions for pure LiCl and NaCl were from the SGTE database compiled by Dinsdale [16], and the Gibbs energy functions for pure $PrCl_3$ were from the optimizing results of Gong et al. [19].

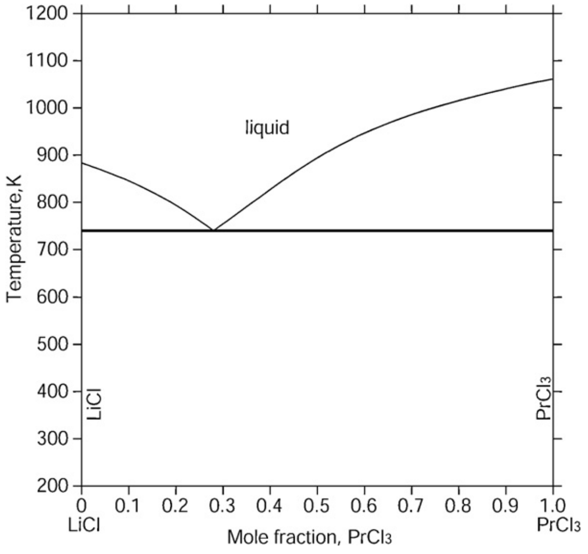

Fig. 2. Calculated LiCl–$PrCl_3$ phase diagram using the thermodynamic parameters from Ref. [19].

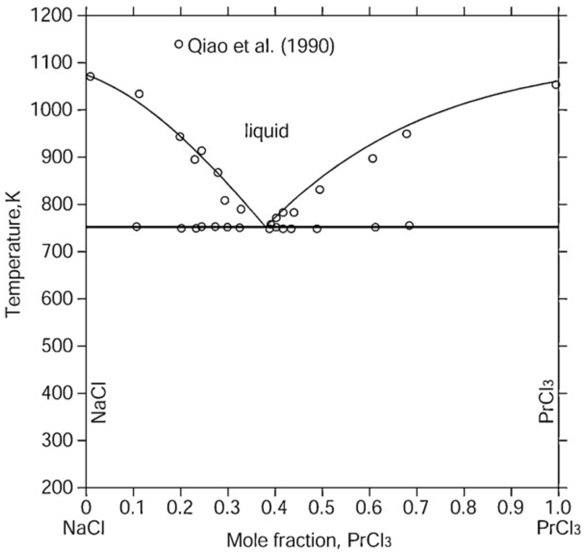

Fig. 3. Calculated NaCl–$PrCl_3$ phase diagram using the present thermodynamic description and comparison with experimental data from Ref. [11].

The liquid phase was described by a two-sublattice solution model [25] $(Li^+, Na^+)_p(Cl^-, {PrCl_6}^{3-}, PrCl_3)_q$ with ${PrCl_6}^{3-}$ cluster included in the anionic site, which was consistent with the model of liquid in the LiCl–$PrCl_3$ system used in Ref. [19].

In this description, p and q were the number of cation and anion sites, respectively, which varied with the composition:

$$p = \sum y_i(-\gamma_i) = y_{Cl^-} + 3y_{{PrCl_6}^{3-}} \tag{2}$$

$$q = \sum y_j\gamma_j = y_{Na^+} + y_{Li^+} \tag{3}$$

where y_i and γ_i, y_j and γ_j, represented the site fraction and charges of anion i and cation j, respectively. The Gibbs energy for liquid was expressed by the following equation:

$$\begin{aligned} G_m^{\text{liquid}} = {} & y_{Li^+}y_{Cl^-}G_{Li^+:Cl^-}^{\text{liquid}} + y_{Na^+}y_{Cl^-}G_{Na^+:Cl^-}^{\text{liquid}} \\ & + y_{Li^+}y_{{PrCl_6}^{3-}}G_{Li^+:{PrCl_6}^{3-}}^{\text{liquid}} y_{Na^+}y_{{PrCl_6}^{3-}}G_{Na^+:{PrCl_6}^{3-}}^{\text{liquid}} \\ & + y_{PrCl_3}G_{PrCl_3}^{\text{liquid}} + qRT(y_{Cl^-}\ \ln y_{Cl^-} + y_{{PrCl_6}^{3-}}\ \ln y_{{PrCl_6}^{3-}} \\ & + y_{PrCl_3}\ \ln y_{PrCl_3}) + pRT(y_{Li^+}\ \ln y_{Li^+} + y_{Na^+}\ \ln y_{Na^+}) + {}^{E}G_m \end{aligned} \tag{4}$$

where $G_{Li^+:Cl^-}^{\text{liquid}}$ and $G_{Na^+:Cl^-}^{\text{liquid}}$ were the Gibbs energies of pure LiCl and NaCl in liquid state, which were selected from the SGTE database [16]. $G_{PrCl_3}^{\text{liquid}}$ was the Gibbs energy of liquid $PrCl_3$, and was from Ref. [19]. $G_{Li^+:{PrCl_6}^{3-}}^{\text{liquid}}$ and $G_{Na^+:{PrCl_6}^{3-}}^{\text{liquid}}$ were the Gibbs energy of the associated Li_3PrCl_6 and Na_3PrCl_6 in liquid state. $G_{Li^+:{PrCl_6}^{3-}}^{\text{liquid}}$ was from Ref. [19], and $G_{Na^+:{PrCl_6}^{3-}}^{\text{liquid}}$ was optimized in the present work according to the experimental data [24]. The Gibbs energy of Na_3PrCl_6 was expressed as follows in Joule per mole:

$$G_{Na^+:{PrCl_6}^{3-}}^{\text{liquid}} = 3G_{Na^+:Cl^-}^{\text{liquid}} + G_{PrCl_3}^{\text{liquid}} + a + bT \tag{5}$$

where a and b were the parameters to be optimized.

The compounds LiCl and NaCl had the same NaCl-type structure, and were treated as one phase “halite” with the formula (Li, Na)Cl in Ref. [16].

Since the mutual solubility between LiCl and $PrCl_3$, and NaCl and $PrCl_3$ was very limited, $PrCl_3$ was treated as stochiometric compound.