Thermodynamic Database Development for the NaCl-UCl_3-UCl_4 System

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1. Introduction

Recent interest in Molten Salt Reactor (MSR) triggers a wide range of thermochemistry research for the fluoride and chloride salt systems. In particular, the chloride system of the NaCl-$MgCl_2$-UCl_3-UCl_4 will be the key salt system for chloride based MSR process. For the investigation on the stable operation condition and possible safety risk of MSR, the phase diagram information and thermodynamic properties such as vapor pressure of U containing gas species, heat capacity of liquid and solid salts and melting enthalpy depending on the chemical composition of salt are essential. Since the experimental determination of such key thermochemical information is costly and time-consuming, thermodynamic database based on CALculation of PHAse Diagram (CAPHAD) type assessment is widely accepted in nuclear research in these days for providing such information.

As a part of a long-term research project to construct the comprehensive thermodynamic database of multicomponent chloride salt system for MSR, the thermodynamic optimization of the NaCl-UCl_3-UCl_4 system was conducted based on the critical review of all the available thermodynamic and phase diagram data. The optimized thermodynamic database can be used to calculate the distribution of U^{3+} and U^{4+} in molten salt depending on oxygen partial pressure. The calculation results can be used to estimate the possible oxidation trend of molten salts in MSR operation condition. All the thermodynamic calculations in this study were performed using the FactSage thermodynamic software [1,2].

2. Thermodynamic Optimization

In this section, overview of the thermodynamic optimization process and the results of the thermodynamic assessments for binary NaCl-UCl_3 and NaCl-UCl_4 system are described.

2.1 Thermodynamic Models

Liquid salt solution was described by the Modified Quasichemical Model (MQM) [3] which takes into account the short-range ordering of the second-nearest neighbors of cations in liquid chloride solution. For example, the following pair exchange reaction can be assumed in the NaCl-UCl_4 solution:

$(Na^+\text{-}Na^+) + (U^{4+}\text{-}U^{4+}) = 2(Na^+\text{-}U^{4+})$: $\Delta g_{Na\text{-}U(IV)}$

where (i-j) represents the pair of i and j cations which contains Cl^- in between. $\Delta g_{Na\text{-}U(IV)}$ is the pair exchange reaction energy being expressed as function of temperature and composition (chemical pair fraction), and it is the main model parameter of the MQM. Then, the Gibbs energy of solution can be expressed by:

$$G^{soln} = \left(n_{NaCl} g^o_{NaCl(l)} + n_{UCl_4} g^o_{UCl_4(l)}\right) - TS^{conf} + \frac{n_{Na-U(IV)}}{2}\Delta g_{Na-U(IV)}$$

where S^{conf} is configuration entropy being changed depending on $\Delta g_{Na\text{-}U(IV)}$. $\Delta g_{Na\text{-}U(IV)}$ is optimized to reproduce all phase diagram and thermodynamic property related to liquid solution.

The Gibbs energy of all stoichiometric solid and liquid compounds can be expressed using the standard Gibbs energy formula including standard enthalpy and entropy at 298 K and heat capacity.

2.2 NaCl-UCl_3 system

Thermodynamic optimization of the NaCl-UCl_3 system was carried out by Benes and Konings [4], and the calculated phase diagram of this system is presented in Fig.1. There is no intermediate compound. As the optimization results from the previous study is accurate enough, so those thermodynamic parameters were taken in this study without any modification.

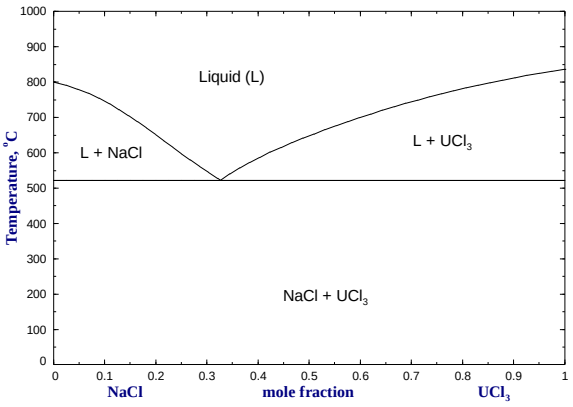

Fig. 1. Calculated phase diagram of the NaCl-UCl_3 using the optimized parameters by Benes and Konings [4].

2.2 NaCl-UCl_4 system

Fig. 2 shows the preliminary thermodynamic optimization results for the NaCl-UCl_4 system. Kuroda and Suzuki[5] and Thoma et al.[6] determined the phase diagram using the thermal analysis method. While Thoma et al. determined the congruent melting of Na_2UCl_5, Kuroda and Suzuki et al. claimed the peritectic melting of Na_2UCl_5. In the present thermodynamic modeling of this system, the phase diagram and thermodynamic property data such as standard formation enthalpy and melting enthalpy of Na_2UCl_5 were considered simultaneously. As can be seen in Fig. 2, the peritectic melting of Na_2UCl_5 was reproduced. However, it is very difficult to reproduce the liquidus of NaCl near Na_2UCl_5 composition. The liquidus of this composition should be re-examined in future. The experimental formation and melting enthalpy values of Na_2UCl_5 were well reproduced in this study.

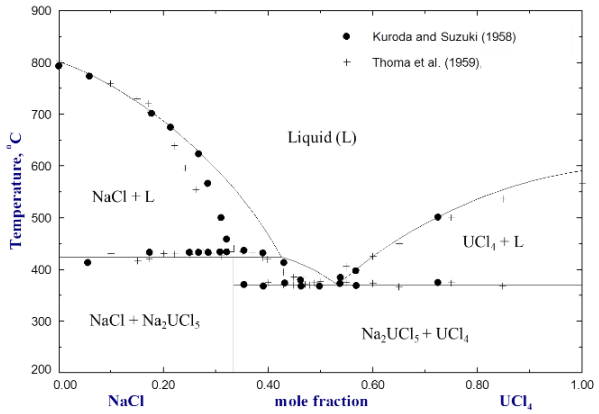

Fig. 2. Calculated phase diagram of the NaCl-UCl_4 using the optimized parameters in this study.

2.3 NaCl- UCl_3-UCl_4 system

The database for the ternary NaCl-UCl_3-UCl_4 system was constructed by integrating binary NaCl-UCl_3, NaCl-UCl_4 and UCl_3-UCl_4 systems, and no ternary compound was considered.

3. Conclusions

Preliminary thermodynamic database for the NaCl-UCl_3-UCl_4 system was constructed based on the critical evaluation and optimization of all available phase diagram and thermodynamic property data in literature. Newly constructed database can be utilized to calculate the phase diagram and thermodynamic properties such as heat capacity, melting enthalpy and equilibrium vapor pressure change of U containing gas species depending on the composition of salts at any given temperature.

The equilibrium vapor pressures of UCl_3 and UCl_4 were calculate in the NaCl-UCl_3-UCl_4 system at MSR operation condition. It is found that internal oxidation of UCl_3 to UCl_4 in liquid salt can significantly influence to the vapor pressure of UCl_4, so the special care should be necessary to keep reducing condition in MSR operation.

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