Prediction of Thermodynamic Property and Phase Diagram of the NaI-UI_3 System

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1. Introduction

With the growing interest in molten salt reactor (MSR), extensive research is being conducted on the thermodynamic properties of salt systems. In MSR operation, the nuclear fuel is mixed with base salt. Fission products can be produced during the MSR operation. The accumulation of fission products can change the physical and chemical properties of fuel salts, such as melting point of molten salt and vaporing species. Iodine is one of the fission products generated after nuclear reactions. As it is a long-lasting substance, iodine can be accumulated in molten salt. Iodine is also more concerned than other nuclear fission products because of its toxicity to humans. Despite the importance of iodides in MSR process, there is a lack of experimental data even for simple iodide salt systems. To overcome this experimental challenge, accurate prediction of thermodynamic properties and phase diagrams containing iodide systems is necessary.

Phase diagrams and thermodynamic properties of salt system can be well predicted by the CALPHAD type thermodynamic database. The key of CALculation of PHAse Diagram (CALPHAD) method is the optimization of thermodynamic functions of phases in the given system, based on the critical evaluation of available thermodynamic and phase diagram data of low order systems. Thermodynamic models with optimized parameters can be used to predict the phase diagram and thermodynamic properties of unexplored systems.

In the present study, we have developed thermodynamic database for the salt systems containing iodides using the systematic analysis of energetics in cationic interactions in molten salts. All thermodynamic calculations were performed by the FactSage thermodynamic software [1,2].

2. Methods and Results

2.1 Solution theory for liquid salts

Several theories have been developed for liquid salt solutions to correlate enthalpy of mixing with other physical properties. Reiss et al. [3] derived a simple model to calculate the enthalpy of mixing of ionic solution using an ionic parameter that is calculated by cation radii of constituent ionic species in liquid solution. The model was improved by Davis [4], which can be applied to a wider range of salt solutions. In Davis's approach, the enthalpy of mixing in dilute solution, which can be referred to the partial enthalpy of mixing, is determined by ionic parameter.

In this study, a new prediction method for the Gibbs energy of molten salts containing iodides was developed based on solution theory by Davis.

2.2 Thermodynamic model for liquid salts

The Gibbs energy of solid and liquid stoichiometric phase can be expressed by the standard enthalpy of formation and entropy at 298 K and heat capacity.

In the present study, liquid solutions are described by the Modified Quasichemical Model (MQM) [5], which has been widely used for molten salt solutions. For the iodide solution (that is, iodine is a common anion in ionic liquid solution), the MQM considers the short-range ordering of the second-nearest neighbor cations in liquid solution. In the NaI-UI_3 iodide salt solution, for example, the following pair exchange reaction can be considered in MQM:

$$(A-A)+(B-B)=2\,(A-B),\ \ \Delta g_{AB} \qquad (1)$$

where A and B refers Na^+ and U^{3+}, respectively, and A-B represents the pair of A and B cations sharing iodine anion in between. Δg_{AB} is the pair-exchange reaction energy, which is a function of temperature and pair fraction. This reaction energy is the model parameter of the MQM. Then the Gibbs energy of solution can be expressed by MQM as following:

$$G^{\text{soln}} = n_A g_A^{\circ} + n_B g_B^{\circ} - T\Delta S^{\text{config}} + \frac{n_{AB}}{2}\Delta g_{AB} \quad (2)$$

where n_i and g_i° are the number of mole and Gibbs energy of i species (such as liquid NaI and UI_3), respectively. ΔS^{config} refers the configuration entropy of mixing, which is given by distribution of pairs in the solution, and n_{AB} is the number of (A-B) pairs in solution. Here, Δg_{AB} can influence to the Gibbs energy of solution and this model parameter should be determined based on available thermodynamic property and phase diagram data. If such data is unavailable, a certain prediction method is necessary to properly determine the parameter.

2.3 Prediction of the thermodynamic property and phase diagram of the NaI-UI_3 system

In spite of its importance in MSR operation, no thermodynamic property and phase diagram have been investigated for the NaI-UI_3 system.

Therefore, the enthalpy of mixing for the molten NaI-UI_3 solution was predicted using the systematic analysis of all available binary molten chloride, bromide, iodide systems based on Davis's approach [4]. Based on this analysis the partial enthalpy of molten NaI-UI_3 solution could be well predicted. Using this data, the MQM parameter (Δg_{AB}) for the liquid solution was determined in this study.

The predicted phase diagram of the NaI-UI_3 system in the present study is shown in Fig. 1. No thermodynamic studies were performed for the NaI-UI_3 system. In this study, neither ternary compound and solid solution of NaI and UI_3 was assumed. The predicted phase diagram of the NaI-UI_3 system shows that this system is a simple eutectic system. Usually, salt systems with Cl, Br, and I show similar phase diagrams. The NaCl-UCl_3 system, which has been well studied, is a simple eutectic system [6]. This result supports the prediction of the phase diagram of the NaI-UI_3 system in Fig. 1.

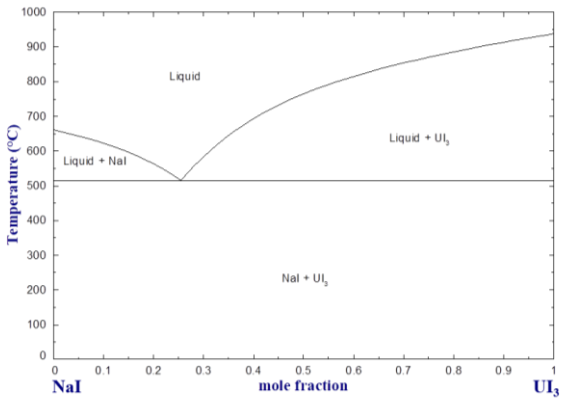

Fig. 1. Predicted phase diagram of the NaI-UI_3 in this study.

2.4 Other iodide salt systems and MSR applications

By employing the same methodology, we already modeled many key iodide salt systems for MSR operation and are constructing the thermodynamic database for the (Na, K, Mg, U) // (Cl, I) system. The constructed database will be used for the various applications of MSR operation prediction. For example, the possible vaporization of iodine species at any temperature and composition can be calculated using the database.

3. Summary

Based on the systematic energetic analysis of all available liquid salt solutions, a method to predict the enthalpy of mixing of liquid iodide solution was developed. This relationship was applied to predict the MQM parameter for the unknown binary iodide system. As an example, the phase diagram of the NaI-UI_3 system was predicted in the present study.

A self-consistent thermodynamic database for (Na, K, Mg, U) // (Cl, I) system is under construction in order to predict behavior of the nuclear fuel in MSR operation.

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