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Thermodynamic Modeling Progress of Uranium Chloride and Uranium Oxide Systems

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1. Introduction

Molten salt reactors (MSRs) employ liquid chloride salts as both coolant and fuel media, typically based on NaCl–KCl–UCl_3 systems. The thermodynamic stability of these multicomponent molten salts governs fuel solubility, redox chemistry, corrosion behavior, and fission product transport during reactor operation.

Under ideal operating conditions, the fuel salt is assumed to consist solely of chloride species in a controlled reducing environment. However, accidental ingress of oxygen, for example during leakage scenarios, may introduce oxide species into the system. Even trace levels of oxygen can significantly shift the redox equilibrium to higher oxidation states [1]. For uranium, U^{3+} may form higher oxidizing states (U^{4+}, U^{6+}), leading to the formation of UO_2, UO_3, and related oxide complexes. These transformations may alter phase equilibria, solubility limits, and precipitation behavior, thereby affecting reactor safety and long-term structural integrity.

Existing thermodynamic databases for chloride-based MSR systems are primarily optimized for halide chemistry, and the oxide subsystem remains insufficiently assessed. In particular, reliable thermodynamic descriptions of oxide-containing systems are essential for predicting oxide precipitation limits or phase stability.

Therefore, the objective of this study is to extend the existing NaCl–KCl–UCl_3 thermodynamic framework to oxide-containing systems using the CALPHAD methodology. The Modified Quasichemical Model (MQM) was adopted to describe ionic liquid interactions, and binary and reciprocal subsystems were systematically evaluated to construct a self-consistent thermodynamic chloride and oxide database. All thermodynamic calculations were performed by the FactSage thermodynamic software [2, 3].

2. Methods and Results

2.1 Thermodynamic model for liquid salts

The Gibbs energy of solid and liquid stoichiometric phases 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 UCl_4-UO_2 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 refer to Cl^- and O^{2-}, respectively, and A-B represents the pair of A and B anions sharing uranium cation 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:

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

where n_i and g_i^o denote the number of moles and standard Gibbs energy of *i* species (such as liquid UCl_4 and UO_2), 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.

2.2 Thermodynamic description of the U-Cl system

Previous thermodynamic assessments of chloride-based MSR systems have primarily focused on UCl_3 as the representative uranium species under reducing conditions. However, when oxygen or moisture ingress is considered, uranium may partially oxidize to higher valence states. In such cases, higher oxidation-state chlorides, such as UCl_4 and UCl_6, must be included to describe the molten salt system consistently.

In this study, the U-Cl binary system was expanded to represent UCl_4 and UCl_6 in addition to UCl_3. The thermodynamic descriptions were assessed to ensure the UCl_3-UCl_6 composition range. The resulting U-Cl phase relations show good agreement with previously reported data in the literature [4]. This expanded U-Cl framework provides a necessary thermodynamic foundation for analyzing redox shifts and phase stability in oxide-contaminated Na–K–U molten salt systems.

2.3 Thermodynamic description of the U-O system

The U-O binary system plays a central role in determining oxide stability under oxygen ingress conditions in MSR. The thermodynamic assessment reported by Chevalier and Fischer [5] was adopted to derive the Gibbs energy for U_2O_3(l) and UO_3(l) through inverse calculation from reported thermodynamic assessment data. Unlike previous Bragg-Williams based descriptions in their work, MQM liquid in the present study considers multiple oxide species simultaneously in the liquid phase. Slight Gibbs energy adjustments were necessary to maintain consistency with experimental phase boundaries. Fig. 1 shows the current modeling result of the U-O binary system.

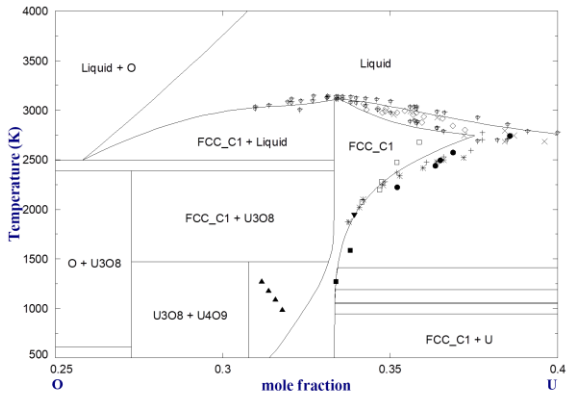

Fig. 1. Thermodynamic modeling result of the U-O binary system in this study.

2.4 Other chloride-oxide systems and applications in MSR operation

Thermodynamic modeling has been performed for several alkali metal chlorides and oxides. By integrating both chloride and oxide systems with thermodynamic modeling for MSR operations, the present database enables quantitative assessment of phase stability in chloride-based MSR fuel salts under oxygen ingress conditions. This integrated thermodynamic database enables quantitative prediction competitive stability between oxides and chlorides, and changes in uranium valence distribution.

3. Summary

In this study, a thermodynamic database combining uranium chloride and uranium oxide systems was developed for chloride-based MSR applications. The U-Cl system was expanded to include higher valence chlorides, ensuring redox consistency under oxidizing conditions. Also, the U-O binary system was reformulated with MQM to represent consistent coupling with chloride containing melts.

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

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