Thermodynamics of soluble fission products cesium and iodine in the Molten Salt Reactor
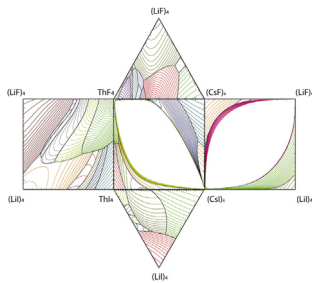
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GRAPHICAL ABSTRACT

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The present study describes the full thermodynamic assessment of the Li,Cs,Th//F,I system. The existing database for the relevant fluoride salts considered as fuel for the Molten Salt Reactor (MSR) has been extended with two key fission products, cesium and iodine. A complete evaluation of all the common-ion binary and ternary sub-systems of the LiF-ThF$_4$-CsF-LiI-ThI$_4$-CsI system has been performed and the optimized parameters are presented in this work. New equilibrium data have been measured using Differential Scanning Calorimetry and were used to assess the reciprocal ternary systems and confirm the extrapolated phase diagrams. The developed database significantly contributes to the understanding of the behaviour of cesium and iodine in the MSR, which strongly depends on their concentration and chemical form. Cesium bonded with fluorine is well retained in the fuel mixture while in the form of CsI the solubility of these elements is very limited. Finally, the influence of CsI and CsF on the physico-chemical properties of the fuel mixture was calculated as function of composition.

1. Introduction

The Molten Salt Reactor (MSR) is one of the promising reactor technologies considered for future nuclear energy development. Fissile and fertile materials are dissolved in a liquid molten salt mixture circulating in the primary circuit and serving both as fuel and as coolant for the fission reaction. Among the various design concepts, the focus in Europe is on the Molten Salt Fast Reactor (MSFR) [1,2] which exploits the advantages of a fast neutron spectrum. The reference salt for this concept is the binary LiF-ThF$_4$ eutectic mixture with addition of either UF$_4$ or PuF$_3$ [3] as fissile

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and small concentration of UF_3 for the redox control.

In case of multi-component mixtures, the physico-chemical properties of the liquid salts can be effectively described by thermodynamic models and an extensive thermodynamic database including the most relevant systems for the MSR is being developed at the Joint Research Centre (JRC) since several years. However, at present the database considers mainly "fresh" fuel compositions, i.e. at the beginning of the reactor operation time. During irradiation, fission products are formed by the fission reaction and accumulate in the fuel matrix. The effect of this composition change on the melting behaviour, solubility limit and vapour pressure of the fuel must be carefully evaluated and could be achieved by extending the present thermodynamic database to the main fission products. The present work considers the effect of two of the most important fission products, cesium and iodine, on the fuel mixture. Both elements are produced with relatively high yield and deserve strong attention due to their volatility and radiological effects in accidental scenarios. Once formed, cesium and iodine are expected to dissolve in the $Li_xTh_{1-x}F_{4-3x}$ liquid solution and bond in the fuel.

In the present work, the modified quasi-chemical model in the quadruplet approximation was applied to describe the reciprocal Li,Cs,Th//F,I system. All the common-ion binary sub-systems have been reviewed and, if needed, newly assessed. Slight modifications have been made for the CsF- and CsI- containing phase diagrams due to a recent re-evaluation of their thermodynamic properties. The ternary common-ion systems (such as the LiF-CsF-ThF$_4$) and the reciprocal systems (Li,Cs//F,I; Cs,Th//F,I and Li,Th//F,I) were extrapolated and optimized in this work based on novel experimental data. The Differential Scanning Calorimetry (DSC) was used to determine the phase equilibria of the selected compositions and to confirm the extrapolated phase diagrams. Finally, the developed model was employed to investigate the behaviour of cesium and iodine in the specific case of the molten salt fuel mixture. The calculations aimed to evaluate the influence of CsF and CsI accumulation in the fuel on its critical thermodynamic properties, such as the melting temperature and the vapor pressure.

2. Experimental

2.1. Sample preparation

In order to complement the existing available data and confirm the developed thermodynamic model, selected compositions of the Li,Cs, Th//F,I system were synthesized and analysed in this work. The samples were prepared starting from the pure compounds lithium fluoride (LiF), cesium fluoride (CsF) and cesium iodide (CsI), obtained for Alfa Aesar, and thorium tetrafluoride (ThF$_4$), obtained from IBI Labs, USA. The details on the provenance of the samples, their purity and the treatments performed prior the mixing are summarized in Table 1. While LiF was provided in anhydrous form, CsF and CsI have been dried at 573 K for several hours under Ar flow to remove the residual moisture, if present. ThF$_4$ is likely to contain, in addition to moisture, oxide and oxyfluoride impurities which can be detected by calorimetric techniques and must be therefore removed from the samples. The purification process is described in details in Ref. [4]

and is based on the conversion of oxides into fluorides using NH_4HF_2 as fluorinating agent. The purity of all the compounds has been confirmed using the DSC technique for the identification of the melting point. As reported in Table 1, the experimental values agree well with the literature values in all cases, within the instrument uncertainty (± 5 K), confirming the purity of the samples.

The samples were prepared by mixing stoichiometric quantities of the end-members and were handled at any time under controlled atmosphere. An argon-filled glove box was used, in which the content of oxygen and water is constantly monitored and kept low, typically below 5 ppm. Moreover, in order to avoid the contact between the corrosive gas formed at high temperature and the environment of the instrument, the samples were encapsulated during the measurements. A gas tight stainless steel crucible internally lined with nickel is used as described in Ref. [8]. This method minimizes also the sample loss and the composition shift due to incongruent vaporization.

2.2. Differential Scanning Calorimetry

The Differential Scanning Calorimetry (DSC) is a widely used technique for the identification of phase equilibria in multi-component systems and was employed in this work to investigate the Li,Cs, Th//F,I system. The detector of the instrument, a Setaram MultiHTC-96 DSC suitable for temperature up to 1400 °C, is composed of two ceramic chambers, one for the sample and one for the reference, linked together by a series of interconnected S-types thermocouples. In this configuration, the heatflow between the two chambers is measured as function of temperature providing information on the occurence of temperature-induced process, such as phase transitions, visualized as peaks. The temperature of the transition and its energy can be determined from the analysis of the peak as the onset temperature and the area, respectively. For this purpose, a temperature calibration is required and was performed by measuring the melting point of several standard materials (In, Sn, Pb, Al, Ag, Au, Zn) with determined uncertainty of ± 5 K. Argon was used as flowing inert purge gas for all measurements.

A standard measurement program was applied for all the samples and consists of four successive heating cycles with constant heating rate of 10 K/min, and different cooling rates (5 K/min, 7 K/min, 10 K/min and 15 K/min). During the first heating ramp, the samples were homogenized while the data were collected during the three following cycles. It is important to mention that CsI and CsF are quite volatile compared to the other components and partial vaporization might occur at high temperature leading to a composition shift. This process will have an effect mainly on the liquidus transition and can be identified by monitoring the variation of the temperature for the same transition in the subsequent cycles.

3. Thermodynamic modeling

3.1. Chemical forms of cesium and iodine

A preliminary thermochemical analysis was performed to identify the relevant species which have to be included in the

Table 1
Details on the provenance, the treatments and the purity of the compounds used in this work.

Compound	Provenance	Purity	Further treatment	$T_{melting}$/K	
				Exp.	Lit.
LiF	Alfa Aesar	99.99%	none (ultradry)	1118 ± 5	1121.3 ± 1 [5]
CsF	Alfa Aesar	99.99%	Drying (Ar atmosphere)	972.7 ± 5	976 ± 2 [5]
CsI	Alfa Aesar	99.999%	Drying (Ar atmosphere)	902.2 ± 5	905 ± 2 [6]
ThF$_4$	IBI Labs	99.99%	Purification using NH_4HF_2	1383.6 ± 5	1383 ± 3 [7]