Effect of Melt Composition on the Reaction of Uranium Dioxide with Hydrogen Chloride in Molten Alkali Chlorides

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The reaction of uranium dioxide with excess hydrogen chloride in alkali chloride melts (LiCl, 3LiCl-2KCl, NaCl-KCl and NaCl-2CsCl) has been studied between 450 and 750 °C, and the reaction products were characterized by electronic absorption and X-ray absorption spectroscopy. Uranium(V), $[UO_2Cl_4]^{3-}$, and uranium(IV), $[UCl_6]^{2-}$, species were formed. They depended upon the temperature and the radius of the alkali cations present. Uranium(V) ions predominated in melts with small cations (LiCl and 3LiCl-2KCl).

Key words: Uranium Dioxide; Hydrogen Chloride; Chloride Melts; Spectroscopy.

1. Introduction

The nature of uranium in alkali chloride melts has attracted considerable attention, since these melts are possible candidates for pyrochemical reprocessing of spent ceramic and metallic nuclear fuels. Uranium can exist in four stable oxidation states in chloride melts: +3 and +4 (normally present as $[UCl_6]^{n-}$, $n = 3$ or 2), +5 and +6 (as the oxychloride species $[UO_2Cl_4]^{n-}$, $n = 3$ or 2).

Uranium dioxide can be dissolved anodically in chloride melts or chemically by reaction with Cl_2 to form $[UO_2Cl_4]^{2-}$-containing melts. The reaction of UO_2 with hydrogen chloride in molten salts has been little studied. Since hydrogen chloride is normally not a strong oxidizing agent, its reaction with metal oxides in fused alkali chlorides usually yields the chloro species in which the oxidation state of the metal remains unchanged. Thus with UO_2, HCl should produce $[UCl_6]^{2-}$-containing melts, and previous studies in NaCl-KCl and NaCl-2CsCl melts showed formation of the U(IV) chloro species [1].

The various oxidation states of uranium in chloride melts can be easily identified by their electronic absorption spectra. Characteristic absorption peaks for U(V, IV and III) are found in the UV-VIS-NIR region together with charge transfer bands. Electronic absorption spectroscopy (EAS) can also be conveniently used for monitoring reactions in molten salts. X-ray absorption spectroscopy (XAS), applied to molten salt systems, provides information concerning coordination numbers and bond lengths of the species of interest.

In the present work EAS and XAS were employed to investigate the products of the reaction of UO_2 with excess HCl in alkali chloride-based melts at various temperatures.

2. Experimental

Chlorination reactions were conducted in molten LiCl, 3LiCl-2KCl and NaCl-2CsCl eutectic mixtures and an NaCl-KCl equimolar mixture between 450 and 750 °C. UO_2 was treated with HCl bubbled (in excess) through the melt at selected temperatures, and the progress of the reaction was followed using in situ electronic absorption spectroscopy. UO_2, in the form of crushed sintered ceramic pellets provided by BNFL, was initially mixed with the alkali chloride salt

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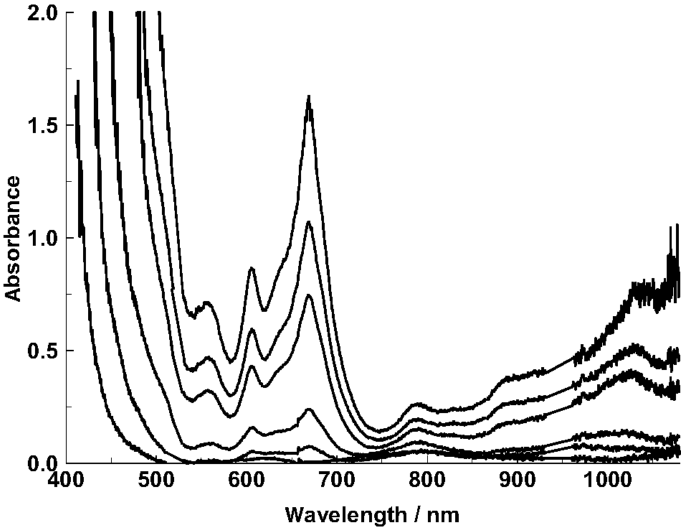

Fig. 1. Electronic absorption spectra recorded during the reaction of UO_2 with HCl in NaCl-KCl melt at 700 °C. Time of HCl bubbling (from bottom to top) was 0, 5, 20, 84, 154 and 259 min.

in a ratio between 0.02 to 0.17 (by weight). Spectra were recorded using an Ocean Optics SD2000 fibre optic spectrometer. The optical furnace and experimental set-up have been described previously [2]. Average oxidation states of uranium, n_U^{ox}, in the rapidly quenched melt samples were determined by oxidimetric titration [3].

Uranium $L_{(III)}$-edge X-ray absorption spectra were recorded for selected molten and quenched samples in transmission and fluorescence modes on stations 9.3 and 16.5 of the CCLRC Daresbury Radiation Source, operating at a typical beam current of 150 mA and an energy of 2 GeV. The monochromic radiation, obtained using an Si 220 double crystal, was detuned to 50% of the maximum intensity to minimize harmonic generation. The experimental set-up has been previously described [4]. The spectra were summed, calibrated, and their background subtracted, using the Daresbury laboratory programs EXCALIB and EXBACK. The EXAFS spectra were simulated using the program EXCURV98.

3. Results and Discussion

The reaction of UO_2 with HCl in NaCl-KCl melt at 700 °C and NaCl-2CsCl eutectic at 600 °C resulted in the formation of the species U(IV). Examples of the spectra in NaCl-KCl melt are shown in Figure 1. The same reaction in molten LiCl, however, produced melts containing U(V) (Fig. 2). Chemical analysis of the quenched melt samples showed that the mean oxidation state of uranium was 5.1 – 5.2, and EXAFS spectroscopy measurements confirmed that "UO_2Cl_4" moieties were present in the melt (Fig. 3 and Tables 1 and 2). Some small amount of U(VI) could also be present in the melt in this particular case.

Table 1. Structural parameters from EXAFS spectra curve fitting of chloride melt samples prepared by the reaction of UO_2 with HCl.

Sample	Shell	CN	Distance, Å	Debye-Waller factor $2\sigma^2$, $Å^2$
UO_2+HCl in LiCl, 750 °C (4.88 wt% U)	U-O	2	1.80	0.011
	U-Cl	4	2.71	0.046
UO_2+HCl in LiCl, 750 °C quenched melt	U-O	2	1.76	0.011
	U-Cl	4	2.76	0.024
	U-U	2	4.04	0.015
UO_2+HCl in 3LiCl-2KCl, 450 °C (0.72 wt% U)	U-Cl	6	2.44	0.028
UO_2+HCl in 3LiCl-2KCl, 450 °C (3.18 wt% U)	U-O	0.8	1.78	0.020
	U-Cl	6	2.65	0.034
	U-U	2	4.96	0.009
UO_2+HCl in 3LiCl-2KCl, quenched melt (11 wt% U)	U-O	1	1.73	0.013
	U-Cl	6	2.69	0.024
UO_2+HCl in 3LiCl-2KCl, quenched melt (1.80 wt% U)	U-O	1	1.79	0.013
	U-Cl	6	2.70	0.027
UO_2+HCl in 3LiCl-2KCl, quenched melt	U-Cl	6	2.61	0.013
	U-K	4	3.13	0.009

In principle, UO_2 can react with HCl in two ways:

$$UO_2 + 4\,HCl \rightarrow UCl_4 + 2\,H_2O, \tag{1}$$

$$2\,UO_2 + 2\,HCl \rightarrow 2\,UO_2Cl + H_2. \tag{2}$$

In a chloride melt the reaction products will dissolve forming $[UCl_6]^{2-}$ and $[UO_2Cl_4]^{3-}$, respectively:

$$UO_2 + 4HCl + 2Cl^- \rightarrow [UCl_6]^{2-} + 2\,H_2O, \tag{3}$$

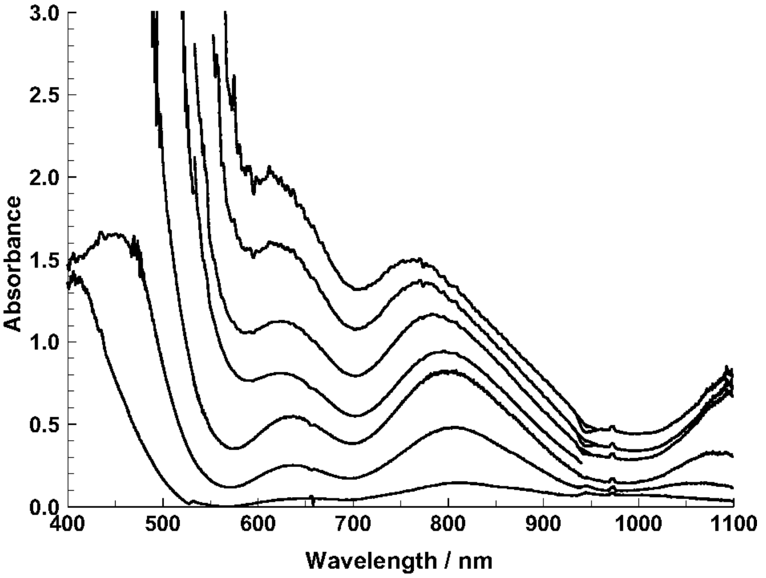

Fig. 2. Electronic absorption spectra recorded during the reaction of UO_2 with HCl in molten LiCl at 750 °C. Time of HCl bubbling (from bottom to top) was 0, 8, 14, 21, 35, 61 and 95 min.

Table 2. Reaction of UO_2 with HCl in molten alkali chlorides.

Melt	$m(UO_2)/$ m(salt)	T, °C	Time, min	Final content of U, wt%	n_U^{ox} in the final melt
LiCl	0.17	750	261	4.88	5.27
	0.02	750	180	0.65	5.09
3LiCl-2KCl	0.01	450	90	0.38	3.91
	0.05	600	60	1.84	4.11
	0.02	750	160	1.06	4.75
NaCl-KCl	0.08	700	259	2.50	4.02
NaCl-2CsCl	0.07	600	162	0.90	3.98

$$2\,UO_2 + 2\,HCl + 6\,Cl^- \rightarrow 2\,[UO_2Cl_4]^{3-} + H_2. \quad (4)$$

The main difference between the used melts (LiCl, NaCl-KCl and NaCl-2CsCl) is the average size of the alkali metal cation. In terms of the cationic size the 3LiCl-2KCl eutectic occupies an intermediate position between LiCl and NaCl-KCl melts. We found that at low temperatures (450 and 600 °C) the reaction of UO_2 with HCl predominantly produces $[UCl_6]^{2-}$ species; the spectra were typical of U(IV) (Fig. 4), and the chemical analysis of the quenched melt samples showed that the mean oxidation state of uranium was around 3.9 – 4.1 (Table 2). Analysis of the EXAFS spectra (Fig. 3 and Table 1) confirmed this but indicated some oxygen contamination in the samples (due to the exceptionally hygroscopic nature of the 3LiCl-2KCl eutectic).

At 750 °C the reaction of UO_2 with HCl in 3LiCl-2KCl melt resulted in the formation of a mixture of U(V) and U(IV), and the electronic spectra recorded in the course of chlorination contained the peaks of both $[UO_2Cl_4]^{3-}$ and $[UCl_6]^{2-}$ (Fig. 5). Initially the spectra were typical of U(V) complex ions, but as the concentration of uranium in the melt increased, absorption peaks of U(IV) started to appear, and the final spectrum of the melt was the superposition of $[UCl_6]^{2-}$ and $[UO_2Cl]^{3-}$ absorption bands. The average oxidation state of uranium in the final melt was around 4.6 – 4.8 (Table 2).

Thus the course of the reaction of UO_2 with HCl in molten alkali chlorides depends on the cationic composition of the melt. Obviously, the strict thermodynamic analysis of the studied reactions (taking into account that the uranium concentration in the melt constantly changes) is an extremely complicated task. Therefore in the present study we limited thermodynamic considerations to the analysis of the system at a particular fixed concentration of uranium in the melt. When calculating ΔG of reactions (3) and (4) one must take into account the effects of dissolution of gaseous reactants and reaction products (HCl, H_2O and H_2) and uranium chlorides (UCl_4 and UO_2Cl) in the melts.

For gaseous species $\Delta G_{(\mathrm{gas})} = \Delta G^0_{(\mathrm{gas})} + \mathrm{R}\cdot\mathrm{T}\cdot\ln(p)$ and $\Delta G_{(\mathrm{melt})} = \Delta G^0_{(\mathrm{l})} + \mathrm{R}\cdot\mathrm{T}\cdot\ln(N) + \Delta G_{(\mathrm{mix})}$, where p is the partial pressure of the gaseous species in the atmosphere above the melt, and N is the gaseous species molar fraction in the melt. Since the partial pressure of HCl is close to one, the system, in respect to the

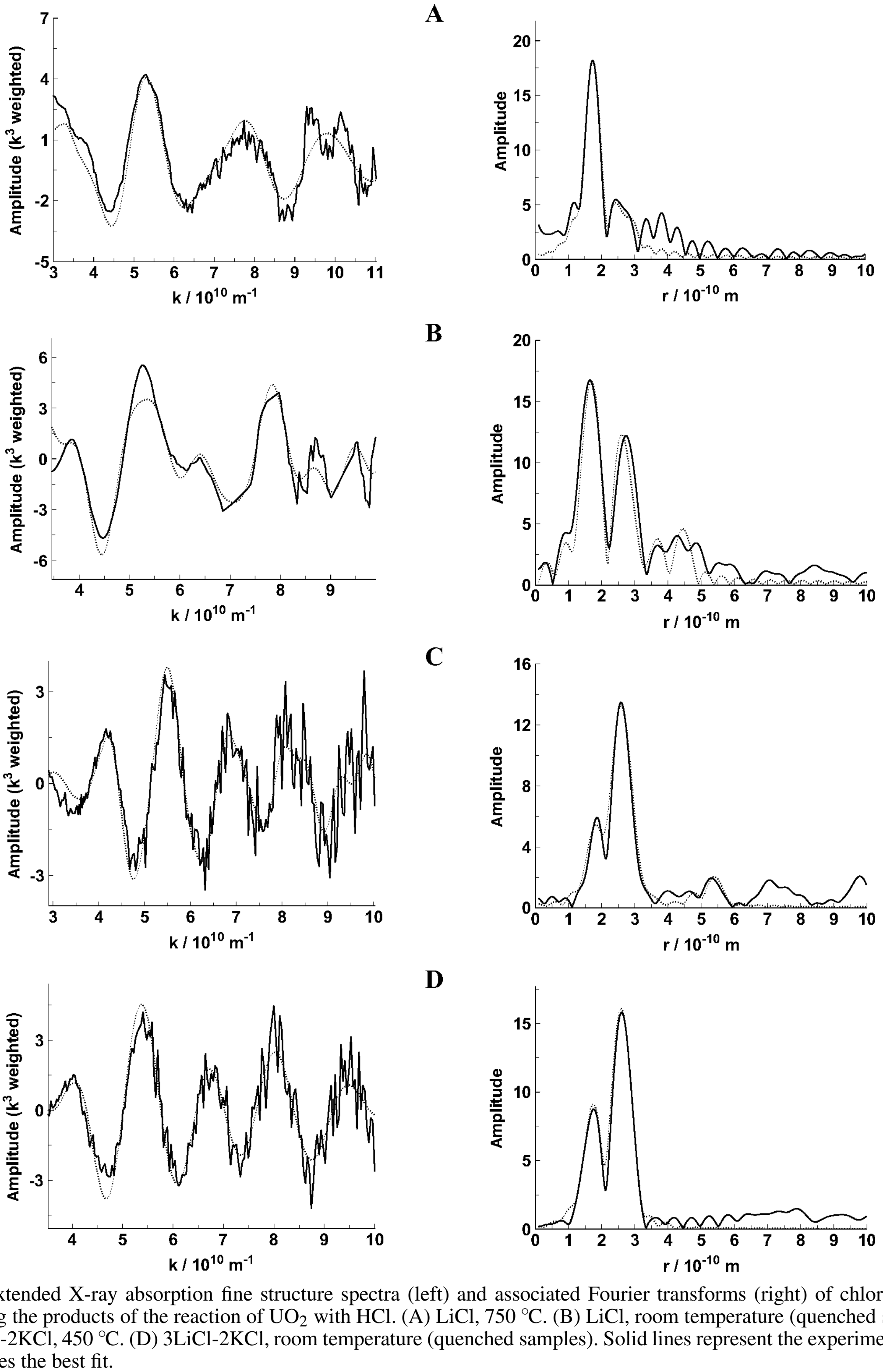

Fig. 3. Extended X-ray absorption fine structure spectra (left) and associated Fourier transforms (right) of chloride melts containing the products of the reaction of UO_2 with HCl. (A) LiCl, 750 °C. (B) LiCl, room temperature (quenched samples). (C) 3LiCl-2KCl, 450 °C. (D) 3LiCl-2KCl, room temperature (quenched samples). Solid lines represent the experimental data, dotted lines the best fit.

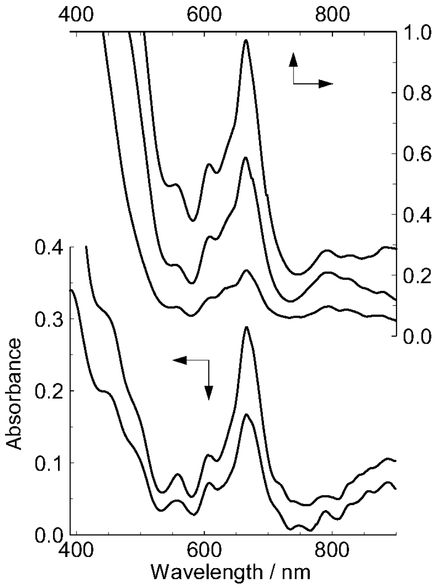

Fig. 4. Electronic absorption spectra recorded during the reaction of UO_2 with HCl in 3LiCl-2KCl melt at 450 °C (bottom) and 600 °C (top). Total time of HCl bubbling was 90 and 60 min, respectively.

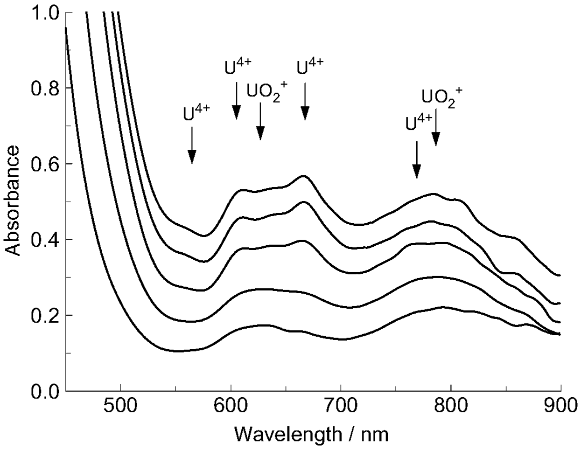

Fig. 5. Electronic absorption spectra recorded during the reaction of UO_2 with HCl in 3LiCl-2KCl melt at 750 °C. Total time of HCl bubbling was 160 min.

gaseous components in a given moment of time, can be considered as close to the equilibrium state. Then it follows for the gaseous reactants and reaction products that $\Delta G_{(\mathrm{melt})} \approx \Delta G_{(\mathrm{gas})}$.

For uranium chlorides $\Delta G_{(\mathrm{melt})} = \Delta G^0_{(\mathrm{l})} + \mathrm{R} \cdot \mathrm{T} \cdot \ln(N) + \Delta G_{(\mathrm{mix})}$. The change of the Gibbs free energy upon mixing uranium chlorides with alkali chlorides, $\Delta G_{(\mathrm{mix})}$, depends on the alkali metal cation size. The value of $\Delta G_{(\mathrm{mix})}$ can be determined from the difference between the Gibbs free energy of the formation of a uranium chloride in the melt, ΔG^*, and the standard Gibbs free energy of the formation of this pure liquid uranium chloride, $\Delta G^0_{(\mathrm{l})}$, at a chosen temperature. ΔG^* can be calculated from known values of the electrode potentials for $\mathrm{U^{III}/U^0}$, $\mathrm{U^{IV}/U^{III}}$ and $\mathrm{UO_2{}^V/UO_2}$ red-ox couples [5–7], measured versus a $\mathrm{Cl_2/Cl^-}$ reference electrode:

$$E^*_{\mathrm{U^{3+}/U}} = -3.50 + \frac{0.52}{r_{\mathrm{Me^+}}} + \left(8.58 - \frac{1.99}{r_{\mathrm{Me^+}}}\right) \cdot 10^{-4} \cdot T. \tag{5}$$

At 700 °C:

$$E^*_{\mathrm{U^{4+}/U^{3+}}} = -2.2173 + \frac{0.9063}{r_{\mathrm{Me^+}}}, \tag{6}$$

$$E^*_{\mathrm{UO_2^+/UO_2}} = -1.214 + \frac{0.53}{r_{\mathrm{Me^+}}} + \left(4.95 + \frac{0.50}{r_{\mathrm{Me^+}}}\right) \cdot 10^{-4} \cdot T. \tag{7}$$

where $r_{\mathrm{Me^+}}$ is the average radius of alkali cations in the melt (in Å), which equals to 0.78 for LiCl, 1.0 for 3LiCl-2KCl, 1.16 for NaCl-KCl and 1.43 for NaCl-2CsCl.

Due to the very low partial pressures of water or hydrogen in the studied systems, their experimental measurements are difficult. In the present work the order of $p(H_2O)$ and $p(H_2)$ was estimated from known volumes of the experimental cells, rate of passing HCl through the system and amounts of H_2O and H_2 formed according to the reactions (3) and (4) during the experiments.

The results of calculations of ΔG of reactions of uranium dioxide with hydrogen chloride, leading to the formation of UCl_4 or UO_2Cl in molten alkali chlorides of various cationic compositions at 750 °C are presented in Figure 6A. At the chosen conditions only in molten LiCl the reaction (4) (resulting in the formation of $[UO_2Cl_4]^{3-}$) is more thermodynamically favourable than the reaction (3). In the 3LiCl-2KCl melt the values of ΔG of both reactions are close, and in the NaCl-KCl and NaCl-2CsCl melts the reaction (3) (leading to $[UCl_6]^{2-}$) will predominantly take place. These conclusions agree well with the experimental results discussed above.

It was also interesting to consider the effect of temperature on ΔG of reactions (3) and (4). The results of calculations for the 3LiCl-2KCl melt between 450

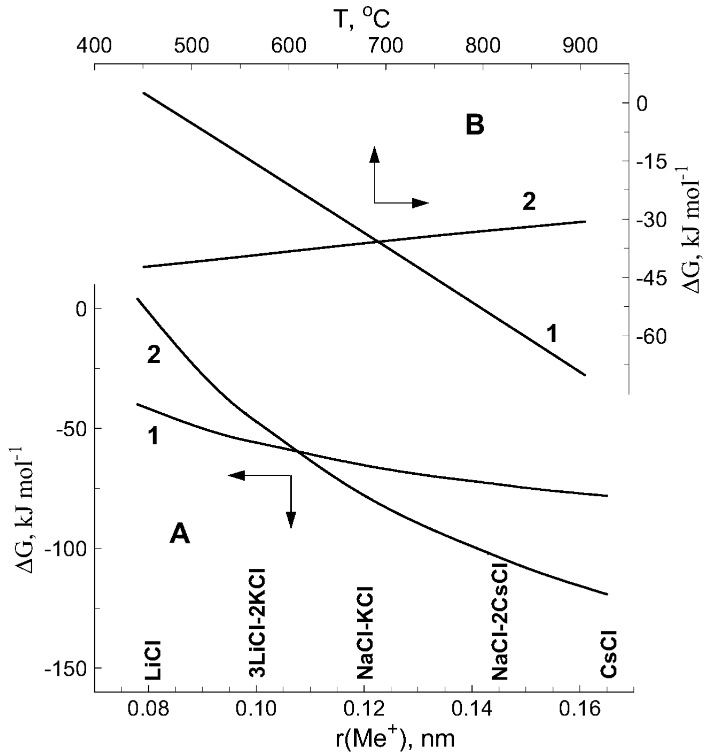

Fig. 6. Calculated values of change of Gibbs free energy ΔG [in kJ/mol(UO_2)] of reactions of UO_2 with HCl leading to the formation of $[UO_2Cl_4]^{3-}$ (1) and $[UCl_6]^{2-}$ (2) in: (A) melts of various cationic compositions at 750 °C, $r(M^+)$ is the average radius of the alkali cation in the melt; (B) 3LiCl-2KCl melt at various temperatures. $p(H_2O) = p(H_2) = 2 \cdot 10^{-4}$ atm; [U] = 1 mol%.

and 900 °C are presented in Figure 6B. At low temperatures the reaction (3) will be predominant, and at high temperatures the reaction (4). The experimental data obtained in the present study agree with that conclusion and show that in 3LiCl-2KCl-based melts at 450 and 600 °C only U(IV) ions were formed (Fig. 4 and Table 2), but at 750 °C around 75% of uranium in the melt was in the form of the U(V) species (Fig. 5 and Table 2).

The results of the calculations carried out in the present study have a somewhat estimative character, taking possible errors in determining the values of the electrode potentials in molten salts into account, especially for the U^{IV}/U^{III} red-ox couple, estimating partial pressures of gaseous species. However, all this can hardly affect the trends in changing thermodynamic values presented in Figure 6.

Therefore we can conclude that the reaction of uranium dioxide with hydrogen chloride in molten alkali chlorides can result in the formation of either U(IV) or U(V) species, depending on the cationic composition of the melt and/or temperature. The results obtained in various melts are summarized in Table 2. At higher temperatures the melts with small cations (LiCl and in somewhat smaller degree 3LiCl-2KCl) favour the formation of the U(V) species, while the U(IV) chloro species are formed in melts with larger alkali cations (NaCl-KCl and NaCl-2CsCl mixtures) and in 3LiCl-2KCl at lower temperatures.

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