

## REACTION OF ZIRCONIUM WITH ALKALI HALIDE MELTS

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The theoretical model was developed for the description of the reactions of a polyvalent metal with melts containing its compounds, which account for the formation of each species in intermediate oxidation states. This theory was applied to the analysis of literature data on the equilibrium potentials of zirconium electrode in chloride and bromide melts (systems:  $Zr-KCl$ ;  $Zr-LiCl-KCl$ ;  $Zr-KBr$ ;  $Zr-NaBr-KBr$ ), and also on the vapor pressure of alkali metal upon the fluoride melt ( $Zr-CsF$ ). The intermediate species were established to form in each chloride and bromide melt. Interaction with evolution of free alkali metal occurs in the fluoride melt, zirconium metal being oxidized to +4 oxidation state. Thermodynamic values for the corresponding reactions were calculated.

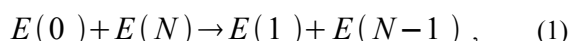
## INTRODUCTION

Reactions of zirconium metal with halide melts are of practical importance considering utilization processes for disposed active fuel elements of nuclear power plants, and also recycling the molten salt fuel compositions. It is known, for example, that zirconium is a reductant for rare earth metal fluorides in molten mixture of sodium and zirconium fluorides, which are basic components of salt carrier in accelerator-governed nuclear reactors [1]. This reaction can be used for the extraction of nuclear fission products.

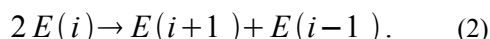
Besides, the information on reactions of metals with molten salts is of interest for understanding of general behavior of polyvalent metal in molten salt media.

This paper presents the results of theoretical analysis of the metal – molten salt reactions. Literature data have been analyzed, and thermodynamic parameters were calculated.

The mechanism of current-less dissolution of a metal in an ionic melt consists in the formation and dissolution of species in different oxidation states  $i = 1, 2, \dots, N$ , where  $N$  is the maximum possible oxidation number, which, in particular, is equal to 4 for zirconium. If the melt contains the dissolved compound in highest oxidation state  $N$ , the metal contacting with the melt should dissolve in form of intermediate species by means of intervalence reactions

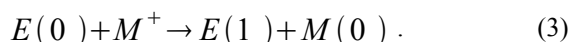


which are represented as a sequence of one-electron elementary steps [2]. Further on, homogeneous intervalence reactions should also occur, the elementary steps also being one-electron exchange between the encountering particles:



As it was shown in [2,3], total number of such reactions is  $N(N-1)$  (for example, 12 for  $N=4$  in case of zirconium). That is why rigorous kinetic description of

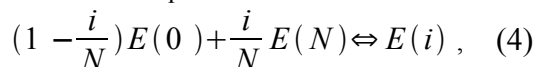
the process at  $N > 2$  is very hard problem – the more so, that in general, not only the reactions (1,2), but possible interaction of the metal with cations of molten solvent (with the formation of free alkali metal if the basic melt is an alkali metal halide) should be considered:



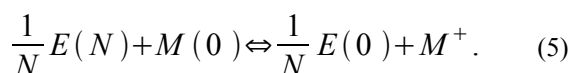
Finally, the reactions (1-3) result in the equilibrium, when the melt contacting with the metal contains the compounds of polyvalent metal in different oxidation states. Relative content of these compounds will depend on its thermodynamic stability.

## 1. THEORY OF POTENTIOMETRY IN METAL – MOLTEN SALT SYSTEM

The problem of description of the equilibrium system is much more simple than the kinetic problem mentioned above. Properties of the system which contains  $N$  species in different oxidation states should be determined by only  $N-1$  independent equations. If we use set of equilibria

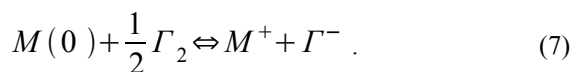
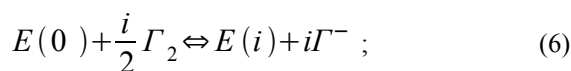


the equilibrium constants of these reactions (or its Gibbs energies) are quantitative measures of the intermediate compounds relatively to reference states, which are zero and maximum oxidation states of the metal. For complete description of the system, the equations (4) should be supplemented with equilibrium encountering the alkali metal cations:



Of course, other than  $E(N)$  reference state can be chosen also for estimation of relative stability of the intermediates. It can be, for example, activity of alkali metal halide in basic melt. The set of independent

equilibrium will then characterize the system, including the oxidation of alkali metal:



In that case, instead of the equilibrium constants of the appropriate reactions, standard potentials are more convenient, which are strictly connected to the values of these constants. We can consider the potentials of red-ox half-reactions



and



vs. the half-reaction



We can then write down N equations for electrode potential

$$\varphi = \varphi_i^0 + \frac{RT}{iF} \ln a_i , \quad (11)$$

one of them corresponds to the reaction (10), others to (8):

$$\varphi = \varphi_M^0 - \frac{RT}{F} \ln a_{M_0} . \quad (12)$$

The activity of species in the melt follows from these equations:

$$\ln a_i = i\Psi - i\Psi_i^0 \quad (13)$$

or

$$a_i = \beta_i \exp(i\Psi) \quad (14)$$

and similarly

$$a_{M_0} = \beta_0^{-1} \exp(-i\Psi) , \quad (15)$$

where

$$\Psi = \frac{\varphi F}{RT} \quad (\text{accordingly, } \Psi^0 = \frac{\varphi^0 F}{RT}) , \quad (16)$$

and

$$\beta_i = \exp(-i\Psi^0) \quad (17)$$

is a coefficient, which contains all information about the relative stability of the appropriate compound in equilibrium system.

Following method for estimation of relative stability of intermediates  $E(i)$  in equilibrium with metal  $E$  stems from the above considerations. If we assume

approximately that concentrations of the appropriate compounds are equal to its activity ( $a_i \approx c_i$ ), and denote  $\exp(i\Psi) = P^i$ , we obtain

$$c_i = \beta_i P^i . \quad (18)$$

Hence, the dependence of equilibrium potential on the total concentration of species containing the metal  $E$  in the melt can be represented in form of polynomial function

$$C = \sum_1^N c_i = \sum_1^N \beta_i P^i , \quad (19)$$

which permits calculations of the values related to the thermodynamic stability of the intermediates – equilibrium constants (4) or standard potentials of half-reactions (8). The (19) is the basic equation for the analysis of experimental data, as it was considered in [4].

However, more common is the situation when we know not the equilibrium but initial concentration  $C_N$  of  $E(N)$  in the melt before its contact with the metal. In that case, the equation

$$NC_N = (\sum iC_i) - C_{M_0} \quad (20)$$

is true, which follows immediately from charge balance condition. Then the equation for the analysis of experimental potentiometric data takes a form:

$$NC_N = (\sum i\beta_i P^i) - \alpha_0 P^{-1} \quad (21)$$

or

$$NC_N P = (\sum i\beta_i P^{i+1}) - \alpha_0 . \quad (21,a)$$

Similar equation is true also for the case when the metal compounds were introduced by electrolytic dissolution and their concentration were recalculated onto the compounds in highest oxidation states  $E(N)$ , as it was done in many experimental works. It was also proved [4,5] that similar equations are valid for the description of *stationary* potential of metal electrode immersed into the melt in the situation when the system as a whole is not in equilibrium and the metal dissolves at the conditions of stationary fluxes of  $E(i)$  into the bulk of melt and  $E(N)$  from the melt. The coefficient  $\beta_i$  in this case must include the correction factor equal to the ratio of diffusion coefficients of the appropriate compounds.

In this work we have applied the obtained equations for the analysis of experimental data on the potentials of zirconium metal electrodes in molten chlorides [6] and bromides [7] of alkali metals.

## 2. MEASUREMENT OF VAPOR PRESSURE AS A METHOD FOR STUDIES OF INTERVALLENCE EQUILIBRIUMS

Concerning application of zirconium in nuclear power plants, the information on its reactions with fluoride melts, which are most promising reaction media

for recycling of fuel [8], is very important. However, potentiometric investigation of such systems is a problem because of the absence of reliable reference electrode. Commonly, quasi-reference electrodes are used in such cases, which electrode function is not exactly known (for example, platinum wire immersed into the melt). Sometimes such approach permits to determine equilibrium constants (4,5), however the calculations of relative stability of different oxidation states against some standard reference system (for example, half-reaction 10) are not possible. In other words, measurements in some arbitrary fixed potential scale allow for estimation of stability for *intermediate* oxidation states  $E(0)$  и  $E(N)$ , only, because the standard potential of species  $E(N)$  can be determined only with the precision up to some arbitrary constant. Such approach was used for estimation of relative stability of silicon intermediates in fluoride melts [4]; we have not found in literature such data on the system zirconium – fluoride melt.

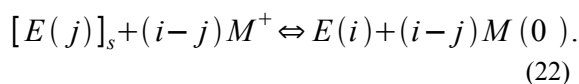
It is known, however, that zirconium in molten fluoride media is very chemically active; see, for example, the data [9] on the corrosion in molten chloride-fluoride mixtures. It was found that Zr can react with the melt with evolution of free alkali metal [10]. Thus, total vapor pressure above the melt should correspond in fact to the vapor pressure of alkali metal. Then, in equilibrium conditions, the value of this pressure can characterize the composition and relative stability of the compounds formed in the system. To make such calculations possible, appropriate algorithm must be developed.

We have derived the equations, which relate the vapor pressure to the composition of the melt, for two particular cases.

### 2.1. CONDENSE PART OF THE SYSTEM IS HETEROGENEOUS; SOLID IS IN EQUILIBRIUM WITH LIQUID MELT AND VAPOR

Not only zirconium metal may form the solid phase. The situation is possible when zirconium is dissolved entirely, and solid phase is represented by its compound in lower oxidation state.

That is why we use a set of equilibriums similar to (5) for description of the system:



Taking into account that solutions are diluted, and  $[E(j)]_s$  is solid, we can write the equilibrium constant of reaction (22) as

$$K_i = C_i p^{i-j}, \quad (23)$$

where  $p$  is vapor pressure of alkali metal above the melt.

If in course of the experiment, along with addition of the compound in highest oxidation state, some amount  $\Delta$  of alkali metal (recalculated on the concentration) was added to or withdrawn from the system, then the charge

balance equation (20) must be modified, and amount of solid phase substance must also be included:

$$NC_N - \Delta = (\sum iC_i) + j[C(j)]_s - C_{M_0}, \quad (24)$$

where  $[C(j)]_s$  is mole fraction of  $[E(j)]_s$  in the system, which can be found from the known value of the mole fraction of all zirconium compounds in the system  $C^0$ :

$$C^0 = (\sum iC_i) + [C(j)]_s. \quad (25)$$

Main formula for the case I follows from (23) – (25):

$$NC_N - \Delta = jC^0 + (\sum (i-j)\alpha_i p^{j-i}) - \beta_0 p. \quad (26)$$

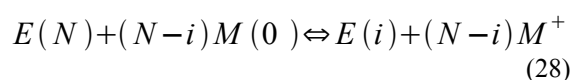
If solid zirconium metal is in equilibrium with the melt ( $j=0$ ), then

$$NC_N - \Delta = (\sum i\alpha_i p^{-i}) - \beta_0 p \quad (27)$$

and it is not necessary to determine total content of zirconium in the system  $C^0$ .

### 3.1. ZIRCONIUM METAL DISSOLVED COMPLETELY, CONDENSED PHASE IS HOMOGENEOUS

Using material balance equations for zirconium and alkali metal, and choosing the set of equilibrium reactions



we finally come to the formula

$$NC_N - \Delta = C^0 \frac{\sum i\beta_i p^{-i}}{\sum \beta_i p^{-i}} - \beta_0 p. \quad (29)$$

Fraction in the right side of the equation (28) has physical meaning of average oxidation number of zirconium species in the melt  $\bar{n}$ , which should not depend significantly on  $p$ . Then the equation for data analysis takes the form:

$$NC_N - \Delta = C^0 \bar{n} - \beta_0 p. \quad (29,a)$$

## 3. EXPERIMENTAL DATA AND ITS ANALYSIS

### 3.1. EQUILIBRIUMS IN ZR – ALKALI METAL BROMIDE SYSTEMS

Experimental data [7] on the equilibrium potential of Zr electrode vs. bromine electrode in KBr and KBr-NaBr equimolar mixture were used. Before measurements, some quantity of zirconium was electrochemically dissolved and total concentration of zirconium compounds in the melt was calculated assuming that its oxidation state is +4.

Such experimental procedure means that the data should be represented in terms of equation (21).

Unfortunately, the dataset is scarce (4 concentrations only), and thus, comprehensive analysis is not possible. However, the main oxidation state of zirconium compounds in the melt can be determined.

In particular, the data on **Zr - KBr** system are most consistent with the case when Zr(II) and Zr(IV) compounds are in equilibrium with Zr metal. As follows from fig. 1, the best approximation formula for concentration dependence of the potential is

$$\frac{4C}{P^2} = a + bP^2, \quad (30)$$

which correspond to the equilibrium

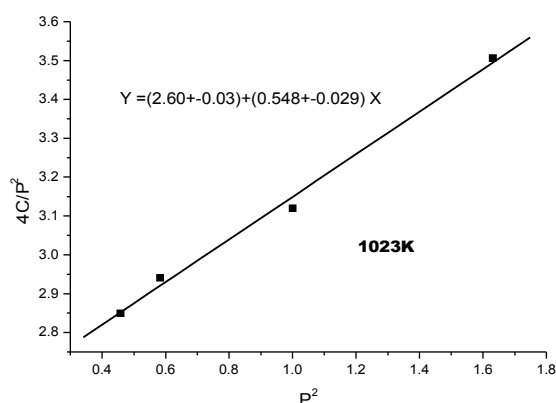
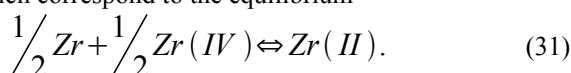


Fig. 1. Concentration dependence of zirconium electrode potential in KBr melt in terms of equation (30)

Determination of *a* and *b* constants in (30) at different temperatures allows us to calculate equilibrium constants of (31) and thus the thermodynamic constants of this reaction. Fig. 2 shows temperature dependency of equilibrium constant (31).

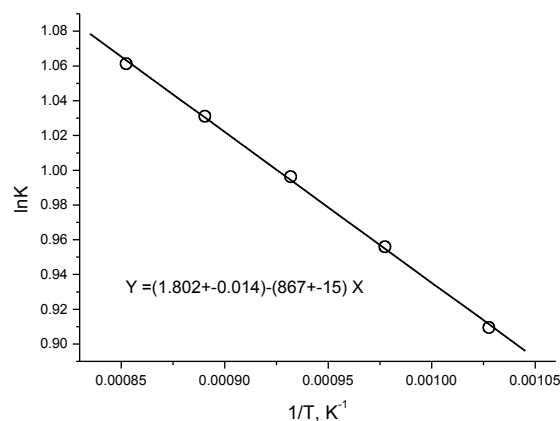


Fig. 2. Logarithm of equilibrium constant of reaction (31) vs. inverse temperature. Straight line is the mean square approximation according to the equation in the graph

Enthalpy and entropy of reaction (31) were calculated from this dependency for temperature range 700-900°C, which are given in Table.

#### Thermodynamic values for some equilibriums in Zr – molten metal halide systems

Reaction	System	Temperature, °C	Enthalpy change, kJ	Entropy change, J/K
$\frac{1}{2} \text{Zr(0)} + \frac{1}{2} \text{Zr(IV)} \rightleftharpoons \text{Zr(II)}$	KBr	700...900	$7,205 \pm 0,125$	$-4,20 \pm 0,03$
$\frac{1}{3} \text{Zr(0)} + \frac{2}{3} \text{Zr(III)} \rightleftharpoons \text{Zr(II)}$	KCl	780...990	82.04	82.3
$\frac{1}{2} \text{Zr} + \text{Me}^+ \rightleftharpoons \frac{1}{2} \text{Zr(II)} + \text{Me(0)}$	LiCl-KCl	500...550	$30.69 \pm 0.28$	$-40.55 \pm 0.35$
$\text{Cs}^0 (\text{melt}) \rightleftharpoons \text{Cs}^0 (\text{vapor})$	CsF	820...950	$66.0 \pm 8.4$	-

The concentration dependence for **NaBr-KBr** melt is essentially different (fig. 3). The coefficient *b* in approximation equation (30) is statistically meaningless, which indicate the presence of mainly Zr(II) in equilibrium with Zr metal.

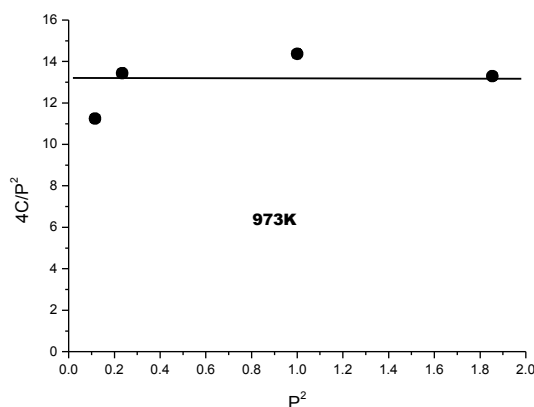
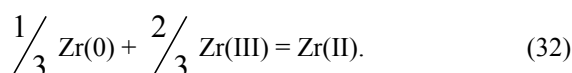


Fig. 3. Concentration dependence of zirconium electrode potential in KBr-NaBr melt in terms of equation (30)

### 3.2. EQUILIBRIUMS IN ZR – ALKALI METAL CHLORIDE SYSTEMS

The data on equilibrium potentials of Zr electrode vs. chlorine reference electrode in KCl (780...990°C) and eutectic LiCl-KCl (500...550°C) melts were taken from the book [6]. The experimental technique was similar to that used for the bromide melts.

The analysis showed that the data are in consistence with the scheme when Zr(III) and Zr(II) species are in equilibrium with Zr metal:



Then, the approximation formula for concentration dependency of the potential takes the form:

$$\frac{4C}{P^2} = a + bP. \quad (33)$$

Fig. 4 shows an example of such dependency.

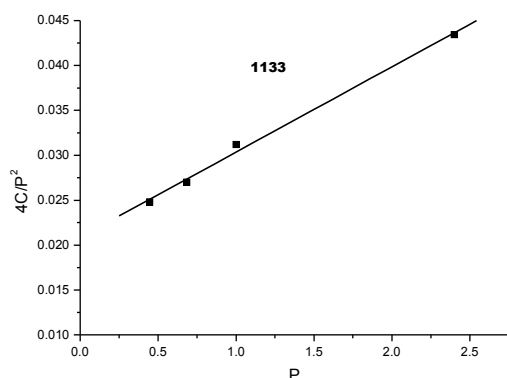


Fig. 4. Concentration dependence of zirconium electrode potential in KCl melt in terms of equation (33)

If we fix the scale of potentials for calculation of the argument  $P = \exp\left(\frac{EF}{RT}\right)$  such, that for coefficient in equation (33)  $b = 3\beta_3$  (see eqn 21) to establish the value  $\beta_3 = 1$ , then the equilibrium constant of the reaction (32) can easily be calculated from the slope of approximation plot.

Fig. 5 shows the temperature dependency for this constant. Thermodynamic values (780...990°C) calculated from this dependency are given in Table. The character of equilibrium changes as the temperature becomes lower and lithium chloride appears in the system.

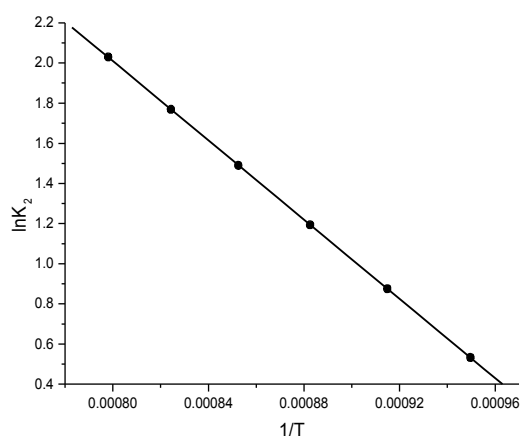
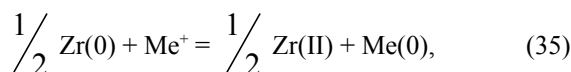


Fig. 5. Logarithm of equilibrium constant of reaction (32) vs. inverse temperature

The appropriate approximation formula for LiCl-KCl experimental data is found to be

$$C * P = -a + bP^3, \quad (34)$$

which corresponds to the equilibrium



where Me is alkali metal.

Fig. 6 shows an example of such dependency. Temperature dependence of equilibrium constant (35), calculated from the concentration dependencies (fig. 6), is a straight line in  $\ln K(1/T)$  coordinates, similar to that shown in fig. 5. Table shows the thermodynamic values calculated for this reaction.

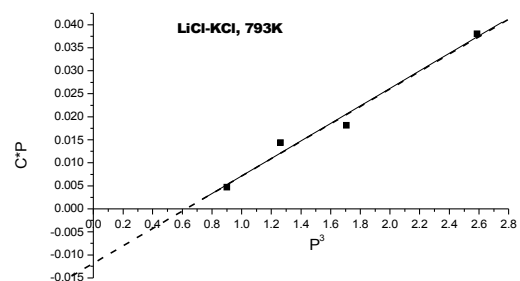


Fig. 6. Concentration dependence of zirconium electrode potential in LiCl-KCl melt in terms of equation (34)

### 3.3. RELATIVE PROPERTIES OF ZR – BROMIDE AND ZR – CHLORIDE SYSTEMS

As follows from the calculations above, the Zr(II) species are rather stable and present in both systems. Besides, Zr(IV) is formed in Zr/KBr, Zr(III) – in Zr/KCl and free alkali metal – in Zr/LiCl-KCl system.

Using equations (16,17), we have calculated the standard potentials of half-reactions (8) for bromide and chloride systems relatively to bromine ( $\text{Br}_2/\text{Br}$ ) and chlorine ( $\text{Cl}_2/\text{Cl}$ ) reference electrodes respectively. These data are shown in Fig. 7 and 8 in form of temperature dependencies.

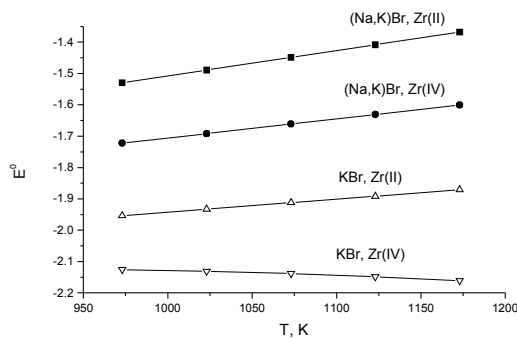


Fig. 7. Standard potentials of Zr(II)/Zr(0) and Zr(IV)/Zr(0) in bromide melts vs. (Br<sub>2</sub>/Br<sup>-</sup>) reference electrode

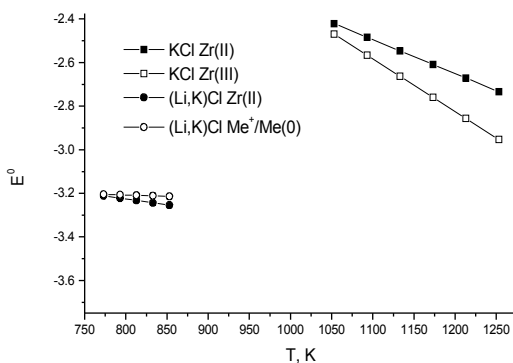


Fig. 8. Standard potentials of Zr(II)/Zr(0) and Zr(III)/Zr(0) in chloride melts vs. (Cl<sub>2</sub>/Cl<sup>-</sup>) reference electrode

As follows from the data, thermodynamic stability of Zr species in different oxidation states decreases in the bromide melts in the order : Zr(II) (NaBr-KBr) > Zr(IV) (NaBr-KBr) > Zr(II) (KBr) > Zr(IV) (KBr). The regularity for chloride melts is: Zr(II) (KCl) > Zr(IV) (KCl) > Zr(II) (LiCl-KCl).

So far as the Zr(II) species are present in all systems, it is worthwhile to compare its stability in chloride and bromide melts. For that, their standard potentials must be represented in the same scale. We have reduced the potentials in bromide melts to the chlorine reference electrode scale using the data on the halogens electrode potentials against sodium reference electrode (700°C) given in [11]:

$$E_{Cl_2}^0 = +3,39 V$$

$$E_{Br_2}^0 = +2,98 V$$

Fig. 9 shows the potentials of electrochemical couple Zr(II)/Zr for all investigated systems vs. Cl<sub>2</sub>/Cl<sup>-</sup> reference electrode.

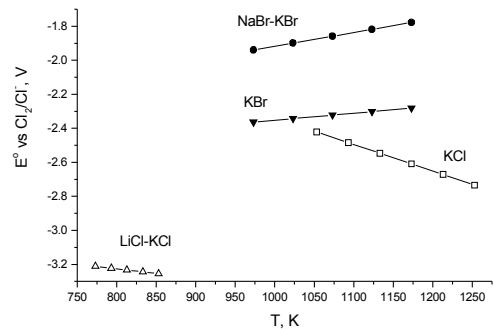


Fig. 9. Temperature dependencies of Zr(II)/Zr potentials in different melts vs. chlorine reference electrode in different melts

As follows from Fig. 9, Zr(II) species are most stable in NaBr-KBr and least stable in LiCl-KCl melt. Stability of Zr(II) in the melts of individual halides is almost the same near the melting point quickly decreasing as temperature increase in KCl and increasing in KBr melts.

### 3.4. CHEMICAL REACTIONS IN ZR-CSF SYSTEM (ACCORDING TO TENSIMETRIC INVESTIGATIONS)

Experimental data for the calculations were taken from work [10]. They are represented in fig. 10.

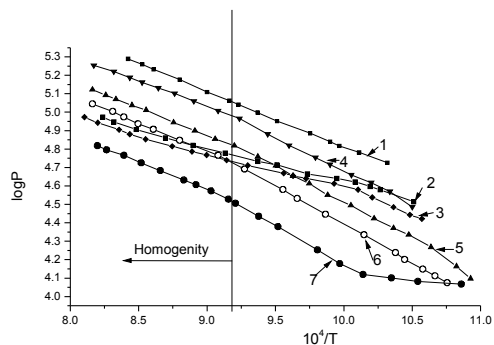


Fig. 10. Experimental data [10] used in the calculations. The digits mean mole fraction of the corresponding component in the initial melt: 1 – 0.029Zr – CsF; 2 – the same, after evacuation of some quantity of free cesium from the system (-0.094Cs); 3 – CsZrF<sub>5</sub> was added to the melt (2) (+0.032Zr(IV)); 4 – Cs metal was added to the melt (3) (+0.082Cs); 5 – CsF – 0.08CsZrF<sub>5</sub> – 0.10Zr; 6 – CsF – 0.112CsZrF<sub>5</sub> – 0.11Zr; 7 – CsF – 0.145CsZrF<sub>5</sub> – 0.11Zr

Left part from the vertical line corresponds to the area where solid phase is absent (the temperatures are higher then about 1090 K). Three phases (vapor, liquid and solid) are in equilibrium at lower temperatures, which corresponds to the inflections on the plots of logarithm of pressure vs. the inverse temperature.

Using the data on vapour pressure in homogeneous system=ms, we have plotted series of isotherms in accordance with the equation (28):

$$4C_N - \Delta = f(C^0, p), \quad (36)$$

where  $C^0$  is total content of Zr in the system;  $p$  – vapor pressure;  $C_N$  content of Zr(IV) in the initial melt.

It was found that the dependence (36), in the limit of experimental error, could be represented by linear equation for homogeneity region (fig. 11)

$$F = 4C_N - \Delta = AC^0 + Bp. \quad (37)$$

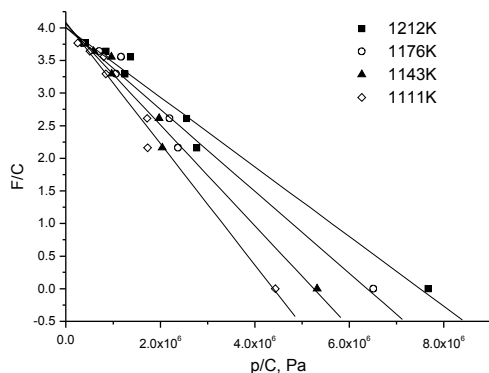
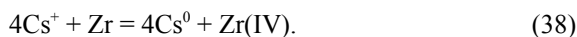
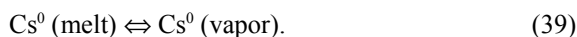


Fig. 11. Isothermal dependencies for homogeneity region, fig.10, presented in form of  $F/C = A + B \frac{p}{C}$  (eqn. 37)

According to the accepted model, the factor  $A$  of linear dependencies, fig. 11, corresponds to average oxidation number of zirconium dissolving in the melt due to the reaction with cesium ions. As follows from fig.11, it is almost precisely equal to 4, which evidences for the reaction



Slopes of the straight lines in fig. 11 corresponds to equilibrium constant of the evaporation process of cesium from the melt:



Analysis of temperature dependence for this factor (fig. 12) confirms this suggestion.

The value of enthalpy of this process, calculated from data fig. 12 (table), is approximately equal to literature value for enthalpy of evaporation of metal cesium (68.2 kJ/mol), which confirm the correctness of the applied analysis of the data.

Thus, dissolution of Zr metal most easily proceeds, and the oxidation state +4 is most stable in fluoride melts. This conclusion follows from the vapor pressure data published in the literature [10].

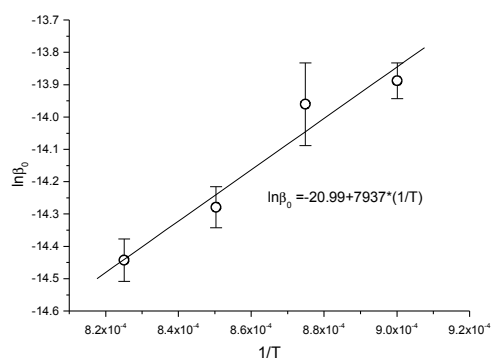


Fig. 12. Logarithm of equilibrium constant of the process (39) vs. inverse temperature

Considering the importance of fluoride melts for nuclear energy systems, the problem of reaction of Zr metal with such media requires further experimental investigations.

## CONCLUSIONS

Applying the developed theoretical approaches, we were able to obtain the information on the oxidation states of zirconium compounds in equilibrium of bromide and chloride melts with zirconium metal. In particular, we have found that Zr(II) species are formed in all systems but its stability is different and decrease in the following order: (NaBr-KBr) > KBr ≥ KCl > (LiCl-KCl). The formation of other valence species has also being established. Its relative stability decrease in the order Zr(II) (NaBr-KBr) > Zr(IV) (NaBr-KBr) > Zr(II) (KBr) > Zr(IV) (KBr) in bromide systems, and Zr(II) (KCl) > Zr(IV) (KCl) > Zr(II) (LiCl-KCl) in the chlorides. The formation of alkali metal by the reaction with zirconium metal is essential in LiCl-KCl melt. Quantitative parameters of the reactions for the formation of low valence Zr species – equilibrium constants and, in some cases, thermodynamic values – were also calculated.

Unfortunately, the information on fluoride systems is much more scarce. High chemical activity of Zr in fluoride melts was established. In particular, analysis of the vapor pressure data [10] shows that it oxidation to highest oxidation state +4 and reduction of cesium cations to free Cs metal in CsF melt. So far, the more detailed information is not yet obtained. The reliable potentiometric method must be developed for fluoride melts. We are working now upon this problem.

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### РЕАКЦІЯ ЦИРКОНІЯ С ГАЛОГЕНІДНИМИ РАСПЛАВАМИ

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Разработаны методы теоретического описания взаимодействия поливалентного металла с расплавами, содержащими соединения этого металла, учитывающие возможное образование всех соединений в промежуточных степенях окисления и взаимодействие с катионами щелочного металла. Эти методы использованы для анализа имеющихся в литературе данных по равновесным потенциалам циркониевого электрода в хлоридных и бромидных расплавах (системы:  $Zr-KCl$ ;  $Zr-LiCl-KCl$ ;  $Zr-KBr$ ;  $Zr-NaBr-KBr$ ), а также по давлению насыщенных паров щелочного металла над фторидным расплавом ( $Zr-CsF$ ). Установлено, что во всех хлоридных и бромидных системах образуются соединения в промежуточных степенях окисления. Во фторидной системе протекает взаимодействие с выделением свободного щелочного металла и образованием соединений циркония в степени окисления +4. Вычислены термодинамические характеристики соответствующих реакций.

### РЕАКЦІЯ ЦИРКОНІЮ З ГАЛОГЕНІДНИМИ РОЗПЛАВАМИ

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Розроблено методи, теоретичного опису взаємодії полівалентного металу з розплавами, які містять сполуки цього металу, що враховують можливість утворення всіх сполук проміжного ступеня окислення та взаємодії з катіонами лужного металу. Ці методи використано для аналізу відомих літературних даних по рівноважним потенціалам цирконієвого електроду в хлоридних та бромідних розплавах (системи:  $Zr-KCl$ ;  $Zr-LiCl-KCl$ ;  $Zr-KBr$ ;  $Zr-NaBr-KBr$ ), а також по тиску насиченої пари лужного металу над фторидним розплавом ( $Zr-CsF$ ). Встановлено, що в усіх хлоридних та бромідних системах утворюються сполуки в проміжному ступеню окислення. У фторидній системі відбувається взаємодія з виділенням лужного металу та сполук цирконію у ступеню окислення +4. Розраховано термодинамічні характеристики відповідних реакцій.