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EQUILIBRIUM POTENTIALS OF ZIRCONIUM IN MIXED FLUORIDE-CHLORIDE MELTS

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In previous works of our laboratory ([1–3]), as well as of other authors ([4]), the temperature and concentration dependences of equilibrium potentials were established for a number of metals in molten mixtures of their chlorides with alkali-metal chlorides. However, the literature contains no data concerning such measurements in mixed fluoride-chloride melts, despite the fact that their results are of undoubted interest for the electrolysis, for example, of K_2TiF_6, K_2ZrF_6, ThF_4, KUF_5, K_2TaF_7 in molten alkali-metal chlorides.

Finding a quantitative dependence of equilibrium potentials on the composition of mixed fluoride-chloride melts can also provide very valuable experimental material on the question of complex formation in molten salt media. As has already been noted in a number of our works ([5–8]), the introduction of fluorine ions into chloride melts markedly shifts the potentials of cathodic deposition and anodic dissolution of beryllium, titanium, and thorium toward more negative values. This indicates that, in mixed fluoride-chloride melts, cations of such metals form strong complex ions with fluorine anions.

In the present communication the main results are given for measurements of the equilibrium potentials of zirconium at 700–950° in an equimolar mixture of sodium and potassium chlorides with additions of various amounts of fluorides.

Salt mixtures $NaCl + KCl + NaF$ of a definite composition were prepared by melting chemically pure salts. Zirconium was introduced into the salt melts by anodic dissolution of metallic iodide directly in the cell, the arrangement of which is shown schematically in Fig. 1. The concentration of zirconium that passed into the melt was checked by chemical analysis of the electrolyte in the crucible after the experiment. The gas space in the test tube above the melt was filled with argon purified of traces of moisture, oxygen, and nitrogen. The cell was heated in an electric resistance furnace with automatic temperature regulation, which could be maintained constant at a prescribed value within $\pm 1.5°$. The potential of the zirconium electrode was measured relative to a chlorine reference electrode by a high-resistance potentiometer. The value of the e.m.f. was taken as reliable if, under the given conditions, it remained constant within ±1 mV for not less than 30 min.

Measurements were carried out with melts containing from 0.17 to 1.05 wt. % Zr and up to 15.82 wt. % F. In this case the ratio of the mole-fraction concentrations of fluorine and zirconium [F]/[Zr] varied from 9 to 75.

Experiments show that the zirconium potential depends not only on its concentration in the electrolyte, but also on the fluorine concentration, and to an even greater degree on the latter. Such a dependence follows from the conditions of thermodynamic equilibrium between the metal and the salt melt, when fluoride complexes are formed in it:

$$\mathrm{Zr} - ne \rightleftarrows \mathrm{Zr}^{n+}\ (\mathrm{melt}),$$

$$\mathrm{Zr}^{n+}\ (\mathrm{melt}) + m\mathrm{F}^{-}\ (\mathrm{melt}) \rightleftarrows \mathrm{ZrF}_m^{(m-n)-}\ (\mathrm{melt}).$$

Here m is the mean number of fluorine ions bound in the complex with a zirconium cation; n is the mean valence of the latter in a melt of the given composition.

The first electrode reaction leads to the following expression for the equilibrium potential:

$$E = E^0_{\mathrm{Zr}/\mathrm{Zr}^{n+}} + \frac{RT}{nF}\ln[\mathrm{Zr}^{n+}],$$

where $[\mathrm{Zr}^{n+}]$ is the mole-fraction concentration of zirconium cations not bound in complex ions. If the instability constant of the latter, expressed in terms of the mole-fraction concentrations of the corresponding ions in the electrolyte, is

$$K = [\mathrm{Zr}^{n+}][\mathrm{F}^{-}]^m/[\mathrm{ZrF}_m^{(m-n)-}],$$

then the equilibrium potential of the zirconium electrode is

$$E = E^0_{\mathrm{Zr}/\mathrm{Zr}^{n+}} + \frac{RT}{nF}\ln K + \frac{RT}{nF}\ln[\mathrm{ZrF}_m^{(m-n)-}] -$$

$$-\frac{m}{n}\frac{RT}{F}\ln[\mathrm{F}^{-}].$$

Under conditions of constant temperature and zirconium concentration in the melt, assuming that practically all zirconium is present in the form of complex ions, we obtain an expression for the dependence of the potential on the concentration of free fluorine ions:

$$E = \text{const} - 1.984 \cdot 10^{-4} T \lg[\text{F}^-].$$

In order to verify this equation, the potentials of zirconium were measured in melts with different fluorine contents (from 2.04 to 15.82 wt. %) at a temperature of 770° and a zirconium concentration of 1.05 ± 0.2 wt. %. In order to compare the results of these experiments with the equation derived, it is necessary to know the mean number of fluorine ions bound in the complex with the zirconium cation. Then the mole-fraction concentration of its free ions can be calculated from the total fluorine content. Only in purely fluoride melts is $m = 6$. In mixtures of these melts with alkali-metal chlorides, $m < 6$, because as the ratio of the mole-fraction concentrations [F]/[Zr] decreases at [Zr] = const, fluorine in the complex ions is gradually replaced by chlorine:

$$\text{ZrF}_6^{(6-n)-} \to \text{ZrClF}_5^{(6-m)-} \to \text{ZrCl}_2\text{F}_4^{(6-n)-} \to \ldots$$

Fig. 1. Cell for measurements.
1, 2 —quartz tubes; 3 —quartz tube with chlorine reference electrode; 4 —auxiliary cathode; 5 —thermocouple; 6 —molybdenum current lead; 7 —molybdenum crucible hangers; 8 —zirconium anode; 9 —zirconium dioxide crucible.

For tetravalent and trivalent zirconium cations, the coordination number in this case remains equal to 6.

If the measured potentials are plotted against the logarithms of the mole-fraction concentrations of free fluorine ions, calculated on the assumption that $m = 6, 5$, and 4, straight lines are obtained, as is seen in Fig. 2, where the plot is constructed for the case $m = 6$. The experimental points fit quite satisfactorily on straight lines described by the empirical equations

$$E = -3.055 - 0.309 \lg[\text{F}^-] \quad \text{for } m = 6,$$

$$E = -3.057 - 0.321 \lg[\text{F}^-] \quad \text{for } m = 5,$$

$$E = -3.062 - 0.334 \lg[\text{F}^-] \quad \text{for } m = 4.$$

From a comparison of the experimental and theoretical values of the prelogarithmic coefficients it follows that, in melts that are in equilibrium with metallic zirconium, under the conditions of our experiments the average valence of its ions is found to be 4.01 if $m = 6$; 3.23 if $m = 5$; and 2.48 if $m = 4$. Consequently, it varies within the limits $4 > n > 2.5$, when the fluorine concentration falls so much that its content in the complex ions decreases from 6 to 4. It should be borne in mind that the average values of m and n characterize the melt as a whole, and not individual ions, which may differ in their valence,

Fig. 2. Change in the equilibrium potential of zirconium as a function of the mole fraction of free fluorine ions in the melt at $t = 770°$ and a zirconium concentration of 1.05 wt. %.

Figure 1: Fig. 2. Change in the equilibrium potential of zirconium as a function of the mole fraction of free fluorine ions in the melt at $t = 770°$ and a zirconium concentration of 1.05 wt. %.

while the complexes may also differ in their composition. In mixed fluoride-chloride melts with a relatively large excess of fluorine ([F]/[Zr] $\gg$ 10), which are in contact with the metal, the predominant fraction of zirconium consists of tri- and tetravalent ions that are part of the anionic complexes $ZrClF_5^{3-}$, ZrF_6^{3-}, and ZrF_6^{2-}. With a decrease in the fluorine concentration ([F]/[Zr] $<$ 10), the equilibria gradually shift:

$$3Zr^{4+}\text{ (melt)} + Zr \rightleftarrows 4Zr^{3+}\text{ (melt)},$$

$$2Zr^{3+}\text{ (melt)} + Zr \rightleftarrows 3Zr^{2+}\text{ (melt)}$$

toward the formation of ions of lower valence: divalent zirconium appears in appreciable amounts in the melt.

Fig. 2. Change in the equilibrium potential of zirconium as a function of the mole fraction of free fluorine ions in the melt at $t = 770°$ and a zirconium concentration of 1.05 wt. %.

We also measured the potentials of the zirconium electrode at different temperatures in melts of five compositions. The ratio of the molar-fraction concentrations of fluorine and zirconium [F]/[Zr] varied from 45 to 9. The results of these experiments are presented graphically in Fig. 3.

The experimental points lie quite satisfactorily on straight lines for each of the electrolytes studied. The empirical equations of these straight lines were found to be

$$E_1 = -3.37 + 6.39 \cdot 10^{-4} T,$$

$$E_2 = -3.50 + 7.92 \cdot 10^{-4} T,$$

$$E_3 = -3.58 + 9.26 \cdot 10^{-4} T,$$

$$E_4 = -3.55 + 8.95 \cdot 10^{-4} T,$$

Fig. 3. Temperature dependence of the equilibrium potential of zirconium in melts containing: 1—0.23 wt. % Zr and 2.16 wt. % F; 2—0.36 wt. % Zr and 2.08 wt. % F; 3—1.05 wt. % Zr and 2.04 wt. % F; 4—0.17 wt. % Zr and 0.75 wt. % F; 5—0.17 wt. % Zr and 0.64 wt. % F

Figure 2: Fig. 3. Temperature dependence of the equilibrium potential of zirconium in melts containing: 1—0.23 wt. % Zr and 2.16 wt. % F; 2—0.36 wt. % Zr and 2.08 wt. % F; 3—1.05 wt. % Zr and 2.04 wt. % F; 4—0.17 wt. % Zr and 0.75 wt. % F; 5—0.17 wt. % Zr and 0.64 wt. % F

$$E_5 = -3.51 + 9.00 \cdot 10^{-4} T.$$

Such a linear dependence follows from the general expression for the equilibrium potential. It is known ([1–3,9]) that $E^0_{\mathrm{Zr/Zr}^{n+}} = a + bT$ and $\lg K = A - B/T$, where a, b, A, and B are constants independent of temperature. Substituting them into the electrode-potential equation, we obtain

$$E = \left(a - \frac{RB}{nF}\right) + \left(b + \frac{RA}{nF} + \frac{R}{nF} \ln \frac{\left[\mathrm{ZrF}_m^{(m-n)-}\right]}{[\mathrm{F}^-]^m}\right) T,$$

or

$$E = \alpha + \beta T.$$

As can be seen, the constant α does not depend on the composition of the electrolyte. In the equations found experimentally for melts of different composition, it varies somewhat within the limits of possible measurement errors: $\alpha = -3.50 \pm 0.07$. The coefficient β, on the contrary, should vary with composition, namely, increase with increasing

ratio of the mole-fraction concentrations of zirconium and free fluoride ions, which is also observed experimentally.

Thus, if it is assumed that mixed fluoride-chloride melts containing up to 10-15 wt. % Zr behave, like melts with thorium ([3]), as ideal solutions, then for determining the magnitude of the equilibrium potential of zirconium we obtain the equation

$$E = -3.50 + 5.4 \cdot 10^{-4} T + \frac{1.984}{n} \cdot 10^{-4} T \lg \frac{[Zr]}{[F^-]^m},$$

where $[Zr]$ and $[F^-]$ are, respectively, the mole-fraction concentrations of zirconium and of fluoride ions not bound in complexes with it. In mixed fluoride-chloride

Fig. 3. Temperature dependence of the equilibrium potential of zirconium in melts containing: **1**–0.23 wt. % Zr and 2.16 wt. % F; **2**–0.36 wt. % Zr and 2.08 wt. % F; **3**–1.05 wt. % Zr and 2.04 wt. % F; **4**–0.17 wt. % Zr and 0.75 wt. % F; **5**–0.17 wt. % Zr and 0.64 wt. % F

electrolytes having a relatively large excess of fluoride ions, $75 > [F]/[Zr] > 10$ (such melts are encountered in practice in the electrolysis of fluorozirconate, when chlorine is evolved at the anode in an amount equivalent to the zirconium deposited at the cathode, and, consequently, over time its ions are gradually replaced by fluoride anions), the average valence of zirconium n and the average number of fluoride ions in the complex m vary within the limits $4 > n > 3$ and $6 > m > 4$. For approximate calculations one may take $m = 5$ and $n = 3.2$.

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1. M. V. Smirnov, V. A. Chemezov, DAN, **120**, 122 (1958).
2. M. V. Smirnov, L. E. Ivanovskii, N. A. Loginov, DAN, **121**, 685 (1958).
3. M. V. Smirnov, L. D. Yushina, Izv. AN SSSR, OKhN, 1959, No. 2, 251.
4. L. Young, R. G. Hudson, Trans. Met. Soc. AIME, **215**, 589 (1959).
5. M. V. Smirnov, L. D. Yushina, Izv. AN SSSR, OKhN, 1956, No. 11, 1285.
6. M. V. Smirnov, L. E. Ivanovskii, ZhFKh, **32**, 2174 (1958).
7. M. V. Smirnov, N. Ya. Chukreev, ZhFKh, **31**, 2165 (1958).
8. M. V. Smirnov, L. A. Tsiovkina, Izv. Sibirsk. otd. AN SSSR, No. 9, 17 (1958).
9. M. V. Smirnov, N. Ya. Chukreev, Zhurn. neorg. khim., **4**, 2536 (1959).

Note: Figure translations are in progress. See original paper for figures.