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EQUILIBRIUM POTENTIALS OF ZIRCONIUM IN CHLORIDE MELTS

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There are no works in the literature devoted to the study of the equilibrium potentials of metallic zirconium in chloride melts. In one of the works of our laboratory (*1*) a dependence was established of the value of the equilibrium potential of thorium on the temperature and concentration of its ions in chloride melts. It was shown that metallic thorium reduces, in such melts, Th^{4+} ions to Th^{2+}. It could be expected that an analogous reduction also takes place for other tetravalent cations of the Ti subgroup. To verify this, we carried out special experiments.

Into a molybdenum crucible we loaded a fused eutectic mixture of lithium and potassium chlorides, previously treated with dry hydrogen chloride, to which a definite amount of zirconium tetrachloride had been added (zirconium tetrachloride was prepared by chlorinating a close mixture of zirconium dioxide with carbon in a stream of chlorine. The reaction product was subjected to threefold sublimation to remove traces of carbon dioxide). The crucible was fastened to a molybdenum rod and placed in a quartz test tube filled with argon. Particular attention was paid to thorough purification of the argon from traces of moisture, nitrogen, and oxygen. The test tube was inserted into a massive metal block serving as a thermostat. It was heated in an electric resistance furnace with automatic temperature regulation, which could be maintained at a specified value constant within ±1°. A zirconium electrode, prepared by the iodide method, was immersed in the salt melt. The metal was weighed before the experiment. The course of reduction of ions in the melt was followed from the change in the potentials of the zirconium and molybdenum (for which the crucible served) electrodes. The potentials were measured relative to a chlorine electrode, which was in a quartz test tube filled with a salt melt of the same composition. To avoid interaction of zirconium ions of lower valences with quartz, the test tube was raised above the electrolyte level. Contact with it was effected by means of a wick-like asbestos diaphragm, tightly closing the opening in the bottom of the test tube with the chlorine electrode. The end of the asbestos wick was immersed in the melt.

Figure 1 presents graphically the results of two experiments carried out at 560 and 585°C. In both cases the melt contained 2.27 wt.% Zr. As can be seen, at first the potential of the indifferent molybdenum electrode was more positive than that of zirconium. As reduction proceeded, the potentials of both chlorides converged and ultimately became equal, having then reached a constant value. This indicated attainment of equilibrium of the reduction reaction:

$$\mathrm{Zr_t} + \mathrm{Zr}^{4+}_{\mathrm{melt}} \rightleftarrows 2\mathrm{Zr}^{2+}_{\mathrm{melt}}.$$

Indeed, at equilibrium the potential of the zirconium electrode, relative to ions of higher and lower valences,

$$E_{\mathrm{Zr}} = E^0_{\mathrm{Zr|Zr^{2+}}} + \frac{RT}{2F}\ln a_{\mathrm{Zr^{2+}}} = E^0_{\mathrm{Zr|Zr^{4+}}} + \frac{RT}{4F}\ln a_{\mathrm{Zr^{4+}}}.$$

must be equal to the oxidation-reduction potential of the system, which is assumed by the indifferent molybdenum electrode:

$$E_{\mathrm{Mo}} = E_{\mathrm{Zr^{2+}/Zr^{4+}}} + \frac{RT}{2F}\ln\frac{a_{\mathrm{Zr^{4+}}}}{a_{\mathrm{Zr^{2+}}}}.$$

The fact that, as a result of reduction, divalent zirconium is formed in the melt in a predominant amount follows from the loss in weight of the zirconium electrode and the increase in the concentration of zirconium in the melt. Within the limits of possible measurement errors (several milligrams), the amount of zirconium in the melt increased twofold in comparison with the initial amount when the potentials of the zirconium and molybdenum electrodes became equal. Zirconium dichloride has not yet been described in the literature. Only in one recent work [2] is the preparation of zirconium trichloride reported. Melts with zirconium dichloride have strongly reducing properties. They react with glass and porcelain. On contact with air, a fine suspension of $\mathrm{ZrO_2}$ rapidly forms in them. Solidified salt mixtures containing $\mathrm{ZrCl_2}$ decompose water with evolution of hydrogen.

Fig. 1. Change in the potentials of zirconium and molybdenum electrodes during the reduction of $\mathrm{Zr^{4+}}$ ions to $\mathrm{Zr^{2+}}$ in the melt.

Fig. 2. Cell for measurements.
1 –quartz-glass test tube, 2 –thermocouple, 3 –quartz-glass test tube, 4 –chlorine electrode, 5 –molybdenum crucible, 6 –asbestos wick, 7 –salt melt, 8 –zirconium powder.

After determining the nature of the zirconium ions present in chloride melts at equilibrium with the metal, the equilibrium potentials of zirconium were measured over wide ranges of temperature (400–820°C) and concentration (from 0.0 to 24.9 wt. % $\mathrm{ZrCl_2}$).

The measurements were carried out in a cell whose design is shown schematically in Fig. 2. The initial electrolyte was a molten eutectic mixture of lithium and

Fig. 3

Figure 1: Fig. 3

potassium chlorides containing a known amount of zirconium tetrachloride. The salt mixture and metallic zirconium powder, the amount of which

exceeded by several times the amount required for the reduction of Zr^{4+} ions to Zr^{2+}. A separate zirconium electrode was not introduced into the melt, since upon attainment of equilibrium the potential of the molybdenum electrode became equal in magnitude to the equilibrium potential of the zirconium electrode. The second electrode of the cell was the chlorine electrode, whose design has been described above. The e.m.f. of the cell was measured with a high-resistance potentiometer of the PPTV-1 type. As the reliable value, we took that which, under the specified conditions, remained constant for a long time (not less than 1 hour) within 1 mV. In the investigated ranges of concentrations and temperatures, no appreciable volatilization of zirconium chloride from the electrolyte was observed. At higher concentrations and temperatures, losses of zirconium from the melt began to appear.

Fig. 3. Temperature dependence of the e.m.f. of a cell with a melt containing 13.95 wt.% Zr^{2+} (1), 4.44 wt.% Zr^{2+} (2), 1.41 wt.% Zr^{2+} (3), 0.26 wt.% Zr^{2+} (4), 0.03 wt.% Zr^{2+} (5); points denoted by triangles are values obtained in a melt without addition of $ZrCl_4$.

The results of the e.m.f. measurements at different temperatures are presented graphically in Fig. 3. For each of the investigated concentrations the experimental points fall on straight lines, which can be expressed by the following empirical equations:

Conc. $ZrCl_2$, wt.%	$\varepsilon_1 \cdot 10^4$, V
24.90	$2.442 - 6.28$
7.90	$2.456 - 5.94$
2.65	$2.474 - 5.54$
0.45	$2.512 - 5.12$
0.05	$2.519 - 4.78$

In Fig. 4 are presented isotherms of the e.m.f. at 700, 800, 900, 1000, and 1100°K, constructed on the basis of the temperature dependences found for the investigated zirconium concentrations in the electrolyte (mole fraction of Zr^{2+}: $8.33 \cdot 10^{-5}$, $7.73 \cdot 10^{-4}$, $4.21 \cdot 10^{-3}$, $1.38 \cdot 10^{-2}$, and $4.74 \cdot 10^{-2}$). At mole-fraction concentrations of zirconium above 10^{-3}, the e.m.f. isotherms are straight lines whose slopes are close to the value $RT/2F$, especially at high temperatures (above 1000°K). This once again confirms that at equilibrium with the metal the predominant amount of zirconium in the melt is present in the form of divalent ions. We measured the e.m.f. of a cell with a molten eutectic mixture of lithium and potassium chlorides without addition of zirconium tetrachloride. In this case, the same potential values were obtained as in the case of a melt containing 0.05 wt.% $ZrCl_2$.

Consequently, the concentration of zirconium in the layer of melt adjacent to it, which is established in the process of self-dissolution of the metal, exceeds 0.05 wt.% $ZrCl_2$. This explains the apparent falling of the experimental points on the e.m.f. isotherms measured in melts with a low zirconium concentration. From the experimental data it is seen that the equilibrium mole-fraction concentration of Zr^{2+} in the near-electrode layer of electrolyte, established through self-dissolution of the metal, is approximately $3 \cdot 10^{-4}$.

The smallest scatter of points was obtained by us in experiments with a melt containing 24.9 wt.% $ZrCl_2$, which is apparently connected with more accurate fixing of the concentration and with smaller relative changes in it during the measurements. The e.m.f. of the cell with this electrolyte varied with tempe-

with temperature according to the empirical equation:

$$\varepsilon_{\text{meas}} = (2.442 - 6.28 \cdot 10^{-4} T) \pm 0.004 \text{ V}.$$

The measured e.m.f., in addition to the electrochemical potential difference, includes the thermoelectromotive force between molybdenum and carbon (the chlorine electrode), with the opposite sign.

As investigations carried out in our laboratory have shown, it varies with temperature according to the equation:

$$\varepsilon_{\text{t}} = (-0.008 + 0.17 \cdot 10^{-4} T) \pm 0.001 \text{ V}.$$

Thus the sought e.m.f. is

$$\varepsilon = (2.434 - 6.11 \cdot 10^{-4} T) \pm 0.005 \text{ V}.$$

From this one can calculate the value $E^0_{\mathrm{Zr/Zr^{2+}}}$, which enters into the thermodynamic equation for the equilibrium potential of zirconium in chloride melts:

$$E = E^0_{\mathrm{Zr/Zr^{2+}}} + \frac{RT}{2F} \ln a_{\mathrm{Zr^{2+}}}.$$

Assuming that a melt with 24.9 wt.% $\mathrm{ZrCl_2}$ behaves as an ideal solution, we obtain

$$E^0_{\mathrm{Zr/Zr^{2+}}} = (-2.434 + 7.42 \cdot 10^{-4} T) \pm 0.005 \text{ V}$$

relative to the chlorine reference electrode.

Fig. 4. Isotherms of the e.m.f. of the cell. 1–700°, 2–800°, 3–900°, 4–1000°, 5–1100°K

Figure 2: Fig. 4. Isotherms of the e.m.f. of the cell. 1–700°, 2–800°, 3–900°, 4–1000°, 5–1100°K

From the previously determined value $E_{\mathrm{Th/Th}^{2+}}$ (1), one can find the difference between the deposition potentials of thorium and zirconium from chloride melts of equal concentrations:

$$E_{\mathrm{Th}} - E_{\mathrm{Zr}} = (-0.80 + 3.55 \cdot 10^{-4} T)\ \mathrm{V}.$$

As can be seen, thorium is more electronegative than zirconium. Thus, at 1000°K it should be deposited at potentials approximately 0.44 V more negative than zirconium, provided, of course, that the electrolysis process is not complicated by the formation of alloys at the cathode. From the temperature dependence of the e.m.f. of the cell

$$\mathrm{Zr} \,|\, 24.9\ \mathrm{wt.\%}\ \mathrm{ZrCl_2},\ \mathrm{KCl},\ \mathrm{LiCl}_{\mathrm{melt}} \,|\, \mathrm{Cl_2},\ \mathrm{C}$$

one can calculate the change in isobaric potential ΔZ for the reaction of formation of molten zirconium dichloride from the elements:

$$\mathrm{Zr_s} + \mathrm{Cl_{2g}} = \mathrm{ZrCl_{2l}},$$

if it is assumed that solutions of $\mathrm{ZrCl_2}$ in the molten eutectic mixture of lithium and potassium behave as ideal ones up to the pure molten salt:

Fig. 4. Isotherms of the e.m.f. of the cell. **1**–700°, **2**–800°, **3**–900°, **4**–1000°, **5**–1100°K

$$\Delta Z = (-112\,300 + 31.82T) \pm 230\ \mathrm{cal/mol}.$$

Hence the heat of formation of liquid zirconium dichloride is

$$\Delta H = -112.3\ \mathrm{kcal/mol},$$

and the entropy change in the reaction is

$$\Delta S = -31.82\ \mathrm{cal/(deg \cdot mol)}.$$

On the basis of literature data (3) on the standard entropy values of metallic zirconium and chlorine, from the value of ΔS found one can calculate the standard entropy of liquid zirconium dichloride:

$$S^0_{\mathrm{ZrCl2}} = \Delta S + S^0_{\mathrm{Zr_s}} + S^0_{\mathrm{Cl_{2g}}}.$$

It is found to be equal to 30.67 cal/(deg · mol).

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CITED LITERATURE

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